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Quantum information description of reactive systems

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Information Theory (IT) of molecular electronic states is applied to describe equilibria in separate reactants and reactive system as a whole. It uses the resultant (quantum) measures of the information content in electronic states, determined by both the classical (probability/density) functionals and their non-classical (phase/current)-related complements. The intra-reactant (fragment) equilibrium state in the separate reactant is uniquely characterized by its equilibrium phase related to its own electron distribution, while the inter-reactant (molecular) equilibrium state reflects the stationary electron density of the whole reactive system. The probability currents of the non-bonded reactants, e.g., the isolated fragments or their mutually-closed analogs in the system "promolecular" reference, and of the bonded (mutually-open) fragments in the whole reactive system, are compared to identify the current-promotion of these subsystems. The illustrative case of the two-orbital (2-electron) system is examined in some detail to generate the combination formula for the overall current and to identify its additive and non-additive components. Electron communications between reactants are examined and IT descriptors of the multiplicity and covalent/ionic composition of chemical bonds are related to the additive and non-additive information contributions in local and atomic orbital resolutions.

Keywords: Communication systems, Current promotion of reactants, Electronic communications in molecules, Information theory, Molecular information channels, Probability currents, Quantum information measures, Reactive systems

The classical Information Theory (IT)[1-8] has been recently applied to explore the electron distributions and chemical bonds in molecules (see Refs 9-15). However, both the electron density, or its shape factor - the probability distribution determined by the wave-function modulus, and the system current distribution, related to the gradient of the wave-function phase, must ultimately contribute to the resultant information content of the molecular electronic state[16-21]. The particle density only reveals the classical information content, while the probability current generates its non-classical complement in the resultant quantum information measures.

In this work we focus on the phase/current descriptors of electronic states in reactive systems. In particular, we examine the current characteristics of the reactant promotion at typical stages of a chemical reaction in representative bimolecular systems. We shall explore implications of the recent results on molecular (horizontal) equilibria, linking the equilibrium phases of molecular fragments to the electron distribution in the whole composite system they belong to[16-21]. A model two-orbital system will be examined in some detail to derive the current combination formula identifying the relevant additive and non-additive contributions. The electronic communications between bonded reactants will be used to determine the inter-rectant IT bond multiplicities and their covalent (communication noise) and ionic (information flow) components.

The following tensor notation is used: A denotes a scalar quantity, $\boldsymbol{A}$ stands for the row- or column-vector, and $\mathbf{A}$ represents a square or rectangular matrix. The logarithm of the Shannon-type 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.

Quantum Complements of Classical Entropy/ Information and Molecular Equilibria

Consider the molecular electron density $(\boldsymbol{r}) = Np(\boldsymbol{r})$ or its shape (probability) factor $p(\boldsymbol{r}) = [A(\boldsymbol{r})]^2$, the square of the distribution classical amplitude $A(\boldsymbol{r})$. Here N stands for the system overall number of electrons. In the simplest case of a single electron in the (complex) state,

$$\vartheta(\boldsymbol{r}) = R(\boldsymbol{r}) \exp[\mathrm{i}\Phi(\boldsymbol{r})] = \vartheta[R, \Phi; \boldsymbol{r}] \qquad ...(1)$$

the modulus part $R(\boldsymbol{r})$ represents the amplitude $A(\boldsymbol{r})$ of probability distribution,

$$p(\boldsymbol{r}) = \vartheta^*(\boldsymbol{r})\ \vartheta(\boldsymbol{r}) = R(\boldsymbol{r})^2; \quad \int p(\boldsymbol{r})\ d\boldsymbol{r} = 1 \qquad ...(2)$$

while the gradient of its phase component $\Phi(\boldsymbol{r})$ generates the density of probability current.

$$\boldsymbol{j}(\boldsymbol{r}) = \frac{\hbar}{2m\mathrm{i}}[\vartheta^*(\boldsymbol{r})\nabla\vartheta(\boldsymbol{r}) - \vartheta(\boldsymbol{r})\nabla\vartheta^*(\boldsymbol{r})] = \frac{\hbar}{m}\mathrm{Im}[\vartheta^*(\boldsymbol{r})\nabla\vartheta(\boldsymbol{r})] = \frac{\hbar p(\boldsymbol{r})}{m}\nabla\Phi(\boldsymbol{r}) \qquad ...(3)$$

One recalls that the stationary state of energy E_i exhibits the purely time-dependent phase,

$$\vartheta_i(\boldsymbol{r}, t) = \langle \boldsymbol{r}|\vartheta_i(t)\rangle = \vartheta_i(\boldsymbol{r}) \exp[-\mathrm{i}(E_i/\hbar)t] \equiv R_i(\boldsymbol{r}) \exp[-\mathrm{i}\ \ _it] \equiv R_i(\boldsymbol{r}) \exp[\mathrm{i}\,\Phi_i(t)] \qquad ...(4)$$

and hence the vanishing current of Eq. (3).

Both the probability distribution and its phase/current density ultimately contribute to the resultant information content of quantum states[16-21]. The non-classical terms allow one to distinguish between the quantum states exhibiting the same electron density but differing in patterns of their probability currents. The wave-function modulus (amplitude of the particle density/probability distribution) and its phase (or phase-gradient generating the current density) thus constitute two fundamental "degrees-of-freedom" in the complete quantum IT description of the system electronic states: $\vartheta \Leftrightarrow (R, \Phi) \Leftrightarrow (p, \boldsymbol{j})$.

The non-classical, phase-related complement to the classical Shannon entropy (Eq. 5),

$$S^{class.}[\vartheta] = -\int p(\boldsymbol{r}) \log p(\boldsymbol{r})\ d\boldsymbol{r} \equiv S[p] \equiv \int p(\boldsymbol{r})\ S^{class.}(\boldsymbol{r})\ d\boldsymbol{r} \qquad ...(5)$$

where $S^{class.}(\boldsymbol{r}) \equiv S_p(\boldsymbol{r}) = -\log p(\boldsymbol{r})$ measures the density per electron of the classical entropy.

$$S^{nclass.}[\vartheta] = \langle\vartheta|\hat{\mathrm{S}}_\Phi|\vartheta\rangle = -2\int p(\boldsymbol{r})\ [\Phi^2(\boldsymbol{r})]^{1/2}\ d\boldsymbol{r} \equiv -2\int p(\boldsymbol{r})\ [\ \ (\boldsymbol{r})]^{1/2}\ d\boldsymbol{r} \equiv S[p, \Phi] \equiv \int p(\boldsymbol{r})\ S^{nclass.}(\boldsymbol{r})\ d\boldsymbol{r} \qquad ...(6)$$

Here the information density $S^{nclass.}(\boldsymbol{r}) \equiv S_\Phi(\boldsymbol{r}) = -2[\Phi^2(\boldsymbol{r})]^{1/2} = -2\ \ (\boldsymbol{r})^{1/2} = -2|\Phi(\boldsymbol{r})|$ measures the non-classical entropy density per electron. It is seen to be proportional to the local magnitude of the phase function, $|\Phi| = [\Phi^2]^{1/2}$, the square root of the phase-density $\ \ = \Phi^2$, with the particle probability p providing the local "weighting" factor in the associated average functional. Since in quantum mechanics the phase of the wave-function is determined only up to an arbitrary constant, its sign is physically irrelevant. In what follows we thus adopt the positive phase convention $\Phi(\boldsymbol{r}) = |\Phi(\boldsymbol{r})| \geq 0$.

