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ORIGINAL PAPER

Chemical bonds from through-*bridge* orbital communications in prototype molecular systems

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Abstract The indirect components of chemical interactions between atomic orbitals are explored within the Orbital Communication Theory of the chemical bond. The conditional probabilities for such through-*bridge* probability propagation and the associated entropy/information measures of the bond covalency are examined. The illustrative example of the bridge components of the chemical bonds between bridgehead carbons in small propellanes is discussed using the hybrid-orbital model. The bridge π-bonds in benzene and butadiene from the inter-orbital communications involving the single intermediate atomic orbitals are probed within the Hückel description and selected higher-orders of orbital bridges, involving several orbital intermediaries, are investigated.

Keywords Chemical bonds · Bonding mechanisms · Entropic bond indices · Information theory · Orbital bridges · *Pi*-electron systems · Propellanes · Through-bridge interactions · Through-space bonds · Wiberg bond-orders

1 Introduction

It has been recently argued [1–3] that the chemical interaction between two Atoms-in-Molecules (AIM) has both the through-*space* and through-*bridge* components. The former reflects the *direct* interactions between such bonded atoms while the latter is realized *indirectly*, through the remaining atoms, which constitute a bridge for an

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

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effective chemical coupling between more distant AIM. The most efficient bridges for such an implicit bonding mechanism realized *via* atomic intermediaries are the real chemical bridges, originating from the basis functions contributed by the chemically bonded atoms connecting such "terminal" atoms in molecular system [3].

Thus, the bonded status of the given pair of atoms can be felt even at relatively large separations provided there exist real bridge(s) of direct chemical bonds connecting them. In other words, atoms exhibiting the vanishing direct chemical interaction can be still bonded indirectly, via AIM bridges. This novel mechanism has already been shown to have important implications for the bonding pattern of the π-interactions in hydrocarbons [3]. For example, in the π-system of benzene the *ortho*-carbons exhibit a strong Wiberg [4] bond-multiplicity measure of almost exclusively through-space origin. The *cross*-ring interactions between the *meta*- and *para*-carbons where shown to be described by much smaller but practically equalized overall resultant bond-orders, being distinguished solely by the direct/indirect composition of these resultant multiplicities: the *meta* interactions are realized exclusively through bridges, while the *para* bonds exhibit strong direct and indirect components.

In the Orbital Communication Theory (OCT) [2,5–9] the "*explicit*" (through-space) bond component originates from the direct probability scattering between the interacting Atomic Orbitals (AO), measured by the corresponding conditional probability related to the square of the relevant element of the system density matrix, which couples the two basis functions, and hence to the associated Wiberg bond-order [4] contribution. In this information-theoretic (IT) [10–13] approach, which uses the standard communication-*noise* and information-*flow* descriptors [1,2] of the bond IT covalency and ionicity, respectively, the bonded atoms "communicate" between themselves in accordance with the electron delocalization pattern implied by the occupied (bonding) subspace of Molecular Orbitals (MO) resulting from the quantum-mechanical description of the system as a whole. In other words, this through-space bonding mechanisms involves a direct "conversation" between the two atoms in question. The "*implicit*" (through-bridges) bond component can be similarly viewed as resulting from the indirect information propagation *via* the bridge AIM. In a sense, while the through-space bonding channel reflects the direct "conversation" between AIM, the through-bridge channel(s) can be compared to a chatty talk reporting "hearsay", the "rumor" spread between the two atoms *via* the connecting chain of the AIM-intermediaries involved in the effective chemical bridge under consideration.

To summarize, one distinguishes in OCT the direct ("dialogue") and indirect ("gossip") origins of the chemical bond, which both contribute to the overall measure of the effective IT bond-order between the given pair of AIM. A similar description follows [1–3] from the Wiberg-type bond-multiplicities formulated in the MO theory [4,14–23]. In MO description the chemical interaction between, say, two (valence) AO or general basis functions originating from different atoms is strongly influenced by their direct overlap and interaction, which both condition the bonding effect experienced by electrons occupying their bonding combination in the molecule, compared to the *non*-bonding reference of electrons on separated AO. The "through-*space*" bonding mechanism is then associated with typical accumulation of valence electrons in the region between the two nuclei, called the bond-charge, due to the constructive interference between the two functions contributed by AIM. Indeed, such "shared" bond-charge is synonymous with the presence of the bond-*covalency* in this familiar (direct) chemical interaction.

This common possession of the spin-paired electrons by both atoms is also reflected by the familiar covalent VB structure. Similar effect of the bonding accumulation of the information densities relative to the promolecular distribution has been detected in maps of alternative measures of the information densities, e.g., of the entropy deficiency or the displacement in Shannon's entropy relative to the promolecular distribution [1–3,24–27]. In this description the complementary *ionicity* aspect is manifested by the MO polarization or—alternatively—by the participation of the orthogonal (independent) component of the ionic VB structure in the ground-state wave function.

The *direct* bonding interaction between neighboring atoms, reflected by the corresponding explicit bond-order of Wiberg, is thus generally associated with the presence of the bond-charge or the increase of information density between the two nuclei. However, for more distant atomic partners such an accumulation of valence electrons can be absent, e.g., in the cross-ring π-interactions in benzene or between the bridgehead carbon atoms in small propellanes, for which the "charge-shift" bonding mechanism [28], involving instantaneous charge fluctuations due to a strong resonance between covalent and ionic VB structures, has been proposed.

Alternatively, such bonding interaction lacking an accumulation of the bond-charge (information) can be also realized *indirectly*, through the neighboring AO intermediaries forming a "bridge" for an effective interaction between distant ("terminal") AO [3]. This indirect (through-bridge) mechanism reflects the *implicit* dependencies between AO resulting from their joint participation in the overall system of chemical bonds determined by the subspace of the occupied MO.

