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On interference of orbital communications in molecular systems

Roman F. Nalewajski

Abstract   The atomic orbitals (AO) contributed by bonded atoms of molecular systems emit or receive the "signals" of electronic allocations to these basis functions, thus acting as the signal *source* (input) or *receiver* (output), respectively, in the associated communication network. Each orbital simultaneously participates in both the *through-space* and *through-bridge* probability propagations: the former involve direct communications between two AO while the latter are realized indirectly *via* orbital intermediates. This work examines the interference effects of the amplitudes of molecular probability scatterings, and introduces the operator representation of AO communications. The eigenvalue problem of the associated Hermitian operator combining the *forward* and *reverse* information propagations defines the stationary modes ("standing" waves) of the molecular propagation of electronic conditional probabilities. The combined effect of interference between the multiple (direct and indirect) information scatterings, which establishes the stationary distribution of electronic probabilities, is probed. The wave-superposition principle for the conditional-probability amplitudes of the generalized through-bridge information propagation is linked to the idempotency relations of the system density matrix. It explicitly demonstrates that the resultant effect of the probability propagations involving bridges containing all basis functions, at arbitrary bridge orders indeed generates the (stationary) molecular distribution of conditional probabilities.

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

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

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components

1 Introduction

The key concept of the *Information-Theoretic* (IT) [1–4] treatment of bond multiplicities and their covalent and ionic components, called the *Communication Theory of the Chemical Bond* (CTCB) [5,6], is the molecular communication (information) system. It can be constructed at alternative levels of resolving the electron probabilities into the underlying elementary "events" determining the channel inputs $a = \{a_i\}$ and outputs $b = \{b_j\}$. For example, they may involve findings of an electron on the specific *Atoms-in-Molecules* (AIM), $a = \{X\}$ and $b = \{Y\}$, or basis functions $\chi = (\chi_1, \chi_2, \ldots, \chi_t)$, e.g., the orthogonalized *Atomic-Orbitals* (AO) used in the molecular *Self-Consistent Field* (SCF) calculations: $a = \{\chi_i \equiv i\}$ and $b = \{\chi_j \equiv j\}$.
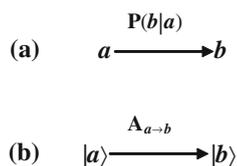
The latter resolution establishes the *Orbital Communication Theory* (OCT) [7–11], in which the chemical bonds originate from molecular communications between AO events determining the channel input and output of Fig. 1a, in accordance with the associated (direct) conditional probability matrix $\mathbf{P}(b|a) = \mathbf{P}(\chi|\chi) = \{P(j|i)\}$. The amplitudes $\mathbf{A}(b|a) = \{A(j|i) \equiv A_{i \to j}\} \equiv \mathbf{A}_{a \to b}$ of such conditional probabilities, $\{P(j|i) \equiv |A_{i \to j}|^2\}$, which define the amplitude channel of Fig. 1b, have been shown to be proportional to elements of the system *Charge-and-Bond-Order* (CBO), density matrix $\boldsymbol{\gamma}$ [9–12].

To summarize, the probability and amplitude channels of Fig. 1 summarize communications between AO events, $a \to b$, and the corresponding state vectors, $|a\rangle \to |b\rangle$, respectively. It should be emphasized that only the information-scattering *states*, defined by communication amplitudes, are capable of "interference" effects which we intend to examine in this work.

It has been recently argued [13,14] that the chemical interaction between AO has both the through-*space* and through-*bridge* components. The former reflects the *direct* interactions (communications) between two orbitals, while the latter is realized *indirectly*, through the single or several consecutive AO intermediates, which constitute an effective bridge for the chemical coupling between spatially sepatated basis functions. Both mechanisms contribute to the resultant multiplicities of chemical bonds reflecting the effective bond "orders".