Together these two components generate the overall Shannon-type measure of the quantum indeterminicity content due to both the probability and current distributions in the complex quantum state ϑ[16-21].

$$S[\vartheta] = S^{class.}[\vartheta] + S^{nclass.}[\vartheta] = \int p(\boldsymbol{r})\ S(\boldsymbol{r})\ d\boldsymbol{r}$$

$$S(\boldsymbol{r}) = S_p(\boldsymbol{r}) + S_\Phi(\boldsymbol{r}) \qquad ...(7)$$

The Fisher information for locality events[1,2], called the intrinsic accuracy, provides the complementary (gradient) measure of the classical information content in $\vartheta(\boldsymbol{r})$.

$$I^{class.}[\vartheta] = \int p(\boldsymbol{r})\ [\nabla \ln p(\boldsymbol{r})]^2\ d\boldsymbol{r} \equiv \int p(\boldsymbol{r})\ I_p(\boldsymbol{r})\ d\boldsymbol{r} = I[p] = \int [\nabla p(\boldsymbol{r})]^2/p(\boldsymbol{r})\ d\boldsymbol{r} = 4\int [\nabla A(\boldsymbol{r})]^2\ d\boldsymbol{r} \equiv I[A]$$

$$I_p(\boldsymbol{r}) = [\nabla \ln p(\boldsymbol{r})]^2 = [\nabla p(\boldsymbol{r})/p(\boldsymbol{r})]^2 = 4[\nabla R(\boldsymbol{r})]^2 \qquad ...(8)$$

The classical-amplitude form $I[A]$ of this functional is naturally generalized into the domain of complex probability amplitudes (wave functions) of molecular quantum mechanics[22].

$$I[\vartheta] = 4\int |\nabla\vartheta(\boldsymbol{r})|^2\ d\boldsymbol{r} = \frac{8m}{\hbar^2}\,T[\vartheta] \qquad ...(9)$$

This overall quantum functional of the gradient information content is related to the expectation value of the system electronic kinetic energy.

$$T[\vartheta] \equiv T[\vartheta] \equiv \langle\vartheta|\hat{\mathrm{T}}|\vartheta\rangle = -\frac{\hbar^2}{2m}\int \vartheta^*(\boldsymbol{r})\Delta\vartheta(\boldsymbol{r})\,d\boldsymbol{r} = \frac{\hbar^2}{2m}\int |\nabla\vartheta(\boldsymbol{r})|^2 d\boldsymbol{r} \qquad ...(10)$$

Therefore, the overall quantum determinicity Fisher information separates into the classical term of Eq. (8) and the associated non-classical complement,

$$I[\vartheta] = I^{class.}[\vartheta] + I^{nclass.}[\vartheta] \equiv \int p(\boldsymbol{r})\,[I^{class.}(\boldsymbol{r}) + I^{nclass.}(\boldsymbol{r})]\ d\boldsymbol{r} = I[p] + 4\int p(\boldsymbol{r})\,[\nabla\Phi(\boldsymbol{r})]^2\,d\boldsymbol{r} \equiv I[p] + I[p, \Phi] = I[p] + 4\left(\frac{m}{\hbar}\right)^2 \int \frac{\boldsymbol{j}^2(\boldsymbol{r})}{p(\boldsymbol{r})}\,d\boldsymbol{r} \equiv I[p] + I[p, \boldsymbol{j}] \qquad ...(11)$$

where the relevant information densities-per-electron is given as

$$I^{class.}(\boldsymbol{r}) = [\nabla p(\boldsymbol{r})/p(\boldsymbol{r})]^2 = 4[\nabla R(\boldsymbol{r})]^2$$
$$I^{nclass.}(\boldsymbol{r}) = 4(m/\hbar)^2[\boldsymbol{j}(\boldsymbol{r})/p(\boldsymbol{r})]^2 = 4[\nabla \Phi(\boldsymbol{r})]^2 \qquad ...(12)$$

Both the classical and *non*-classical densities-per-electron of the complementary Shannon and Fisher measures of the quantum information content are mutually related via the common-type dependence[16-21].

$$I^{class.}(\boldsymbol{r}) = [\nabla \ln p(\boldsymbol{r})]^2 = [\nabla S^{class.}(\boldsymbol{r})]^2$$

and

$$I^{nclass.}(\boldsymbol{r}) = \left(\frac{2m\,\boldsymbol{j}(\boldsymbol{r})}{\hbar p(\boldsymbol{r})}\right)^2 \equiv [\nabla S^{nclass.}(\boldsymbol{r})]^2 \qquad ...(13)$$

The extremum of the resultant (quantum) entropy content combining both the classical and non-classical contributions, subject only to the "geometric" constraint of the wave-function normalization,

$$\Delta\{S[\vartheta] - \ \langle\vartheta|\vartheta\rangle\} = \Delta\{\int \vartheta^*(\boldsymbol{r})[S(\boldsymbol{r}) - \ ]\,\vartheta(\boldsymbol{r})\, d\boldsymbol{r} = 0 \qquad ...(14)$$

give the equilibrium phase related to the system probability distribution[16-21]. The arbitrary variations $\{\Delta\vartheta^*(\boldsymbol{r})\}$ then imply $S(\boldsymbol{r}) - \ = 0$, or

$$\Phi_{eq.}[\boldsymbol{r}; p] = -(½)\ln p(\boldsymbol{r}) \equiv \Phi_{eq.}(\boldsymbol{r}) \qquad ...(15)$$

and hence

$$\vartheta_{eq.}[\boldsymbol{r}; p] = R(\boldsymbol{r}) \exp[\mathrm{i}\,\Phi_{eq.}(\boldsymbol{r})]$$
$$= R(\boldsymbol{r}) \exp[-\mathrm{i}(½)\ln p(\boldsymbol{r})] \equiv \vartheta_{eq.}(\boldsymbol{r}) \qquad ...(16)$$

We call such states the molecular phase-equilibria. Notice that the resultant equilibrium entropy $S[\vartheta]$ exactly vanishes: $S[\vartheta] = S^{class.}[\vartheta] + S^{nclass.}[\vartheta] = 0$. Also, for the given stationary probability distribution $p_i = |\vartheta_i|^2 = R_i^2$ in ϑ_i [Eq. (4)], one reaches the maximum value of $S[p_i, \Phi] = 0$ for the stationary-state solution $\Phi = 0$, i.e., $\vartheta_i = R_i$.