Thus, in the generalized outlook on the bond-order concept one identifies the chemical bond multiplicity as a measure of the statistical "*dependence*" (*non*-additivity) between orbitals on different atomic centers [1–3]. On one hand, this dependence between basis functions on different atoms is realized *directly* (through space), by the constructive interference of orbitals (probability amplitudes) on two atoms, which generally increases the electron density between them. On the other hand, it also has an *indirect* origin, through the dependence on orbitals of the remaining AIM used to construct the whole system of the occupied MO. Indeed, the mutually-bonding status of two basis functions can be felt even at large distances due to their involvement in chemical bonds with the chemically interacting AO intermediaries, which strongly participate in the localized bonds of the AIM bridge connecting the parent atoms, from which the two reference basis functions originate. These dependencies are due to the orthonormality relations involving the bonding subspace of the occupied MO, which determine the entire framework of chemical bonds in the molecule.

To summarize, each pair of AO or AIM exhibits the partial through-*space* and through-*bridge* components [3]. The bond-order of the former quickly vanishes with increasing *inter*-atomic separation, when the interacting AO are heavily engaged in forming chemical bonds with other atoms or remain *non*-bonding, thus describing the lone electron pairs. The latter can still assume appreciable values, when the remaining atoms form an effective bridge of the neighboring, chemically bonded atoms, which links the specified terminal AO/AIM in question [3]. Thus, the *non*-vanishing density-matrix element coupling the two AO in the molecule, which in MO theory reflects their directly-bonding status, is not essential for the existence of their through-bridge interaction. The latter may exist even when the direct interaction vanishes, provided the two AO strongly couple to the chemically bonded chain of orbitals connecting them.

The previous analysis [3], using mainly the Wiberg [4] measure of bond multiplicities, has explicitly identified both these components in chemical interactions between AO by using the appropriate projections of basis functions onto the bonding subspace of MO, the scalar products of which determine in the SCF MO theory the associated elements of the system *charge-and-bond-order* (CBO) density matrix. It is the main purpose of the present analysis to develop the conditional probabilities between the specified pairs of AIM originating from communications through the remaining AO. The corresponding IT-covalencies originating from such indirect probability propagation in the molecule will be examined within OCT and illustrative applications to small propellanes and π-electron systems will be reported.

2 Indirect conditional probabilities

Let us reexamine probability scattering through AO bridges in the standard SCF MO theory. The network of chemical bonds is then determined by the occupied MO in the system ground-state. For simplicity we assume the *closed*-shell (*cs*) configuration of $N = 2n$ electrons in the standard spin-restricted Hartree-Fock (RHF) description, which involves n lowest, *doubly*-occupied (orthonormal) MO. In the LCAO MO approach they are generated as linear combinations of the (Löwdin-orthogonalized) AO (basis functions) $\boldsymbol{\chi} = (\chi_1, \chi_2, \ldots, \chi_m) = \{\chi_i\}$, $\langle \boldsymbol{\chi} | \, \boldsymbol{\chi} \rangle = \{\delta_{i,j}\} \equiv \mathbf{I}$, contributed by the system constituent atoms:

$$\boldsymbol{\varphi} = \{\varphi_s\} = [(\varphi_1, \varphi_2, \ldots, \varphi_n), (\varphi_{n+1}, \ldots \varphi_m)] \equiv \left(\boldsymbol{\varphi}^o, \boldsymbol{\varphi}^v\right) = \boldsymbol{\chi}\mathbf{C} = \boldsymbol{\chi}(\mathbf{C}^o|\mathbf{C}^v). \quad (1)$$

Here, the rectangular matrices $\mathbf{C}^o = \langle \boldsymbol{\chi} | \, \boldsymbol{\varphi}^o \rangle$ and $\mathbf{C}^v = \langle \boldsymbol{\chi} | \, \boldsymbol{\varphi}^v \rangle$ group the expansion (LCAO) coefficients of the n occupied and $(m - n)$ virtual MO, respectively, to be determined from the iterative self-consistent-field (SCF) procedure. The full SCF LCAO MO matrix $\mathbf{C}$ is unitary, $\mathbf{C}^\dagger = \mathbf{C}^{-1}$, since it "rotates" orthonormal AO into the orthonormal MO, and hence the inverse transformation reads: $\boldsymbol{\chi} = \boldsymbol{\varphi}\mathbf{C}^\dagger$. The basis set projections onto the *bond*-subspace $\boldsymbol{\varphi}^o$,

$$\left|\boldsymbol{\chi}^b\right\rangle = \hat{\mathrm{P}}^o_{\boldsymbol{\varphi}} \, |\boldsymbol{\chi}\rangle = \left|\boldsymbol{\varphi}^o\right\rangle\left\langle\boldsymbol{\varphi}^o|\boldsymbol{\chi}\right\rangle = \left|\boldsymbol{\varphi}^o\right\rangle \mathbf{C}^{o\dagger} = \left\{\hat{\mathrm{P}}^o_{\boldsymbol{\varphi}} \, |i\rangle = \left|i^b\right\rangle\right\}, \quad (2)$$

then determine the 1-density (CBO) matrix $\boldsymbol{\gamma}$:

$$\begin{aligned}\boldsymbol{\gamma} &= \mathbf{C}\mathbf{d}\mathbf{C}^\dagger = 2\left\langle\boldsymbol{\chi}|\boldsymbol{\varphi}^o\right\rangle\left\langle\boldsymbol{\varphi}^o|\boldsymbol{\chi}\right\rangle = 2\mathbf{C}^o\mathbf{C}^{o\dagger} \equiv 2\left\langle\boldsymbol{\chi}\left|\hat{\mathrm{P}}^o_{\boldsymbol{\varphi}}\right|\boldsymbol{\chi}\right\rangle \\ &= 2\left(\langle\boldsymbol{\chi}|\,\hat{\mathrm{P}}^o_{\boldsymbol{\varphi}}\right)\left(\hat{\mathrm{P}}^o_{\boldsymbol{\varphi}}\,|\boldsymbol{\chi}\rangle\right) \equiv 2\left\langle\boldsymbol{\chi}^b|\boldsymbol{\chi}^b\right\rangle, \end{aligned} \quad (3)$$