In the *Molecular Orbital* (MO) theory, with MO expanded in terms of AO contributed by the system constituent AIM, within the familiar LCAO 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/interaction,

Fig. 1 The molecular orbital
channels in the probability (**a**)
and amplitude (**b**)
representations

(a) $a \xrightarrow{\mathbf{P}(b|a)} b$

(b) $|a\rangle \xrightarrow{\mathbf{A}_{a \to b}} |b\rangle$

(a)
$$|\chi\rangle \xrightarrow{\ \gamma\ } |\chi\rangle$$

(b)
$$|\chi\rangle \xrightarrow{\ \gamma\ } |\chi\rangle^{(1)} \xrightarrow{\ \gamma\ } |\chi\rangle \qquad \Rightarrow |\chi\rangle \xrightarrow{\ \gamma_{(S)} = \gamma^2\ } |\chi\rangle$$

(c)
$$|\chi\rangle \xrightarrow{\ \gamma\ } \{ |\chi\rangle^{(1)} \xrightarrow{\ \gamma\ } |\chi\rangle^{(2)} \} \xrightarrow{\ \gamma\ } |\chi\rangle \qquad \Rightarrow |\chi\rangle \xrightarrow{\ \gamma_{(D)} = \gamma^3\ } |\chi\rangle$$

....

(d)
$$|\chi\rangle \xrightarrow{\ \gamma\ } \{ |\chi\rangle^{(1)} \xrightarrow{\ \gamma\ } \cdots \xrightarrow{\ \gamma\ } |\chi\rangle^{(t)} \} \xrightarrow{\ \gamma\ } |\chi\rangle \qquad \Rightarrow |\chi\rangle \xrightarrow{\ \gamma_{(t)} = \gamma^{t+1}\ } |\chi\rangle$$
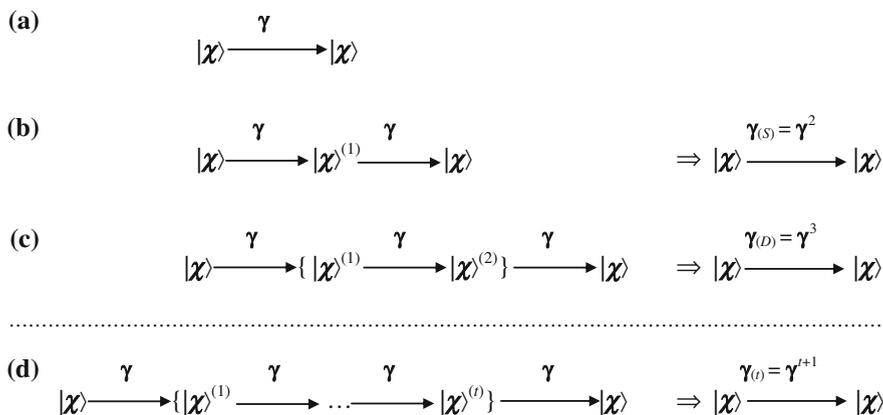
Fig. 2 Hierarchy of the amplitude channels between the AO states $|\chi\rangle$, the basis set of molecular cal-culations: direct communications (**a**); *single* (*S*)-AO bridges $|\chi\rangle_{(1)} \equiv \chi^{(1)}$ (**b**); *double* (*D*)-AO bridges $|\chi\rangle_{(2)} \equiv \{|\chi\rangle^{(1)} \rightarrow |\chi\rangle^{(2)}\}$ (**c**); *t*-AO bridges $|\chi\rangle_{(t)} \equiv \{|\chi\rangle^{(1)} \rightarrow |\chi\rangle^{(2)} \rightarrow \cdots \rightarrow |\chi\rangle^{(t)}\}$ (**d**). The resultant amplitudes of such *multi*-step propagations are shown to be proportional to consecutive powers of the CBO (density) matrix $\boldsymbol{\gamma}$: $\mathbf{A}_{(t)} = \left\{ A_{i \rightarrow j}^{(t)} \right\} \propto \boldsymbol{\gamma}_{(t)} = \boldsymbol{\gamma}^{t+1}$

which conditions 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 typi-cal accumulation of valence electrons in the region between the two nuclei, called the bond-charge, due to the constructive interference between the two functions contrib-uted by AIM. For more distant bond partners such an accumulation of valence electrons can be absent, e.g., in the cross-ring π-interactions in benzene or between the bridge-head carbon atoms in small propellanes [1,2,13–15]. Such bonding interaction lacking an accumulation of the bond-charge (information) can be realized *indirectly*, through the neighboring AO intermediaries forming a "bridge" for an effective interaction between distant ("terminal") AO. 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. These dependencies are due to the orthonormality relations involving the bonding sub-space of the occupied MO, which determine the entire framework of chemical bonds in the molecule.