To summarize this illustrative one-electron development, the square of the gradient of the local Shannon probe in the state resultant quantum "indeterminicity" (disorder) generates the density of the corresponding Fisher measure of the state quantum "determinicity" (order). The system electron distribution, related to the wave-function modulus, reveals the probability (classical) aspect of the molecular information content, while the phase (current) facet of the molecular state gives rise to the specifically quantum (non-classical) entropy/information terms.

An appropriate generalization to many-electron case[18-21] is effected using the determinantal wave-functions for the specified (or p) of Harriman[23], Zumbach & Maschke[24] (HZM), used in the Levy[25] definition of the universal density functional for the sum of molecular kinetic and repulsion energies of N electrons. This construction has used crucial insights due to Macke[26] and Gilbert[27]. It introduces the complete set of the density-conserving Slater determinants build using the (plane-wave)-type equidensity orbitals.

$$\{\vartheta_{\boldsymbol{k}}(\boldsymbol{r}) = R(\boldsymbol{r}) \exp[\mathrm{i}\,\Phi_{\boldsymbol{k}}(\boldsymbol{r})]\} \qquad ...(17)$$

These orbitals adopt equal, density-dependent modulus part $R(\boldsymbol{r}) = p(\boldsymbol{r})^{1/2}$ and the spatial phase,

$$\Phi_{\boldsymbol{k}}(\boldsymbol{r}) = \boldsymbol{k}\cdot\boldsymbol{f}(\boldsymbol{r}) + \Phi(\boldsymbol{r}) \equiv F_{\boldsymbol{k}}(\boldsymbol{r}) + \Phi(\boldsymbol{r}) \qquad ...(18)$$

with the density-dependent vector function $\boldsymbol{f}(\boldsymbol{r}) = \boldsymbol{f}[\boldsymbol{r};p]$, common to all equidensity orbitals, linked to the Jacobian of the $\boldsymbol{r}\rightarrow\boldsymbol{f}(\boldsymbol{r})$ transformation. The optimum HZM orbitals for the specified ground-state probability distribution $p_0(\boldsymbol{r}) = [R_0(\boldsymbol{r})]^2$,

$$\vartheta_{\boldsymbol{k}}(\boldsymbol{r}) = [p_0(\boldsymbol{r})]^{1/2} \exp\{\mathrm{i}[\boldsymbol{k}\cdot\boldsymbol{f}[\boldsymbol{r}; p_0] + \Phi(\boldsymbol{r})]\}$$
$$\equiv R_0(\boldsymbol{r}) \exp(\mathrm{i}\,\Phi_{\boldsymbol{k}}[\boldsymbol{r}; p_0]) \equiv \vartheta_{\boldsymbol{k}}[\boldsymbol{r}; p_0] \qquad ...(19)$$

are shaped by the "orthogonality" phase $F_{\boldsymbol{k}}[\boldsymbol{r}; p_0] = \boldsymbol{k}\cdot\boldsymbol{f}[\boldsymbol{r}; p_0]$, with the wave-vector (reduced momentum) $\boldsymbol{k}$ and the the density-dependent spatial vector field $\boldsymbol{f}_0(\boldsymbol{r}) = \boldsymbol{f}[\boldsymbol{r}; p_0]$ resulting from the ordinary variational principle for the system minimum electronic energy, e.g., in the familiar Self-Consistent Field (SCF) theories.

The optimum form of the remaining part $\Phi(\boldsymbol{r})$ of $\Phi_{\boldsymbol{k}}(\boldsymbol{r})$, common to all orbitals and called the "thermodynamic" phase, results from the extremum (maximum) principle of the quantum entropy, for the given ground-state density $_0$ or the associated probability distribution p_0 determined at the energy optimization stage. The result recovers Eq. (15) thus confirming its validity for general systems. These equilibrium thermodynamic phases of orbitals then imply the resultant current of N electrons[18,19],

$$\boldsymbol{j}[\boldsymbol{r}; \Phi_{eq.}[p_0]] = N\frac{\hbar p_0(\boldsymbol{r})}{m}\nabla\Phi_{eq.}[p_0;\boldsymbol{r}]$$
$$= -\frac{\hbar}{2m}\nabla\ _0(\boldsymbol{r}) \qquad ...(20)$$

with the orthogonality phases $\{F_k(\boldsymbol{r})\}$ contributing the vanishing overall contribution. Therefore, in the system phase-equilibrium, the average resultant electronic current is completely determined by the molecular electron density $_0$, in agreement with the Hohenberg-Kohn theorem[28].

Phase/Current Promotion of Reactants

This approach to equilibria in molecules and reactive systems offers a new perspective on the promoted states of molecular fragments {M }, e.g., reactants {R = (A, B)}, Atoms-in-Molecules (AIM) {X }, etc., which determine the mutully exclusive pieces { $= N\ p$ }, $N = \int (\boldsymbol{r})d\boldsymbol{r}$, of the system overall density $= Np$ in the isoelectronic molecular (M) or promolecular (M^0) systems as a whole,

$$(\boldsymbol{r}) = \sum (\boldsymbol{r}) = \sum N\ p\ (\boldsymbol{r}) = Np(\boldsymbol{r})$$

or

$$p(\boldsymbol{r}) = \sum (N\ /N)\, p\ (\boldsymbol{r}) \equiv \sum P\ p\ (\boldsymbol{r})$$

$$\sum P = \int p\ (\boldsymbol{r})\, d\boldsymbol{r} = 1, \sum N = N = \sum N^0 = N^0 \qquad ...(21)$$

The (isoelectronic) promolecular system consists of its (molecularly) placed free (non-bonded, mutually closed) fragments.