where the diagonal matrix $\mathbf{d} = \{(2, s \le n; 0, s > n)\delta_{s,s'}\}$ groups the MO occupations. The CBO matrix thus constitutes the AO representation of the projection operator $\hat{\mathrm{P}}^o_{\boldsymbol{\varphi}}$

onto the bond-subspace $\boldsymbol{\varphi}^o$. It thus satisfies the idempotency relation:

$$(\boldsymbol{\gamma})^2 = 4\,\langle \boldsymbol{\chi} |\, \hat{\mathrm{P}}^o_{\boldsymbol{\varphi}}\, | \boldsymbol{\chi} \rangle \, \langle \boldsymbol{\chi} |\, \hat{\mathrm{P}}^o_{\boldsymbol{\varphi}}\, | \boldsymbol{\chi} \rangle = 4\,\langle \boldsymbol{\chi} |\, (\hat{\mathrm{P}}^o_{\boldsymbol{\varphi}})^2\, | \boldsymbol{\chi} \rangle = 4\,\langle \boldsymbol{\chi} |\, \hat{\mathrm{P}}^o_{\boldsymbol{\varphi}}\, | \boldsymbol{\chi} \rangle = 2\boldsymbol{\gamma}, \tag{4}$$

since, in the molecular Hilbert space spanned by the basis set $\boldsymbol{\chi}$, $|\boldsymbol{\chi}\rangle \langle \boldsymbol{\chi} |\, \hat{\mathrm{P}}^o_{\boldsymbol{\varphi}} = \hat{\mathrm{P}}^o_{\boldsymbol{\varphi}}$ or $|\boldsymbol{\chi}\rangle \langle \boldsymbol{\chi} | = 1$.

The square of the *off*-diagonal CBO matrix element $\gamma_{i,j}$ linking two different AO χ_i and χ_j, contributed by atoms A and B, respectively, determines the contribution

$$\mathcal{M}_{i,j} = \gamma_{i,j}\gamma_{j,i} = 4\left\langle j^b | i^b \right\rangle \left\langle i^b | j^b \right\rangle = 4\left\langle j^b \middle| \hat{\mathrm{P}}^b_i \middle| j^b \right\rangle = 4\left| \left\langle i^b | j^b \right\rangle \right|^2 \equiv 4|S^b_{i,j}|^2 \tag{5}$$

to the overall Wiberg index [4] of the molecular *bond*-multiplicity between these atoms:

$$\mathcal{M}_{\mathrm{A,B}} = \Sigma_{i\in \mathrm{A}} \Sigma_{j \in \mathrm{B}} \mathcal{M}_{i,j}. \tag{6}$$

This *quadratic* bond-multiplicity concept has been subsequently extended [14–16] and generalized in terms of the bond-orders from the *two*-electron difference approach [17–23]. It follows from Eq. 5 that this "through-*space*" dependence between two AO located on different atoms originates from the *direct* "overlap" $S^b_{i,j}$ between the bond-projections $\left|i^b\right\rangle$ and $\left|j^b\right\rangle$ of the interacting orbitals,

$$S^b_{i,j} = \left(\langle i |\, \hat{\mathrm{P}}_{\boldsymbol{\varphi}} \right) \left(\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\, | j \rangle \right) = \left\langle i^b | j^b \right\rangle = \gamma_{i,j}/2, \tag{7}$$

which reflect the overall involvement of these two basis functions in all chemical bonds in the molecular system under consideration.

The 1-matrix reflects the promoted, *valence* state of AO in the molecule, with the diagonal elements measuring the effective electron occupations of these basis functions, $\{N_i = \gamma_{i,i} = Np_i\}$, with probabilities $\boldsymbol{p} = \{p_i = \gamma_{i,i}/N\}$ of the basis functions occupancy in molecule: $\mathrm{Tr}\,\boldsymbol{\gamma} = N\Sigma_i p_i = N$. The *off*-diagonal CBO elements between AO on different atoms similarly reflect the bonding status of the *direct* interaction of the specified AO pair in the molecule, with the positive (negative) values signifying the bonding (*anti*-bonding) coupling between basis functions, and the vanishing bond-order $\gamma_{i,j} = 0$ identifying their directly *non*-bonding chemical interaction, when $\left|i^b\right\rangle = 0$ or $\left|j^b\right\rangle = 0$. Thus, the "constructive" (bonding) interference between two AO, the basis functions of SCF MO calculations, requires the two AO in question to exhibit the positive product of their direct bond-projections, while the negative product value identifies their resultant "destructive" interference in the molecular bond system.

The 1-density matrix also determines the conditional probabilities for the *direct* information propagation in the AO information system, the key concept of OCT [2,5–9], in which the basis functions of SCF MO calculations provide a natural resolution level of the electron-assignment "events", appropriate for discussing the information scattering via the system chemical bonds. This AO communication network is then described by standard quantities developed in IT for real communication devices [10–13].

Due to the electron delocalization throughout the network of chemical bonds the transmission of "signals" about the electron-assignments to AO becomes randomly disturbed in the molecule, thus exhibiting typical communication "noise". Indeed, an electron initially attributed to the given AO in the channel "input" $\boldsymbol{a} = \{\chi_i\}$ can be later found with a *non*-zero probability at several locations in the molecular "output" $\boldsymbol{b} = \{\chi_j\}$. This feature of the electron delocalization is embodied in the conditional probabilities of the "outputs-given-inputs",

$$\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \{P(j|i) = P(i \wedge j)/p_i\}, \qquad \Sigma_j P(j|i) = 1. \tag{8}$$

The probabilities of simultaneously observing two AO in the system chemical bonds $\mathbf{P}(\boldsymbol{a} \wedge \boldsymbol{b}) = \{P(i \wedge j)\}$ satisfy the following normalization:

$$\Sigma_i P(i \wedge j) = p_j, \;\; \Sigma_j P(i \wedge j) = p_i, \;\; \Sigma_i \Sigma_j P(i \wedge j) = 1, \tag{9}$$

where $p_i = \gamma_{i,i}/N$ stands for the AO probability in the molecule. These AO-pair probabilities are determined from the superposition-principle of quantum mechanics [29], supplemented by the "physical" projection onto the bond-subspace [2,6–9]:

$$\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \{P(j|i) = (2\gamma_{i,i})^{-1}\gamma_{i,j}\gamma_{j,i} = (2\gamma_{i,i})^{-1}(\gamma_{i,j})^2\}. \tag{10}$$