This work examines the generalized (*consecutive*) bridges (see Fig. 2) for the AO probability propagation in molecules, which involve the (*parallel*) set of all basis func-tions at each scattering step. In other words, any propagation stage involves all AO inputs, each communicating with all AO outputs (Fig. 1). We develop the operator representation of the AO communications in molecules and examine the interference effects accompanying the multiple probability scatterings in the amplitude informa-tion channels involving the generalized AO bridges. The superposition principle is established for amplitudes of the conditional probabilities determining such through-bridge information propagation in molecules. The idempotency of the density matrix is then used to show that such generalized probability scatterings conserve the stationary

distribution of molecular communications, thus demonstrating the internal consistency of OCT as quantum theory of the molecular electronic structure.

2 Probability scattering states and stationary communication modes

Let us summarize the direct probability scattering of Fig. 1 in the standard SCF MO theory. For simplicity we assume the *closed*-shell ground-state configuration of $N = 2n$ electrons in the standard spin-*Restricted Hartree–Fock* (RHF) description, which involves n lowest, *doubly*-occupied (orthonormal) MO. In this orbital approximation the network of chemical bonds is thus fully determined by this occupied subspace $\boldsymbol{\varphi}^o$ of MO. In the LCAO MO approach they are generated as linear combinations of the (Löwdin-orthogonalized) AO, $\boldsymbol{\chi} = \{\chi_i\}$, $\langle \boldsymbol{\chi} \mid \boldsymbol{\chi} \rangle = \{\delta_{i,j}\} \equiv \mathbf{I}$, contributed by the system constituent atoms:

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

Here, the rectangular matrices $\mathbf{C}^o = \langle \boldsymbol{\chi} \mid \boldsymbol{\varphi}^o \rangle$ and $\mathbf{C}^v = \langle \boldsymbol{\chi} \mid \boldsymbol{\varphi}^v \rangle$ 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 $\boldsymbol{\varphi}^o$,

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

subsequently determine the CBO matrix $\boldsymbol{\gamma}$:

$$\boldsymbol{\gamma} = 2\langle\boldsymbol{\chi}|\hat{\mathrm{P}}^o_\varphi|\boldsymbol{\chi}\rangle = 2(\langle\boldsymbol{\chi}|\hat{\mathrm{P}}^o_\varphi)(\hat{\mathrm{P}}^o_\varphi|\boldsymbol{\chi}\rangle) = 2\langle\boldsymbol{\chi}^b|\boldsymbol{\chi}^b\rangle \equiv 2\mathbf{d}, \quad (3)$$

and the *bond-overlap* matrix $\mathbf{d} = \langle\boldsymbol{\chi}|\boldsymbol{\varphi}^o\rangle\langle\boldsymbol{\varphi}^o|\boldsymbol{\chi}\rangle = \mathbf{C}^o\mathbf{C}^{o\dagger} = \langle\boldsymbol{\chi}^b|\boldsymbol{\chi}^b\rangle$. The CBO matrix constitutes the AO representation of the projection operator $\hat{\mathrm{P}}^o_\varphi$ onto the bond subspace $\boldsymbol{\varphi}^o$, thus satisfying the associated idempotency relations,

$$\boldsymbol{\gamma}^2 = 4\langle\boldsymbol{\chi}^b|\boldsymbol{\chi}^b\rangle\langle\boldsymbol{\chi}^b|\boldsymbol{\chi}^b\rangle = 4\langle\boldsymbol{\chi}^b|\boldsymbol{\chi}^b\rangle = 2\boldsymbol{\gamma} \quad \text{or} \quad (4a)$$
$$\mathbf{d}^2 = \langle\boldsymbol{\chi}^b|\boldsymbol{\chi}^b\rangle\langle\boldsymbol{\chi}^b|\boldsymbol{\chi}^b\rangle = \langle\boldsymbol{\chi}^b|\boldsymbol{\chi}^b\rangle = \mathbf{d}, \quad (4b)$$

and hence:

$$\boldsymbol{\gamma}^n = 2^{n-1}\boldsymbol{\gamma} \quad \text{or} \quad \mathbf{d}^n = \mathbf{d}, \quad n > 2. \quad (4c)$$