By linking the equilibrium thermodynamic phase to the system electron distribution (Eq. (15)), one explicitly specifies the molecular/promolecular origins of such subsystems, thus distinguishing the separated fragments, surrounded by an empty space, from their molecular/promolecular analogs[19]. Indeed, the latter represent constituent parts of a larger (composed) system, being surrounded by their respective molecular/promolecular remainders. Thus, the internal equilibrium states of isolated species are fully determined by their own densities alone, while phases of molecular fragments are fixed by the density of a larger, composed system they belong to.

For example, the free (isolated, infinitely separated) reactants $\{R^0(\infty)\}$ exhibiting the ground-state densities,

$$\{\ ^0 = N^0 p^0\},\ N^0 = \text{integer}$$

are characterized by their equilibrium phases,

$$\{\Phi^0_{,eq.}(\infty) = \Phi_{eq.}[\boldsymbol{r}; N^0, p^0]\}$$

while their promolecular analogs, of the same (molecularly placed) densities, correspond to the inter-fragment equalized promolecular phase,

$$\{\Phi^0_{,eq.}(M^0) = \Phi_{eq.}[\boldsymbol{r}; N^0, p^0]\}$$

determined by the overall density or probability distribution of the whole composed system M^0.

$$p^0(\boldsymbol{r}) = \ ^0(\boldsymbol{r})/N^0$$

$$^0(\boldsymbol{r}) = \sum \ ^0(\boldsymbol{r}) = \sum N^0 p^0(\boldsymbol{r}) = N^0 p^0(\boldsymbol{r})$$

or

$$p^0(\boldsymbol{r}) = \sum (N^0/N)\, p^0(\boldsymbol{r}) \equiv \sum P^0 p^0(\boldsymbol{r})$$

$$\sum P^0 = \int p^0(\boldsymbol{r})\, d\boldsymbol{r} = 1 \qquad ...(22)$$

The equilibrium states of molecular fragments, e.g., the bonded (mutually open) reactants {R } corresponding to densities { $(\boldsymbol{r})$}, i.e., the reactant pieces of the molecular ground-state density $_0 = Np_0$, are similarly specified by the equilibrium phase of the whole molecule M, $\{\Phi_{,eq.}(M) = \Phi_{eq.}[\boldsymbol{r}; N, p_0]\}$, determined by the molecular ground-state probability distribution p_0, while the isolated bonded fragments, in an empty space, exhibit the subsystem phases.

$$\{\Phi_{,eq.}(\infty) = \Phi_{eq.}[\boldsymbol{r}; N\ , p\ ]\}$$

Therefore, the present approach provides a full specification of molecular fragments, including both the density/probability distribution of the fragment itself and its equilibrium phase identyfying the composed system from which this subsystem originates. The "frozen", molecularly placed "free" reactants in the promolecular reference $M^0 = A^0$—B^0 of the reactive system M = A—B, are thus phase-promoted compared to their isolated analogs. The promolecule density $^0(\boldsymbol{r})$ then induces the associated local currents in the molecularly placed free reactants $R^0(M^0)$,

$$\boldsymbol{j}^0(M^0) = \frac{\hbar}{m} p^0\, \nabla \Phi^0_{,eq.}(M^0)$$
$$= -\frac{\hbar}{2m}\left(\frac{p^0}{p^0}\right)\nabla p^0 \equiv -\frac{\hbar}{2m} d^0\, \nabla p^0 \qquad ...(23)$$

which differs from the equilibrium current in the isolated reactant $R^0(\infty)$.

$$\boldsymbol{j}^0(\infty) = \frac{\hbar}{m} p^0 \, \nabla \Phi^0_{,eq.}(\infty) = -\frac{\hbar}{2m} \nabla p^0 \qquad ...(24)$$

A similar current-distinction is observed between the equilibrium state of the isolated reactants {R (∞)} and of the corresponding bonded analogs {R (M)}.

$$\boldsymbol{j}\ (\infty) = \frac{\hbar}{m} p\ \nabla \Phi_{,eq.}(\infty) = -\frac{\hbar}{2m} \nabla p$$

$$\boldsymbol{j}\ (\mathrm{M}) = \frac{\hbar}{m} p\ \nabla \Phi_{,eq.}(\mathrm{M})$$

$$= -\frac{\hbar}{2m}\left(\frac{p}{p}\right)\nabla p \equiv -\frac{\hbar}{2m} d^{\mathrm{M}}\, \nabla p \qquad ...(25)$$

The current promotion of R due to bond formation in the reactive system M is thus characterized by the following induced electronic flow in this bonded reactant relative to its isolated status.

$$\Delta \boldsymbol{j}\ (\mathrm{M};\infty) = \boldsymbol{j}\ (\mathrm{M}) - \boldsymbol{j}^0(\infty) = \frac{\hbar}{2m}(\nabla p^0 - d^{\mathrm{M}} \nabla p) \qquad ...(26)$$

Of interest also is the current displacement of the bonded reactant relative to its free analogs in the promolecule of reactive system.

$$\Delta \boldsymbol{j}\ (\mathrm{M};\mathrm{M}^0) = \boldsymbol{j}\ (\mathrm{M}) - \boldsymbol{j}^0(\mathrm{M}^0)$$

$$= \frac{\hbar}{2m}(d^0\, \nabla p^0 - d^{\mathrm{M}}\, \nabla p) \qquad ...(27)$$

Let us finally examine how the current due to the A—B bond formation partitions into its additive (add.) and non-additive (nadd.) components in the reactant resolution of the reactive system density[22]. As an illustration we again consider the simplest two-orbital model of such an inter-reactant chemical bond, in which each reactant contributes a single electron occupying the (complex) reactant orbitals,

$$_{\mathrm{A}}(\boldsymbol{r}) = R_{\mathrm{A}}(\boldsymbol{r}) \exp[\mathrm{i}\Phi_{\mathrm{A}}(\boldsymbol{r})], \qquad _{\mathrm{B}}(\boldsymbol{r}) = R_{\mathrm{B}}(\boldsymbol{r}) \exp[\mathrm{i}\Phi_{\mathrm{B}}(\boldsymbol{r})]$$

generating the corresponding densities and currents of the non-bonded (isolated) species.

$$^0 = p\ ^0 = R\ ^2, \quad \boldsymbol{j}\ ^0 = (\hbar/m)\, p\ \nabla\Phi, \quad = \mathrm{A, B} \qquad ...(28)$$

In the non-bonded reference the molecularly placed orbitals of reactants generate the promolecular density ^{0} and the associated equilibrium phase $\Phi_{eq.}[\boldsymbol{r}; N^0, p^0] \equiv \Phi^0$.

$$^0 = \ _{\mathrm{A}}{}^0 + \ _{\mathrm{B}}{}^0 = 2p^0, \qquad \Phi^0 = -(1/2)\ln p^0 \qquad ...(29)$$