Hence the associated *joint*-probability matrix:

$$\mathbf{P}(\boldsymbol{a} \wedge \boldsymbol{b}) = \{P(i \wedge j) = p_i P(j|i) = (2N)^{-1}\,\gamma_{i,j}\gamma_{j,i} = (2/N)\,\langle i|\,\hat{\mathrm{P}}^o_{\boldsymbol{\varphi}}\,|j\rangle\,\langle j|\,\hat{\mathrm{P}}^o_{\boldsymbol{\varphi}}\,|i\rangle\}. \tag{11}$$

The indirect probability scattering through the remaining basis functions $\boldsymbol{\chi}'=\{\chi_{k\neq(i,j)}\}$, which constitute the effective bridge for the specified AO pair χ_i (input) and χ_j (output) can be then determined as conditional probabilities of the underlying *information cascade* of Fig. 1, in which the input signal emitted at the input $a_i = \chi_i$ is propagated into the specified output $b_j = \chi_j$ through the admissible single-orbital bridges including all remaining AO: $\boldsymbol{c}(i, j) = \{c_k(i, j) = \chi_{k\neq(i,j)}\}$. The associated conditional probability for such a through-bridges propagation thus reads:

$$\begin{aligned} P[(j|i) \mid (\boldsymbol{c}(i,j)] &= \sum_{k\neq(i,j)} P(k\,|i\,)P(j|k) \\ &= \sum_{l} P(l\,|i\,)P(j\,|l\,) - P(j\,|i\,)[P(i\,|i\,) + P(j\,|j\,)] \\ &= P^2(j\,|i\,) - \frac{1}{2}P(j\,|i\,)[\gamma_{i,i} + \gamma_{j,j}] \\ &\equiv P^2(j\,|i\,) - P(j\,|i\,)\gamma^{av.}(i,j), \end{aligned} \tag{12}$$

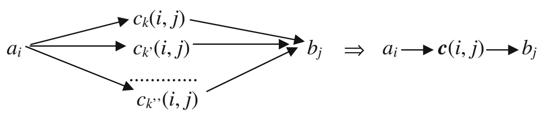

Fig. 1 The intermediate probability scattering between the specified AO events a_i and b_j, in the channel input and output, respectively, through the AO intermediates $\boldsymbol{c}(i, j) = \{c_k(i, j)\}$

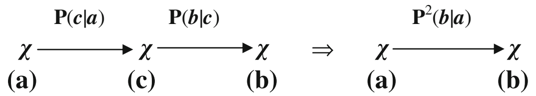

Fig. 2 Effective sequential cascade of two information systems in AO resolution

where the square of the AO conditional probabilities,

$$\mathbf{P}^2(\boldsymbol{b}|\boldsymbol{a}) = \{P^2(j|i) = \left[\mathbf{P}^2(\boldsymbol{\chi}|\boldsymbol{\chi})\right]_{i,j} = \mathbf{P}(\boldsymbol{c}|\boldsymbol{a})\mathbf{P}(\boldsymbol{b}|\boldsymbol{c})]_{i,j} = \sum_l P(l\,|i\,)P(j\,|l\,)$$
$$= \sum_l \frac{\gamma_{i,l}^2 \gamma_{j,l}^2}{4\gamma_{i,i}\gamma_{l,l}}, \tag{13}$$

characterizes the complete sequential AO-cascade (Fig. 2) involving *all* orbital intermediaries [30]. It follows from Eq. 12 that the intermediate probability propagation via the full "bridge" consisting off all the remaining AO, $\chi_i \to \boldsymbol{c}(i, j) \to \chi_j$, is determined by the corresponding squared-matrix probability $P^2(j|i)$ of the sequential AO cascade corrected by the product of the direct-scattering probability $P(j|i)$ and the average occupation $\gamma^{av\cdot}(i, j)$ of the specified input and output AO in the molecule.

Of interest also are the dominating partial bridges consisting of AO contributed by the sequence of the chemically bonded AIM connecting the specified two atoms in the molecular input and output, respectively. Such probabilities, be it for the different normalization convention, have been preliminarily examined in the previous analysis [3], using the appropriate sequence of the AO projections.

It follows from Eq. 9 that for the single AO χ_k in the bridge the present sequential approach gives:

$$P[(j|i) \mid k] = P(k\,|i\,)P(j\,|k\,) = \frac{\gamma_{i,k}^2 \gamma_{j,k}^2}{4\gamma_{i,i}\gamma_{k,k}}, \qquad \Sigma_j P[(j|i) \mid k] = P(k|i). \tag{14}$$

For the *parallel* two AO intermediaries of Fig. 3a one similarly finds:

$$P[(j|i) \mid (k,l)] = P(k\,|i\,)P(j\,|k\,) + P(l\,|i\,)P(j\,|l\,) = \frac{1}{4\gamma_{i,i}}\left(\frac{\gamma_{i,k}^2\gamma_{j,k}^2}{\gamma_{k,k}} + \frac{\gamma_{i,l}^2\gamma_{j,l}^2}{\gamma_{l,l}}\right), \tag{15}$$

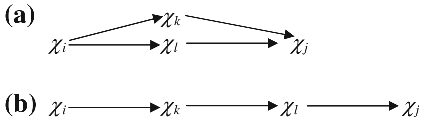

Fig. 3 The intermediate probability scattering from χ_i to χ_j *via* the *two*-AO bridges $\{\chi_k, \chi_l\}$: parallel (Panel **a**) and sequential (Panel **b**)

while the *sequential two*-AO bridge of Fig. 3b gives:

$$P[(j|i) \mid k \rightarrow l] = P(k\,|i\,)P(l\,|k\,)P(j\,|l\,) = \frac{\gamma_{i,k}^2 \gamma_{l,k}^2 \gamma_{j,l}^2}{8\gamma_{i,i}\gamma_{k,k}\gamma_{l,l}}. \qquad (16)$$