The CBO matrix $\boldsymbol{\gamma} = N\langle\boldsymbol{\chi}|\hat{\mathrm{D}}^o_\varphi|\boldsymbol{\chi}\rangle \equiv N\mathbf{D}^o_\varphi$ is thus proportional to the AO representation $\mathbf{D}^o_\varphi$ of the Hermitian density operator defining the bond *ensemble* generated by all occupied MO:

$$\hat{D}_{\varphi}^{o} = \sum_{s=1}^{n} |s\rangle \, p_s \, \langle s| = \frac{1}{n} \hat{P}_{\varphi}^{o} = \frac{1}{N} |\chi\rangle \, \boldsymbol{\gamma} \, \langle \chi|. \tag{5}$$

This matrix reflects the promoted, *valence* state of AO in the molecule, with the diagonal elements measuring the effective electron occupations of these basis functions, $\{N_i = \gamma_{i,i} = 2\langle i_b | i_b \rangle = N p_i\}$, tr$\boldsymbol{\gamma} = N$, with the probabilities $\boldsymbol{p} = \{p_i = \gamma_{i,i}/N\}$ of the basis functions occupancy in molecule. The *off*-diagonal CBO elements between AO on different atoms similarly reflect the bonding status of the *direct* chemical interaction of the specified AO pair in the molecule, with the positive (negative) values signifying the resultant bonding (*anti*-bonding) coupling between the two basis functions in question, and the vanishing bond-order $\gamma_{i,j} = 2\langle i_b | j_b \rangle = 0$ identifying their directly *non*-bonding chemical interaction, when $|i_b\rangle = 0$ or $|j_b\rangle = 0$. Thus, the "constructive" (bonding) interference between two AO, the basis functions of SCF MO calculations, implies the positive (*in phase*) product of their direct bond-projections, while its negative (*out of phase*) 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 [7–12], the key concept of OCT, 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 [1–4]. Due to 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 (direct) conditional probabilities of the "outputs-given-inputs",

$$\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \left\{ P(j|i) = \left(2\gamma_{i,i}\right)^{-1} \gamma_{i,j}\gamma_{j,i} = \left(2\gamma_{i,i}\right)^{-1} |\gamma_{i,j}|^2 \right.$$
$$\left. = \left(d_{i,i}\right)^{-1} |d_{i,j}|^2 \equiv A_{i \to j} A_{i \to j}^{*} = |A_{i \to j}|^2 \right\}, \tag{6}$$

where the normalization constant results from the requirement $\sum_j P(j|i) = 1$. They have been determined [9] from the superposition principle of quantum mechanics [16] supplemented by the "physical" projection onto the bond subspace of the occupied MO. The preceding equation also introduces the quantum-mechanical *amplitude* $A(j|i) \equiv A_{i \to j}$ associated with the conditional probability $P(j|i)$. It is seen to be determined by the corresponding (renormalized) element of the CBO/density matrix,

$$A_{i \to j} = \gamma_{i,j}/\sqrt{2\gamma_{i,i}} \equiv \gamma_{i,j} N_{i \to j} = d_{i,j}/\sqrt{d_{i,i}}, \quad |A_{i \to j}| \leq 1, \tag{7}$$

since $|\langle i_b | j_b \rangle| \leq \langle i_b | i_b \rangle$.