Consider now the chemical bond due to both electrons occupying the bonded combination of two reactant orbitals.

$$\vartheta = 2^{-1/2}[\ _{\mathrm{A}} + \ _{\mathrm{B}}] \qquad ...(30)$$

The associated molecular probability density $p = \ /2$,

$$p = |\vartheta|^2 = (1/2)(p_{\mathrm{A}}{}^0 + p_{\mathrm{B}}{}^0) - (p_{\mathrm{A}}{}^0 p_{\mathrm{B}}{}^0)^{1/2} \cos(\ \ + \vartheta_{\mathrm{M}})$$
$$\equiv R^2 \equiv p^{add.} + p^{nadd.}$$

$$\vartheta_{\mathrm{M}} = \Phi_{\mathrm{A}} - \Phi_{\mathrm{B}} \qquad ...(31)$$

which reflects the resultant modulus factor $R = |\vartheta|$ of the bonding combination of Eq. (30), also identifies the first (additive) and second (non-additive, interference) contributions in this molecular distribution. The resultant phase of the bonding state of Eq. (30),

$$\vartheta = \arctan\left[\frac{R_{\mathrm{A}}\ \sin\vartheta_{\mathrm{A}} + R_{\mathrm{B}}\ \sin\vartheta_{\mathrm{B}}}{R_{\mathrm{A}}\ \cos\vartheta_{\mathrm{A}} + R_{\mathrm{B}}\ \cos\vartheta_{\mathrm{B}}}\right] \qquad ...(32)$$

then generates the resultant current in the bonded system:

$$\boldsymbol{j} = (\hbar/m)\, p\nabla\Phi = (1/2)(\boldsymbol{j}_{\mathrm{A}}{}^0 + \boldsymbol{j}_{\mathrm{B}}{}^0)$$
$$+ (1/2)\{[(p_{\mathrm{B}}{}^0/p_{\mathrm{A}}{}^0)^{1/2}\, \boldsymbol{j}_{\mathrm{A}}{}^0 + (p_{\mathrm{A}}{}^0/p_{\mathrm{B}}{}^0)^{1/2}\, \boldsymbol{j}_{\mathrm{B}}{}^0] \cos\vartheta_{\mathrm{M}}$$
$$+ [(p_{\mathrm{B}}{}^0/p_{\mathrm{A}}{}^0)^{1/2}\nabla p_{\mathrm{A}}{}^0 - (p_{\mathrm{A}}{}^0/p_{\mathrm{B}}{}^0)^{1/2}\, \nabla p_{\mathrm{B}}{}^0] \sin\vartheta_{\mathrm{M}}\}$$

$$\equiv \boldsymbol{j}^{add.} + \boldsymbol{j}^{nadd.} \qquad ...(33)$$

The equal weigting factors in the first, additive component are in fact conditional probabilities of orbitals in their bonding combination: $P(\ _{\mathrm{A}}|\vartheta) = P(\ _{\mathrm{B}}|\vartheta) = 1/2$.

Molecular Communication Systems and Their Bond Descriptors

The Communication Theory of the Chemical Bond (CTCB) uses the orbitally or locally resolved information channels[11-13]. The Atomic Orbital (AO) channel propagates probabilities of electron assignments to the basis functions $\boldsymbol{\chi} = (\ _1,\ \ _2,\ \ldots,\ \ _m)$ of typical SCF LCAO MO calculations, while the local communication network scatters the information between the infinitesimal volume elements $\{d\boldsymbol{r}\}$. The AO set $\boldsymbol{\chi}$ and $\{\boldsymbol{r}\}$ identify the the associated varieties of the mutually exclusive events in the molecular bond system.

The underlying conditional probabilities of the output AO events, given the input AO events, $\mathbf{P}(\chi'|\chi) = \{P(\ _j|\ _i) \equiv P(j|i) \equiv P(i,\ j)/p_i \equiv |A(j|i)|^2\}$, or the associated scattering amplitudes $\mathbf{A}(\chi'|\chi) = \{A(j|i)\}$ of the emitting (input) states $\boldsymbol{a} = |\chi\rangle = \{|\ _i\rangle\}$ among the monitoring/receiving (output) states $\boldsymbol{b} = |\chi'\rangle = \{|\ _j\rangle\}$, which define the AO network, result from the bond-projected superposition principle of quantum mechanics[11-13]; here $P(i,\ j)$ stands for the joint probability of simultaneously observing $\ _i$ and $\ _j$ in the bond system.

The local description (LCT) similarly invokes the basis functions $\{|\boldsymbol{r}\rangle\}$ of the position representation, identified by the continuous labels of spatial coordinates determining current location $\boldsymbol{r}$ of an electron. This complete basis set then determines both the input $\boldsymbol{a} = \{|\boldsymbol{r}\rangle\}$ and output $\boldsymbol{b} = \{|\boldsymbol{r}'\rangle\}$ events of the *local* molecular channel determined by the molecular kernel of conditional-probabilitities: $P(\boldsymbol{r}'|\boldsymbol{r}) = P(\boldsymbol{r},\ \boldsymbol{r}')/p(\boldsymbol{r}) = |A_{\boldsymbol{r}\rightarrow\boldsymbol{r}'}|^2$, where again $P(\boldsymbol{r},\ \boldsymbol{r}')$ denotes the associated joint probability.

Consider the single-configuration approximation of typical Hartree-Fock (HF) or Kohn-Sham (KS) Self-Consistent Field (SCF) calculations, with the occupied Molecular Orbitals (MO) $\boldsymbol{\varphi} = (\vartheta_1,\ \vartheta_2,\ \ldots,\ \vartheta_N)$ expanded in the (orthogonalized) AO basis: $\boldsymbol{\varphi} = \boldsymbol{\chi}\mathbf{C}$; here the column $\boldsymbol{C}_s$ of the unitary matrix $\mathbf{C}$, $\mathbf{C}^\dagger\mathbf{C} = \mathbf{I}$, groups the expansion coefficients of ϑ_s. The bond subspace $\boldsymbol{\varphi}$ is then defined by the MO projector $|\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}|$, which gives rise to the (idempotent) Charge and Bond-Order (CBO) matrix in AO representation.

$$\gamma = \{\ _{i,j}\} = \langle\chi|\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}|\chi\rangle = \mathbf{CC}^\dagger$$

$$\gamma^2 = \mathbf{C}(\mathbf{C}^\dagger\mathbf{C})\mathbf{C}^\dagger = \mathbf{CC}^\dagger = \gamma \qquad ...(34)$$

The molecular joint AO probabilities, of the given pair of the input-output AO in the bond system, are then proportional to the square of the corresponding CBO matrix element.

$$P(\ _i\wedge\ _j) \equiv P(i, j) = \ _{i,j}\ _{j,i}/N = (\ _{i,j})^2/N$$

$$\textstyle\sum_j P(i, j) = N^{-1}\sum_j\ _{i,j}\ _{j,i} = \ _{i,i}/N = p_i \qquad ...(35)$$

The conditional probabilities between AO, $\mathbf{P}(\chi'|\chi) = \{P(\ j|i) = P(i, j)/p_i\}$,

$$P(j|i) = (\ _{i,j})^2/\ _{i,i},\ \textstyle\sum_j P(j|i) = 1 \qquad ...(36)$$

then reflect the electron delocalization throughout all AO used to represent the occupied MO.