3 Orbital model of the central bond in small propellanes

Let us examine the patterns of chemical bonds in the representative [1.1.1] and [2.2.2] propellanes (Fig. 4), incuding a single and double carbon bridges, respectively. In the minimum basis set the bond structure in these two molecular systems can be understood in terms of the localized MO resulting from interactions between *directed* (hybrid) orbitals on neighboring atoms and the *non*-bonding electrons occupying such hybrid AO. In the smallest [1.1.1] system the nearly tetrahedral ($h = sp^3$) hybridization on both bridgehead and bridging carbons is required to form chemical bonds of the three carbon bridges and to accommodate two hydrogens on each bridge-carbons. Thus three sp^3 hybrids on each of the bridgehead atoms are used to form the chemical bonds with the bridge carbons and the fourth hybrid is directed away from the central-bond region, between the two bridgehead carbons, thus remaining *non*-bonding and *singly*-occupied. In the [2.2.2] propellane the two central carbons acquire a nearly trigonal ($h' = sp^2$) hybridization, to form bonds with the bridge neighbours, each with a single $2p_\sigma$ orbital directed along the central-bond axis, which has not been used in this hybridization scheme, now being available to form a strong through-space component of the overall multiplicity of the C′–C′ bond. This explains the missing through-space component in the smaller (diradical) propellane and its presence in the larger system [1–3,24]. The same conclusion follows from the information-probes of the direct bonding pattern in these molecules [1,2,24,27].

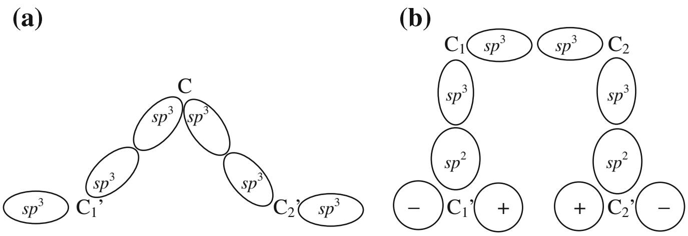

Fig. 4 Schematic diagrams rationalizing the patterns of the localized bonds in [1.1.1] (Panel **a**) and [2.2.2] (Panel **b**) propellanes; the bridgehead carbon atoms are primed

In this qualitative picture each directed AO participates in a single localized, *two*-centre (*doubly*-occupied) bonding MO, which allows one to estimate the diatomic CBO matrix elements determining the direct and indirect components of the central bonds in these two propellanes:

$$\gamma_{p,p} = (1 + S^{\sigma}_{p,p})^{-1} \approx 0.78, \quad \gamma_{h,h} = \left(1 + S_{h,h}\right)^{-1} \approx 0.60,$$
$$\gamma_{h,h'} = (1 + S_{h,h'})^{-1} \approx 0.60, \tag{17}$$

where $S^{\sigma}_{p,p}$, $S_{h,h}$ and $S_{h,h'}$ stand for the overlap integrals between two $2p_{\sigma}$ orbitals and between the indicated hybrid-AO, respectively. In the preceding equation these orbital overlaps have been realistically estimated using the standard overlap integrals between valence orbitals on carbon atoms in ethane (single C—C bond): $S_{s,s} = 0.36$, $S^{\sigma}_{s,p} = 0.42$, $S^{\sigma}_{s,p} = 0.42$, $S^{\sigma}_{p,p} = 0.28$, giving rise to the associated standard overlaps between hybrid AO : $S^{\sigma}_{h,h} = 0.66$, $S^{\sigma}_{h,h'} = 0.67$.

Hence, the direct Wiberg component of the central bond in the [2.2.2] system,

$$\mathcal{M}_{1',2'} \approx (1 + S^{\sigma}_{p,p})^{-2} = 0.62, \tag{18}$$

and the indirect contribution due to three (*double*-carbon) bridges [3],

$$\mathcal{M}_{1',2'}(bridges) = 3\mathcal{M}_{C_1',C_1}\mathcal{M}_{C_1,C_2}\mathcal{M}_{C_2,C_2'} \approx 3(1+S^{\sigma}_{h,h'})^{-4}(1+S^{\sigma}_{h,h})^{-2} = 0.14, \tag{19}$$

which give rise to the total bond multiplicity:

$$\mathcal{M}(1' - 2') = \mathcal{M}_{1',2'} + \mathcal{M}_{1',2'}(bridges) \approx 0.76. \tag{20}$$

The corresponding indirect (total) component for the [1.1.1] system reads:

$$\mathcal{M}_{1',2'}(bridges) = 3\mathcal{M}_{C_1',C}\mathcal{M}_{C,C_2'} \approx 3(1 + S^{\sigma}_{h,h})^{-4} = 0.40 = \mathcal{M}(1' - 2'). \tag{21}$$

Therefore, the smaller system is predicted to exhibit higher through-bridge component, compared to larger propellane, with the latter generating greater overall bond-order. This trend is also reflected by numerical SCF and DFT calculations [1–3,24].

Finally, let us examine the associated conditional entropy (communication noise) contributions, reflecting the associated IT bond-orders due to through-bridge covalencies. The conditional probabilities of Eqs. 14 and 16, due to a single bridge in the [1.1.1] and [2.2.2] propellanes, respectively, read:

$$P[\left(C_2'|C_1'\right) \mid C] \approx \frac{1}{4}(\gamma_{h,h})^4 = 0.0333 \qquad \text{and}$$
$$P[\left(C_2'|C_1'\right) \mid C_1 \to C_2] \approx \frac{1}{8}(\gamma_{h,h})^2(\gamma_{h,h'})^4 = 0.0058. \tag{22}$$

They again reflect a higher through-bridge propagation of electron probability in the single carbon bridge. These probabilities generate the associated entropies due to three identical (parallel) bridges, which measure the bridge IT-covalencies (in bits) of the central bond in these two molecular systems:

$$\mathsf{S}_{1',2'}(bridges) \approx 3\left(-0.0333 \log_2 0.0333\right) = 0.49 \qquad \text{and}$$
$$\mathsf{S}_{1',2'}(bridges) \approx 3(-0.0058 \log_2 0.0058) = 0.13, \tag{23}$$

which compare favorably with the corresponding Wiberg estimates of Eqs. 21 and 19, respectively.