The (*non*-Hermitian) matrix $\mathbf{A}_{a \to b} = \{A_{i \to j}\}$ of all "*forward*" (*input* → *output*) communications then determines the AO scattering states of the amplitude channel of Fig. 1b. It can be viewed as the AO representation of the associated communication operator $\hat{A} \equiv \hat{A}(a \to b) : \mathbf{A}_{a \to b} \equiv \langle b | \hat{A} | a \rangle$. Therefore, the input states scattered into the channel output read:

$$\hat{A} | a \rangle = \mathbf{A}_{a \to b} | a \rangle. \tag{8}$$

The Hermitian conjugate matrix $(\mathbf{A}_{a \to b})^\dagger = \{A_{j \to i}\}$, $\hat{A}^\dagger \equiv \hat{A}_{(b \to a)}$, then combines the AO amplitudes of the "*reverse*" (*output* → *input*) probability propagations, with the conjugate operator generating the output states scattered into the channel input:

$$\hat{A}^\dagger | b \rangle = \mathbf{A}_{b \to a} | b \rangle. \tag{9}$$

These directed-scattering operators can be combined into the symmetrized (Hermitian) communication operator of AO amplitudes:

$$
\begin{aligned}
\hat{B} &= 1/2(\hat{A} + \hat{A}^\dagger) = 1/2[\hat{A}(a \to b) + \hat{A}(b \to a)] \quad \text{or} \\
\mathbf{B} &= \langle \boldsymbol{\chi} | \hat{B} | \boldsymbol{\chi} \rangle = 1/2(\mathbf{A}_{a \to b} + \mathbf{A}_{b \to a}).
\end{aligned} \tag{10}
$$

Its eigenvalue (diagonalization) problem then determines the decoupled modes $| \boldsymbol{\psi} \rangle = | \boldsymbol{\chi} \rangle \mathbf{D}$ of the information propagation between AO:

$$\hat{B} | \boldsymbol{\psi} \rangle = \boldsymbol{\lambda} | \boldsymbol{\psi} \rangle, | \boldsymbol{\psi} \rangle = \{| \psi_\alpha \rangle\}, \quad \langle \boldsymbol{\psi} | \hat{B} | \boldsymbol{\psi} \rangle = \boldsymbol{\lambda} = \{\lambda_\alpha \delta_{\alpha, \beta}\}, \tag{11a}$$

or

$$\mathbf{D}^\dagger \mathbf{B} \mathbf{D} = \boldsymbol{\lambda}, \quad \mathbf{D} = \langle \boldsymbol{\chi} | \boldsymbol{\psi} \rangle. \tag{11b}$$

The stationary states $\{| \psi_\alpha \rangle\}$ combine the forward and reverse probability scatterings into the corresponding (delocalized) "standing waves" of AO communications in molecules, with the eigenvalues $\{\lambda_\alpha\}$ providing the *principal* propagation amplitudes of the associated (diagonal) spectral resolution of the AO-communication operator:

$$\hat{B} = | \boldsymbol{\psi} \rangle \boldsymbol{\lambda} \langle \boldsymbol{\psi} | = \sum_\alpha | \psi_\alpha \rangle \lambda_\alpha \langle \psi_\alpha |. \tag{12}$$

The conditional-probability amplitude of Eq. 7 determines the associated scattered state

$$| i \to j \rangle = | i \rangle + A_{i \to j} | j \rangle, \tag{13}$$

for the unit probability of the incident input state $|i\rangle$. Accordingly, the scattering state originating from the output state $|j\rangle$ reads:

$$|j \to i\rangle = |j\rangle + A_{j \to i}|i\rangle. \tag{14}$$

These equations thus identify the forward and reverse propagation amplitudes as the scalar products of the corresponding scattering states and the relevant final ("detection") AO state:

$$A_{i \to j} = \langle j|i \to j\rangle \quad \text{and} \quad A_{j \to i} = \langle i|j \to i\rangle. \tag{15}$$

In this interpretation the elementary conditional probabilities $P(j|i) = P_{i \to j}$ and $P(i|j) = P_{j \to i}$ of the specified forward and reverse conditional events represent the expectation values of the corresponding projection operators:

$$
\begin{aligned}
P(j|i) &= |A_{i \to j}|^2 = \langle j|i \to j\rangle\langle i \to j|j\rangle \equiv \langle j|\hat{P}_{i \to j}|j\rangle \\
&= \langle i \to j|j\rangle\langle j|i \to j\rangle \equiv \langle i \to j|\hat{P}_j|i \to j\rangle, \\
P(i|j) &= |A_{j \to i}|^2 = \langle i|j \to i\rangle\langle j \to i|i\rangle \equiv \langle i|\hat{P}_{j \to i}|i\rangle \\
&= \langle j \to i|i\rangle\langle i|j \to i\rangle \equiv \langle j \to i|\hat{P}_i|j \to i\rangle.
\end{aligned}
\tag{16}
$$

Thus, the AO conditional probabilities in the molecular bond system can be interpreted as the expectation value in the relevant scattering state of the projection operator onto the detection AO state in question. Alternatively, these probabilities are seen to determine the expectation values in the reference detection state of the projection operators onto the scattering state.