This discrete development can be straightforwardly generalized into the ultimate continuous (local) resolution, in which the simultaneous $P(\boldsymbol{r},\boldsymbol{r}')$ and conditional $P(\boldsymbol{r}'|\boldsymbol{r})$ probabilities of observing the input ($\boldsymbol{r}$) and output ($\boldsymbol{r}'$) electron locations in the molecular bond system are determined by the corresponding elements of the (idempotent) 1-electron density matrix.

$$(\boldsymbol{r},\ \boldsymbol{r}') = \langle\boldsymbol{r}|\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}|\boldsymbol{r}'\rangle = \boldsymbol{\varphi}(\boldsymbol{r})\boldsymbol{\varphi}^\dagger(\boldsymbol{r}')$$

$$\int (\boldsymbol{r},\ \boldsymbol{r}')\ (\boldsymbol{r}',\ \boldsymbol{r}'')\ d\boldsymbol{r}' = \ (\boldsymbol{r},\ \boldsymbol{r}'') \qquad ...(37)$$

$$P(\boldsymbol{r},\ \boldsymbol{r}') = N^{-1}\ (\boldsymbol{r},\ \boldsymbol{r}')\ (\boldsymbol{r}',\ \boldsymbol{r})$$

$$\int P(\boldsymbol{r},\ \boldsymbol{r}')\ d\boldsymbol{r}' = N^{-1}\ (\boldsymbol{r},\ \boldsymbol{r}) = p(\boldsymbol{r}) \qquad ...(38)$$

$$P(\boldsymbol{r}'|\boldsymbol{r}) = \ (\boldsymbol{r},\ \boldsymbol{r}')\ (\boldsymbol{r}',\ \boldsymbol{r})/\ (\boldsymbol{r},\ \boldsymbol{r})$$

$$\int P(\boldsymbol{r}'|\boldsymbol{r})\ d\boldsymbol{r}' = 1 \qquad ...(39)$$

In CTCB the entropy/information indices of the covalent/ionic components of the system overall IT-multiplicities of chemical bonds represent the complementary descriptors of the average communication- noise and amount of information-flow, respectively, in the molecular channel. The molecular input $\boldsymbol{P}(\boldsymbol{a}) \equiv \boldsymbol{p}$ generates the same distribution in the output of the AO network, $\boldsymbol{q} = \boldsymbol{p}\ \mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \{\sum_i p_i\,P(j|i) \equiv \sum_i P(i,\ j) = p_j\} = \boldsymbol{p}$, thus identifying $\boldsymbol{p}$ as the stationary vector of AO-probabilities in the molecular ground state. The same applies to local channels.

$$\int p(\boldsymbol{r})\ P(\boldsymbol{r}'|\boldsymbol{r})\ d\boldsymbol{r} = \int P(\boldsymbol{r},\ \boldsymbol{r}')\ d\boldsymbol{r} = p(\boldsymbol{r}')$$

This purely molecular communication channel is devoid of any reference (history) of the chemical bond formation and generates the average noise index of the IT bond-covalency measured by the average conditional-entropy of the system outputs-given-inputs.

$$S(\boldsymbol{P}(\boldsymbol{b})|\boldsymbol{P}(\boldsymbol{a})) = S^{\mathrm{AO}}(\boldsymbol{q}|\boldsymbol{p}) \equiv S^{\mathrm{AO}} = -\textstyle\sum_i\sum_j P(i,\ j)\ \log P(j|i)$$

or

$$S[p(\boldsymbol{r}')|p(\boldsymbol{r})] = S^{loc.}[p'|p] \equiv S^{loc.} = -\iint P(\boldsymbol{r},\ \boldsymbol{r}')\ \log P(\boldsymbol{r}'|\boldsymbol{r})\ d\boldsymbol{r}\ d\boldsymbol{r}' \qquad ...(40)$$

The molecular channel with the promolecular input signal, $\boldsymbol{P}(\boldsymbol{a}^0) = \boldsymbol{p}^0 = \{p_i^0\}$ or $\{p^0(\boldsymbol{r})\}$, of elementary input events in the non-bonded system of the molecularly placed free constituent atoms, refers to the initial stage in the bond-formation process. It corresponds to the ground-state occupations of AO contributed by the constituent atoms of a molecule to the system chemical bonds, before their mixing into MO. These reference probabilities give rise to the average information flow index of the system IT bond-ionicity, given by the mutual-information in the channel promolecular inputs and molecular outputs.

$$I(\boldsymbol{P}(\boldsymbol{a}^0):\boldsymbol{P}(\boldsymbol{b})) = I^{\mathrm{AO}}(\boldsymbol{p}^0:\boldsymbol{q})$$
$$= \sum_i\sum_j P(i, j)\log[P(i, j)/(p_i^0 q_j)]$$
$$= \sum_i\sum_j P(i, j)\log[p_i P(i, j)/(p_i q_j p_i^0)]$$
$$= \sum_i\sum_j P(i, j)[-\log q_j + \log(p_i/p_i^0) + \log P(j|i)]$$
$$= S^{\mathrm{AO}}(\boldsymbol{q}) + \Delta S^{\mathrm{AO}}(\boldsymbol{p}|\boldsymbol{p}^0) - S^{\mathrm{AO}}$$
$$\equiv I^{\mathrm{AO}} + \Delta S^{\mathrm{AO}}(\boldsymbol{p}|\boldsymbol{p}^0) \equiv I_0^{\mathrm{AO}}$$