We thus conclude that the entropic and Wiberg measures of the through-bridge component of the central bond covalency in this simple model of the electronic structure in the representative [1.1.1] and [2.2.2] propellanes are in general agreement with one another thus providing consistent insights into the novel through-bridge bond components in these prototype molecular systems.

4 Communications in π-electron systems through single-AO bridges

Next, let us reexamine the indirect π-bonds between carbon atoms in benzene and butadiene, using the occupied MO from the familiar Hückel theory. We begin with a brief summary of the main predictions from the previous analysis [3] of the Wiberg bond-orders in these molecules.

The density matrix in benzene is summarized by the following elements of the CBO matrix:

$$\gamma_{i,i} = 1, \qquad \gamma_{i,i+1} = 2/3, \qquad \gamma_{i,i+2} = 0, \qquad \gamma_{i,i+3} = -1/3. \tag{24}$$

This density matrix generates the following through-space π bond-orders of Wiberg:

$$\mathcal{M}_{i,i+1} = 0.44, \qquad \mathcal{M}_{i,i+2} = 0, \qquad \mathcal{M}_{i,i+3} = 0.11, \tag{25}$$

predicting the vanishing direct bond-multiplicities between the two *meta*-carbons. In the previous study [3] we have demonstrated that these explicit π-bonds are supplemented by the indirect interactions *via* the remaining carbon atoms in the benzene ring:

$$\mathcal{M}_{i,i+1}(bridges) = 0.06, \;\; \mathcal{M}_{i,i+2}(bridges) \cong 0.30, \;\; \mathcal{M}_{i,i+3}(bridges) \cong 0.18, \tag{26}$$

thus predicting the associated total measures of the chemical π interactions in benzene:

$$\mathcal{M}(para) \cong \mathcal{M}(meta) = 0.3 < \mathcal{M}(ortho) = 0.5. \tag{27}$$

One observes the differences in their compositions: the *para* interactions exhibit comparable through-space and through-bridge components, the *meta* multiplicities are realized through bridges only, while the strongest *ortho* bond-orders have practically direct, through-space origin.

For the consecutive numbering of carbon atoms in butadiene the *off*-diagonal part of the CBO matrix in Hückel approximation is fully characterized by the following elements:

$$\gamma_{1,2} = \gamma_{3,4} = 2/\sqrt{5}, \quad \gamma_{1,3} = \gamma_{2,4} = 0, \quad \gamma_{1,4} = -1/\sqrt{5}, \quad \gamma_{2,3} = 1/\sqrt{5}, \tag{28}$$

which determine the associated through-space bond-orders of Wiberg:

$$\mathcal{M}_{1,2} = \mathcal{M}_{3,4} = 0.80, \quad \mathcal{M}_{1,3} = \mathcal{M}_{2,4} = 0, \quad \mathcal{M}_{1,4} = \mathcal{M}_{2,3} = 0.20. \tag{29}$$

Again, this artificial distinction of the (1–3) and (2–4) interactions as π *non*-bonding is remedied by the inclusion of the indirect bond components:

$$\mathcal{M}_{1,2}(bridges) = 0.03, \quad \mathcal{M}_{1,3}(bridges) = 0.32, \quad \mathcal{M}_{1,4}(bridges) = 0.13, \tag{30}$$

which generate the following resultant bond orders:

$$\mathcal{M}(1-2) = \mathcal{M}(3-4) = 0.83, \quad \mathcal{M}(1-3) = \mathcal{M}(2-4) = 0.32, \\ \mathcal{M}(1,4) = \mathcal{M}(2,3) = 0.33. \tag{31}$$

The strongest, terminal bonds (1–2) and (3–4) are almost exclusively of the through-space origin, the π-bonds (1–3) and (2–4) connecting the *second*-neighbors exhibit the pure through-bridge character, while the remaining bonds (1–4) and (2–3) include comparable direct and indirect components.

Turning now to the orbital communications we recall, that the symmetry-unrelated, direct conditional probabilities [Eq. 10] in benzene,

$$P(i|i) = 1/2, \quad P(i+1|i) = 2/9, \\ P(i+2|i) = 0, \quad P(i+3|i) = 1/18, \tag{32}$$

define the through-space AO-communications for this molecule. The *non*-vanishing probabilities for butadiene read:

$$P(i|i) = 1/2, \quad P(2|1) = P(4|3) = 2/5, \\ P(3|1) = P(4|2) = 0, \quad P(4|1) = P(3|2) = 1/10. \tag{33}$$

The corresponding elements of the squared conditional probability matrices [Eq. 13], characterizing the sequential cascade of Fig. 2, for benzene,

$$P^2(i|i) = 19/54, \quad P^2(i+1|i) = 2/9, \\ P^2(i+2|i) = 2/27, \quad P^2(i+3|i) = 1/18, \tag{34}$$

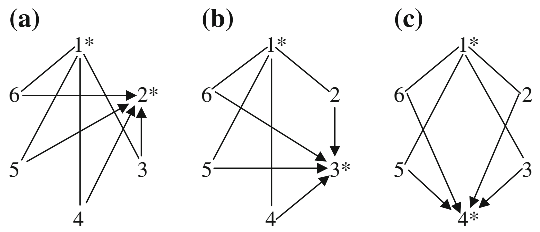

Fig. 5 Indirect communications between terminal (identified by *asterisk*) *ortho* (Panel **a**), *meta* (Panel **b**) and *para* (Panel **c**) carbons in benzene, through the single π-AO intermediate

and butadiene,

$$\begin{aligned} &P^2(i|i) = 21/50, && P^2(2|1) = P^2(4|3) = 2/5, \\ &P^2(3|1) = P^2(4|2) = 2/25, && P^2(4|1) = P^2(3|2) = 1/10, \end{aligned} \tag{35}$$

then determine the indirect probability scatterings between these orbitals through all admissible single AO bridges including the remaining AO.