3 Multiple probability scatterings and their interference

The conditional probabilities of Eq. 5 describe the delocalized electrons in the molecular bond system and originate from the standard (Slater determinant) wave function of the molecule in the adopted MO approximation. This stationary distribution must effectively combine contributions from both the direct and generalized indirect probability propagations between AO. It is therefore vital for the internal consistency of OCT to show that an inclusion of the generalized through-bridge communications preserves the molecular conditional probabilities of AO. Such a demonstration is the main goal of this section.

We recall that in the Born (statistical) interpretation of quantum mechanics the state probability distribution is given by the squared modulus of the corresponding (complex-valued) amplitude, the system wave function. This wave function "power" is then interpreted as the probability density over the representation elementary events. Thus, it is the superposition of the wave-functions (quantum states) that gives rise to the interference of *micro*-objects. Therefore, it is both natural and indeed compulsory that in the reconstruction of the underlying AO communications behind the stationary (ground-state) probability distribution *via* the multiple probability propagations

between the basis functions one must insist on the *wave* character of such elementary molecular communications, which are capable of the interference.

Indeed, the classical combination rules of conditional probabilities determining the molecular communications between AO would fail to reconstruct this molecular probability distribution and the underlying wave function (probability amplitude) of the system as a whole. Instead, one must combine the AO probability amplitudes in order to recover the stationary probabilities of Eq. 5. The amplitudes of such elementary steps of the information propagations between AO have been shown to be proportional to the corresponding elements of the CBO matrix, which exhibit both positive and negative values, thus being perfectly capable of both the constructive and destructive interference in the scattering states of Eqs. 13 and 14.

Consider the generalized through-bridge (forward) probability propagations $\{i \rightarrow j\}$ of Fig. 2. Each output in the *direct* information network of Fig. 2a can subsequently emit the signal to any of the system basis functions in the sequential cascade of Fig. 2b, in which the events of the secondary output are linked to the original input *via* all *single(S)*-AO intermediates $\chi^{(1)}$. This intermediate scattering can be repeated still further, e.g., by adding the *double(D)*-AO bridges $\chi_{(2)} \equiv \{\chi^{(1)} \rightarrow \chi^{(2)}\}$, additionally including the AO intermediates $\chi^{(2)}$ in the sequential cascade of Fig. 2c, or in general t-AO bridges $\chi_{(t)} \equiv \{\chi^{(1)} \rightarrow \chi^{(2)} \rightarrow \cdots \rightarrow \chi^{(t)}\}$ shown in Panel *d* of the figure. In principle, this order of the intermediate probability propagation can be extended to infinity, $t \rightarrow \infty$, with the combined effect of all propagation orders $t = 0, 1, 2, \ldots$, where $t = 0$ corresponds to the direct molecular communications, eventually establishing the stationary molecular communications between AO. Examining this overall interference is the main purpose of this section. In this multi-scattering perspective the stationary distribution of electronic probabilities in molecular systems is thus seen as the net result of all such elementary (multiple) probability propagations, in which the communications $i \rightarrow j$ between two specified basis functions effectively involve bridges of all orders.

In the *classical* sequential cascade of several information channels the resultant conditional probability matrix between the initial input and the final output is given by the product of conditional probabilities of all constituent *sub*-channels [14,17]. As we have argued above, this classical combination rule would fail to reconstruct the molecular distributions of electrons, quantum particles capable of interference, since inclusion of such products does not conserve the molecular probability distribution of the direct AO communications. For such *micro*-objects one has to propagate the probability amplitudes at each bridge order (see Fig. 2) and then determine the effective amplitude due to interference of amplitudes from all orders t. In determining the overall effect of the superposition of the scattering states corresponding to all bridge orders one has to add the resultant amplitudes for each order.