$$I[p^0(\boldsymbol{r}):p(\boldsymbol{r}')] = I^{loc.}[p^0:p']$$
$$= \iint P(\boldsymbol{r}, \boldsymbol{r}') \log\{P(\boldsymbol{r}, \boldsymbol{r}')/[p^0(\boldsymbol{r})\, p(\boldsymbol{r}')]\}\, d\boldsymbol{r}\, d\boldsymbol{r}'$$
$$= \iint P(\boldsymbol{r},\boldsymbol{r}') \log\{p(\boldsymbol{r})P(\boldsymbol{r},\boldsymbol{r}')/[p(\boldsymbol{r})p^0(\boldsymbol{r})p(\boldsymbol{r}')]\}\, d\boldsymbol{r}\, d\boldsymbol{r}'$$
$$= \iint P(\boldsymbol{r}, \boldsymbol{r}')\, \{-\log p(\boldsymbol{r}') + \log[p(\boldsymbol{r})/p^0(\boldsymbol{r})] + \log P(\boldsymbol{r}'|\boldsymbol{r})\}\, d\boldsymbol{r}\, d\boldsymbol{r}'$$
$$= S^{loc.}[p'] + \Delta S^{loc.}[p|p^0] - S^{loc.}$$
$$\equiv I^{loc.} + \Delta S^{loc.}[p|p^0] \equiv I_0^{lo.} \qquad ...(41)$$

Here $\Delta S^{\mathrm{AO}}(\boldsymbol{p}|\boldsymbol{p}^0)$ and $\Delta S^{loc.}[p|p^0]$ denote the molecular information-distances[5,6] relative to the associate promolecular distributions. The mutual information reflects the fraction of the initial (promolecular) information content $S(\boldsymbol{p}^0)$ which has not been dissipated as noise in the molecular communication system. In particlular, for the molecular inputs, $\boldsymbol{p}^0 = \boldsymbol{p}$ or $p^0(\boldsymbol{r}) = p(\boldsymbol{r})$, and hence the vanishing information distances $\Delta S^{\mathrm{AO}}(\boldsymbol{p}|\boldsymbol{p}^0)$ or $\Delta S^{loc.}[p|p^0]$,

$$I^{\mathrm{AO}}(\boldsymbol{p}:\boldsymbol{q}) = S^{\mathrm{AO}}(\boldsymbol{q}) - S^{\mathrm{AO}} \equiv I^{\mathrm{AO}}$$

and

$$I^{loc.}[p:p'] = S^{loc.}[p'] - S^{loc.} \equiv I^{loc.} \qquad ...(42)$$

The sum of the "noise" and "flow" bond components,

$$M^{\mathrm{AO}}(\boldsymbol{p}^0; \boldsymbol{q}) = S^{\mathrm{AO}} + I_0^{\mathrm{AO}}$$
$$= S^{\mathrm{AO}}(\boldsymbol{q}) + \Delta S^{\mathrm{AO}}(\boldsymbol{p}|\boldsymbol{p}^0) \equiv M_0^{\mathrm{AO}}$$

or

$$M^{loc.}[p^0; p'] = S^{loc.} + I_0^{loc.}$$
$$= S^{loc.}[p'] + \Delta S^{loc.}[p|p^0] \equiv M_0^{loc.} \qquad ...(43)$$

measures the absolute overall IT bond-multiplicity index relative to the promolecular reference, for all bonds in the molecular system under consideration. For the molecular input this quantity preserves the Shannon entropy of the molecular probabilities.

$$M^{\mathrm{AO}}(\boldsymbol{p}; \boldsymbol{q}) = S^{\mathrm{AO}} + I^{\mathrm{AO}} = S^{\mathrm{AO}}(\boldsymbol{q}) \equiv M^{\mathrm{AO}}$$

and

$$M^{loc.}[p; p'] = S^{loc.} + I^{loc.} = S^{loc.}[p'] \equiv M^{loc.} \qquad ...(44)$$

The IT-descriptors of the overall bond-multiplicity and its covalent/ionic components can be further decomposed into the additive and non-additive terms, appropriate for the resolution in question[29]. For example, the AO noise (covalency) contribution represents the difference between total and additive communication contributions, defining the associated non-additive component of the Shannon entropy in the CBO matrix $\boldsymbol{\gamma}$.[29]

$$S^{\mathrm{AO}}(\boldsymbol{q}|\boldsymbol{p}) = -\sum_i \sum_j P(i, j) \log[P(i, j)/p_i]$$
$$= N^{-1}\,[-\sum_i\sum_j \;{}_{i,j}\;{}_{j,i} \log(\;{}_{i,j}\;{}_{j,i}) + \sum_i \;{}_{i,i} \log \;{}_{i,i}]$$
$$\equiv N^{-1}\{S^{total}(\gamma) - S^{add.}(\gamma)\} \equiv N^{-1}S^{nadd.}(\gamma) \qquad ...(45)$$

A similar partitioning of the information-flow (iconicity) index identifies it as the difference between the two components of $S^{total}(\gamma) = S^{add.}(\gamma) + S^{nadd.}(\gamma)$.

$$I^{\mathrm{AO}}(\boldsymbol{p}:\boldsymbol{q}) = \sum_i \sum_j P(i, j) \log[P(i, j)/(p_i\, q_j)]$$
$$= N^{-1}\{2S^{add.}(\gamma) - S^{total}(\gamma) + \log N\}$$
$$= N^{-1}\{S^{add.}(\gamma) - S^{nadd.}(\gamma) + \log N\} \qquad ...(46)$$

These two components thus generate the following overall IT bond-multiplicity index,

$$M^{\mathrm{AO}}(\boldsymbol{p}; \boldsymbol{q}) = N^{-1}\{S^{add.}[\gamma] + \log N\} \qquad ...(47)$$

which reflects the additive component alone.

To summarize, in this single-determinant approximation of molecular states the additive part of the Shannon entropy due to molecular AO communications represents the overall bond-multiplicity index, the non-additive part reflects the channel covalent (noise) descriptor, while their difference measures the complementary ionic (deterministic) descriptor.