These additional degrees-of-freedom for communications between different π-AO, through the single member of the AO subset $\boldsymbol{c}(i, j)$ combining all remaining basis functions, are then given by the associated probabilities of Eq. 12. All these intermediate π-AO communications in benzene are illustrated in Fig. 5.

For benzene one finds

$$\begin{aligned} &P[(i+1|i) \mid \boldsymbol{c}(i, i+1) = P[(i+3|i) \mid \boldsymbol{c}(i, i+3)] = 0, \\ &P[(i+2|i) \mid \boldsymbol{c}(i, i+2)] = 2/27, \end{aligned} \tag{36}$$

while these implicit communications in butadiene read:

$$\begin{aligned} &P[(2|1) \mid (3,4)] = P[(4|3) \mid (1,2)] = P[(4|1) \mid (2,3)] = P[3|2) \mid (1,4)] = 0, \\ &P[(3|1) \mid (2,4)] = P[(4|2) \mid (1,3)] = 2/25, \end{aligned} \tag{37}$$

Therefore, these results for the complete bridge of sequential probability propagation between two π-AO through the *single* orbital of the set combining the remaining basis functions predict vanishing *single*-AO bridge communications between the two *ortho*- and *para*-carbons, with only *meta*-carbons exhibiting a *non*-vanishing indirect probability scattering. A similar trend is observed for butadiene, with only the $1 \to 3$ and $2 \to 4$ communications, which exhibit the vanishing *direct* component, now acquiring the *indirect* communication links.

The additional, indirect IT-covalency between two *meta* carbons in benzene is thus reflected by the associated conditional entropy (noise) descriptor:

$$\mathsf{S}_{i,i+2}[c(i, i+2)] = -(2/27)\log_2(2/27) = 0.28 \text{ bits.} \tag{38}$$

The indirect entropic covalency of the 1–3 and 2–4 IT bond-orders in butadiene similarly reads:

$$\mathsf{S}_{1,3}(2,4) = \mathsf{S}_{2,4}(1,3) = -(2/25)\log_2(2/25) = 0.29 \text{ bits.} \tag{39}$$

These implicit (total) bond IT-covalencies can be compared with the direct (total) entropies of the remaining two-orbital interactions in benzene,

$$\begin{aligned} \mathsf{S}_{i,i+1} &= -(2/9)\log_2(2/9) = 0.48 \text{ bits}, \\ \mathsf{S}_{i,i+3} &= -(1/18)\log_2(1/18) = 0.23 \text{ bits}, \end{aligned} \tag{40}$$

and in butadiene:

$$\begin{aligned} \mathsf{S}_{1,2} = \mathsf{S}_{3,4} &= -(2/5)\log_2(2/5) = 0.53 \text{ bits}, \\ \mathsf{S}_{1,4} = \mathsf{S}_{2,3} &= -(1/10)\log_2(1/10) = 0.33 \text{ bits}. \end{aligned} \tag{41}$$

Therefore, the present perspective, combining the entropy-covalencies due to the direct AO communications and indirect probability propagations *via single*-AO bridges of all remaining basis functions, gives even more dichotomous distinction of diatomic π-interactions in these two molecules, compared to that resulting from all admissible bridges in the AO information system [3]. The bridge contributions now correct only the atomic pairs, which do not interact directly: in benzene $\mathsf{S}_{i,i+2}[\boldsymbol{c}(i, i+2)] \cong 0.3$ bits and in butadiene $\mathsf{S}_{1,3}(2,4) = \mathsf{S}_{2,4}[1,3] \cong 0.3$ bits. One again observes, that this *indirect* correction is of the order of the weaker *direct* bonds in these molecules.

5 Higher orders of bridge communications in benzene

It follows from Eq. 36 that the effective probabilities $\mathbf{Q}^S = \{Q^S_{i\to j}\{k \neq (i,j)\}$ of the information scattering between the specified pair of the input (i) and output (j) AO, through the *single* (S)-AO bridges including all the remaining basis functions $\{k_{\neq}(i,j)\}$ (see Fig. 6a) read:

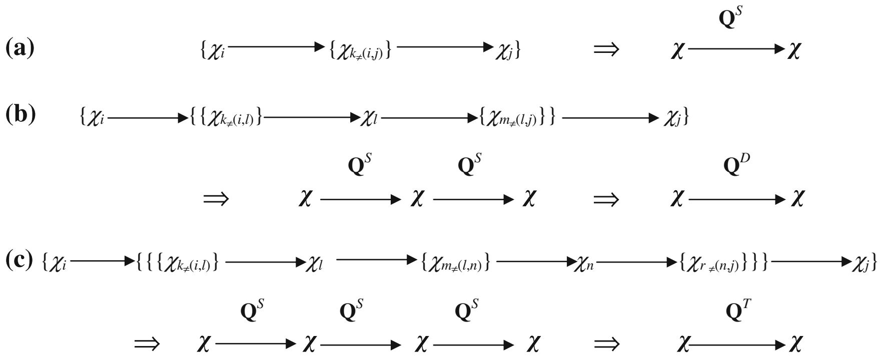

Fig. 6 The intermediate probability scattering $\chi_i \to \chi_j$ *via* the AO bridges including all $single(S)\{\chi_k\}$ (Panel **a**), $double(D)\{\chi_k \to \chi_m\}$ (Panel **b**), and $triple(T)\{\chi_k \to \chi_m \to \chi_r\}$ (Panel **c**) AO in the benzene ring, generating the associated conditional-probability matrices $\mathbf{Q}^S$, $\mathbf{Q}^D$, $\mathbf{Q}^T$, respectively

$$\mathbf{Q}^S = \begin{bmatrix} 0 & 0 & q & 0 & q & 0 \\ 0 & 0 & 0 & q & 0 & q \\ q & 0 & 0 & 0 & q & 0 \\ 0 & q & 0 & 0 & 0 & q \\ q & 0 & q & 0 & 0 & 0 \\ 0 & q & 0 & q & 0 & 0 \end{bmatrix}, \qquad q = 2/27. \tag{42}$$