The generalization of the amplitude for the direct conditional-probability propagation (Eqs. 13, 14) into the bridge propagations [13], *via* the sequential sets of all AO used in SCF MO calculations (see Fig. 2), involves the corresponding powers of the projection operator onto the bonding subspace. For example, the amplitude for the communication $i \rightarrow j$ through the bridge order t (see Fig. 2d) reads:

$$A_{i\to j}^{(t)} = N_{i\to j}^{(t)} \langle i|\hat{P}_{\varphi}^{o}\rangle \left(\hat{P}_{\varphi}^{o}\right)^{t} (\hat{P}_{\varphi}^{o}|j\rangle = \left[N_{i\to j}^{(t)}/2^{t+1}\right] (\gamma^{t+1})_{i,j}$$
$$= N_{i\to j}^{(t)} \langle i^{b}|(\hat{P}_{\varphi}^{o})^{t}|j^{b}\rangle \equiv N_{i\to j}\langle i^{b}|j^{b}\rangle = A_{i\to j}, \qquad (17)$$

since by the idempotency of the bond projection $(\hat{P}_{\varphi}^{o})^{m} = \hat{P}_{\varphi}^{o}$ and $\hat{P}_{\varphi}^{o}|j^{b}\rangle = |j^{b}\rangle$ and $\hat{P}_{\varphi}^{o}|i^{b}\rangle = |i^{b}\rangle$. Thus, at each order of the through-bridge scattering involving the entire set of AO the amplitude for the representative propagation $i \to j$ stays the same as in the direct propagation.

Therefore, the resultant amplitude from the interference of all bridge-orders, the normalized linear combination of amplitudes generated at each bridge order, is identical with the direct amplitude, which generates the stationary conditional-probability distribution in the molecule:

$$A_{i\to j}^{res.} = \sum_{m=0}^{\infty} C^{(m)} A_{i\to j}^{(m)} = A_{i\to j}, \quad \sum_{m=0}^{\infty} \left|C^{(m)}\right|^{2} = 1. \qquad (18)$$

Hence, the square of the modulus of the amplitudes thus obtained, reflecting the net effect of the amplitude superposition at all bridge orders, generates the stationary molecular probability. Indeed, in accordance with the quantum superposition principle any combination of the state with itself represents the same state of the system.

We thus conclude, that the interference of the quantum amplitudes for the generalized conditional probabilities of AO, resulting from the multiple through-bridge scatterings at each stage involving *all* basis functions, do not alter the stationary communications resulting from the direct information scattering in the molecular ground-state. This explicitly demonstrates the internal consistency of OCT as the *quantum* theory of molecular electronic structure.

4 Conclusion

The quadratic indices of the chemical bond multiplicity [18–28] and the IT descriptors of the bond order [5–8], as well as their through-bridge generalizations [13,14] are related to molecular probabilities, squares of the corresponding quantum amplitudes. However, in an attempt to reconstruct such stationary probability distributions from generalized probability scatterings between the elementary AO events one has to superpose the corresponding communication amplitudes. In this work we have examined such interference effects of the information propagation in molecules. The operator representation of such processes has facilitated the vector interpretation of amplitudes of the forward and reverse scattering states, eventually leading to the establishment of the independent modes (standing ways) of the molecular conditional-probability propagation between basis functions of SCF MO calculations, linked to the eigenvalue problem of the associated AO-communication operator.

The interference of amplitudes of the generalized, multiple scatterings through all basis functions at arbitrary bridge-order has also resolved the apparent paradox that in quantum mechanics the resultant effect of the superposition of such scattering

states must ultimately recover the stationary conditional probability distribution of the molecular ground-state. This consistency requirement is not satisfied when the bridge conditional probabilities are determined classically, as products of probabilities of each consecutive *sub*-channel. Only the wave-like superposition of the sub-channel scattering amplitudes was explicitly shown to satisfy this stationary condition at any bridge order. The idempotency of the molecular density matrix was shown to be vital for the fulfillment of this conditional-probability preservation principle. This demonstrates that OCT provides the internally-consistent *quantum* description of the molecular electronic structure and AO communications provided that the elementary scattering amplitudes are superimposed, rather than probabilities.

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