One can also envisage higher orders of AO bridges in which the specified $i \to j$ probability is propagated *via* the consecutive scatterings involving *two* (Fig. 6b) or *three* (Fig. 6c) AO bridges in the benzene ring. The associated conditional probability matrices are then determined by the corresponding powers of $\mathbf{Q}^S$ (see Fig. 6b,c):

$$\begin{aligned} \mathbf{Q}^D &= \left(\mathbf{Q}^S\right)^2 = \{Q^D_{i\to j}[\{k \neq (i,l)\} \to \{m \neq (l,j)\}] \\ &= \sum_l Q^S_{i\to l}\{k \neq (i,l)\} Q^S_{l\to j}\{m \neq (l,j)\}\} \\ &= \begin{bmatrix} 2q^2 & 0 & q^2 & 0 & q^2 & 0 \\ 0 & 2q^2 & 0 & q^2 & 0 & q^2 \\ q^2 & 0 & 2q^2 & 0 & q^2 & 0 \\ 0 & q^2 & 0 & 2q^2 & 0 & q^2 \\ q^2 & 0 & q^2 & 0 & 2q^2 & 0 \\ 0 & q^2 & 0 & q^2 & 0 & 2q^2 \end{bmatrix}, \end{aligned} \tag{43}$$

$$\begin{aligned} \mathbf{Q}^T &= \left(\mathbf{Q}^S\right)^3 = \{Q^T_{i\to j}[\{k \neq (i,l)\} \to \{m \neq (l,n)\} \to \{r \neq (n,j)\}] \\ &= \sum_l \sum_n Q^S_{i\to l}\{k \neq (i,l) Q^S_{l\to n}\{m \neq (l,n)\} Q^S_{n\to j}\{r \neq (n,j)\}\} \\ &= \begin{bmatrix} 2q^3 & 0 & 3q^3 & 0 & 3q^3 & 0 \\ 0 & 2q^3 & 0 & 3q^3 & 0 & 3q^3 \\ 3q^3 & 0 & 2q^3 & 0 & 3q^3 & 0 \\ 0 & 3q^3 & 0 & 2q^3 & 0 & 3q^3 \\ 3q^3 & 0 & 3q^3 & 0 & 2q^3 & 0 \\ 0 & 3q^3 & 0 & 3q^3 & 0 & 2q^3 \end{bmatrix}, \end{aligned} \tag{44}$$

These expressions demonstrate that these indirect communications fast decay with the bridge order $O = S, D, T, \ldots \equiv 1, 2, 3, \ldots$, with the *non*-vanishing terms of $\mathbf{Q}^O$ being determined by contributions of the order $\mathrm{O}(q^O)$. This enhances the importance of conclusions in Sect. 4, based upon the single bridges $O = S$, which determine the largest contributions to indirect communications between AO.

6 Conclusion

In this work we have further explored the through-bridge mechanism of bonding interactions in molecular systems, which has been first conjectured to explain the numerical bond orders for propellane systems [1–3]. The present IT analysis and previous Wiberg-type treatment [3] of both the explicit and implicit chemical interactions in molecules confirm the presence of both these bond components. The former, more familiar bonding mechanism is associated with an accumulation of the electronic charge between bonded atoms. As conditioned by the direct overlap between the interacting orbitals it is possible only at relatively short distances between AIM. The latter does not require the presence of such a bond-charge and depends on the existence of the real bridge of chemically bonded atoms between the interacting AIM. As such it can be effected at larger separations between atoms, which may have important implications for biological and solid-state systems.

The bottom-line of both these studies is that the chemical bonding between two AO can in fact be realized despite the vanishing CBO matrix element coupling directly these basis functions in the molecule, provided that they both exhibit the *non*-vanishing density matrix elements with the bridge basis functions. In other words, the two AO may exhibit the indirect chemical bonding when they strongly couple to other directly bonded basis functions.

The simple orbital model of such direct and indirect interactions in small propellanes further confirms the apparent existence of the trough-bridge bond even in the smallest [1.1.1] system lacking the direct bond component, thus offering an explanation of the experimentally conjectured central bonding in this molecule despite the absence of the charge/information accumulation between central (bridgehead) carbons. This constitutes an additional insight into the bond pattern in these molecules, alternative to the VB-inspired *charge-shift* mechanism [28] of the instantaneous charge fluctuations between the central carbon atoms, invoked to explain the existence of “some” chemical bonding between the central carbons in the smallest propellane.

Both the Wiberg-type bond-order description and OCT treatment of such indirect bonding mechanism through the orbital/AIM intermediaries called “bridges” has been shown to also rationalize the π-bonding patterns in benzene and butadiene, by removing some artifacts of the traditional (direct) bond-order description, e.g., of the *cross*-ring interactions in benzene. The overall interactions of the two *meta*-carbons, lacking the direct (through-space) component, have been shown to amount to about 0.3 bond-order, thus being approximately of the same magnitude as the resultant bond multiplicity predicted for the two carbons in the mutual *para*-positions. The same extra IT-covalency follows from the OCT using the conditional-probability corrections due to bridging orbitals in the carbon ring. The dominant *ortho*-interactions in benzene and terminal π bonds in butadiene have been shown to be almost exclusively of the through-space character, while the *second*-neighbor interactions in butadiene and *meta* interactions in benzene were found to be of the pure through-bridges origin.

The novel, indirect mechanism adds to the diversity and complexity of the chemical interactions in molecular systems, and offers an alternative perspective on some controversial chemical bonds in molecules, e.g., the central bond problem in propellanes. We recall that both the Shannon-type information densities [1,2,24] and the *contragradience* criterion [2,31–35], related to the *Electron Localization Function* [27,36–38], fail to detect the presence of the direct chemical bond in the smallest propellane. The indirect bond concept has also been shown to remove some artifacts of the over-simplified approach to conjugated π bonds based solely upon the through-space mechanism.

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