A similar partition applies to the local average IT descriptors of the system chemical bonds.

$$S^{loc.}[p'|p] = -\iint P(\boldsymbol{r}, \boldsymbol{r}')\log[P(\boldsymbol{r}', \boldsymbol{r})/p(\boldsymbol{r})]\, d\boldsymbol{r}' d\boldsymbol{r}$$
$$= N^{-1}\{-\iint (\boldsymbol{r},\boldsymbol{r}')\ (\boldsymbol{r}',\boldsymbol{r})\log[\ (\boldsymbol{r},\boldsymbol{r}')\ (\boldsymbol{r}',\boldsymbol{r})]\, d\boldsymbol{r}' d\boldsymbol{r}$$
$$+ \int (\boldsymbol{r}, \boldsymbol{r})\log\ (\boldsymbol{r}, \boldsymbol{r})\, d\boldsymbol{r}\}$$
$$= N^{-1}\{S^{total}[\ ] - S^{add.}[\ ]\} \equiv N^{-1}S^{nadd.}[\ ] \quad ...(48)$$

$$I^{loc.}[p{:}p'] = \iint P(\boldsymbol{r}, \boldsymbol{r}')\log\{P(\boldsymbol{r}', \boldsymbol{r})/[p(\boldsymbol{r})p(\boldsymbol{r}')]\, d\boldsymbol{r}' d\boldsymbol{r}$$
$$= N^{-1}\{S^{add.}[\ ] - S^{nadd.}[\ ] + \log N\} \quad ...(49)$$

$$M^{loc.}[p; p] = N^{-1}\{S^{add.}[\ ] + \log N\} \quad ...(50)$$

The constant term $S[\mathrm{MO}] \equiv -N^{-1}\log N^{-1}$ in the ionicity and overall IT descriptors measures the entropy of the equalized probability $P_\vartheta = N^{-1}$ of finding an electron on any of the N singly-occupied spin-MO, which together determine the system bond system.

A presence of the non-classical, (phase/current)-related supplements of the classical measures of the information content in quantum molecular states impresses the need for supplementing the classical communication system, i. e., the molecular probability channel, with an appropriate non-classical companions, the current or phase molecular channels[29], which generate the non-classical Fisher- and Shannon-type descriptors of the system chemical bonds, respectively.

Communications in Reactive Systems

Let us qualitatively examine general communications in typical bimolecular reactive system M = A—B (Fig. 1). In the discrete (orbital) resolution the subsets of AO contributed by each subsystem, $\boldsymbol{\chi} = (\boldsymbol{\chi}_\mathrm{A}, \boldsymbol{\chi}_\mathrm{B})$, determine the relevant orbital events in each reactant and their molecular $\boldsymbol{p}(\boldsymbol{a}) = (\boldsymbol{p}_\mathrm{A}, \boldsymbol{p}_\mathrm{B}) = \boldsymbol{p}$ and promolecular $\boldsymbol{p}^0(\boldsymbol{a}) = (\boldsymbol{p}_\mathrm{A}^0, \boldsymbol{p}_\mathrm{B}^0) = \boldsymbol{p}^0$ input probabilities, giving rise to the reactant partition of a general AO communication system for M as a whole (Fig. 1A). The latter is determined by the conditional probabilities $\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \{\mathbf{P}(\boldsymbol{\chi}\ |\boldsymbol{\chi}\ ),\ \ ,\ \ = \mathrm{A, B}\}$ which produce the associated output signals: $\boldsymbol{p}(\boldsymbol{b}) = \boldsymbol{q}(\boldsymbol{p}) = \boldsymbol{p}\,\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \boldsymbol{q} = (\boldsymbol{q}_\mathrm{A}, \boldsymbol{q}_\mathrm{B})$ and $\boldsymbol{p}^0(\boldsymbol{b}) = \boldsymbol{q}(\boldsymbol{p}^0) = \boldsymbol{p}^0\,\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \boldsymbol{q}^0 = (\boldsymbol{q}_\mathrm{A}^0, \boldsymbol{q}_\mathrm{B}^0)$.

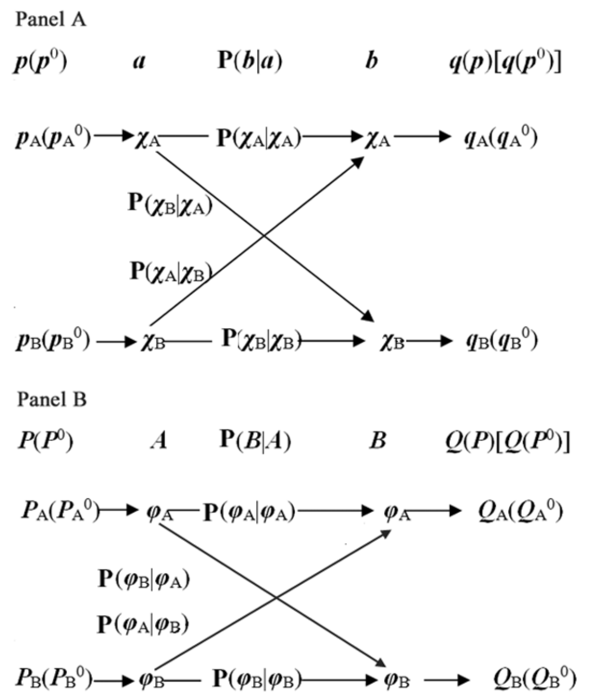

Fig.1 – Orbitally resolved communication system in the bimolecular reactive system M = A—B: AO-resolved (Panel A) and MO-resolved (Panel B).

Alternatively, the MO of the separated subsystems $\boldsymbol{\varphi}^0 = (\boldsymbol{\varphi}_\mathrm{A}, \boldsymbol{\varphi}_\mathrm{B})$ can be used to partition the reactive system (Fig. 1*B*). They generate the associated input signals: molecular $\boldsymbol{P}(\boldsymbol{A}) = (\boldsymbol{P}_\mathrm{A}, \boldsymbol{P}_\mathrm{B}) = \boldsymbol{P}$ and promolecular $\boldsymbol{P}^0(\boldsymbol{A}) = (\boldsymbol{P}_\mathrm{A}^0, \boldsymbol{P}_\mathrm{B}^0) = \boldsymbol{P}^0$. The conditional probabilities $\mathbf{P}(\boldsymbol{B}|\boldsymbol{A}) = \{\mathbf{P}(\boldsymbol{\varphi}\ |\boldsymbol{\varphi}\ ),\ \ ,\ \ = \mathrm{A, B}\}$, which define the relevant communications, ultimately determine the associated output signals: $\boldsymbol{P}(\boldsymbol{B}) = \boldsymbol{Q}(\boldsymbol{P}) = \boldsymbol{P}\,\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \boldsymbol{Q} = (\boldsymbol{Q}_\mathrm{A}, \boldsymbol{Q}_\mathrm{B})$ and $\boldsymbol{P}^0(\boldsymbol{B}) = \boldsymbol{Q}(\boldsymbol{P}^0) = \boldsymbol{P}^0\mathbf{P}(\boldsymbol{B}|\boldsymbol{A}) = \boldsymbol{Q}^0 = (\boldsymbol{Q}_\mathrm{A}^0, \boldsymbol{Q}_\mathrm{B}^0)$.

The blocks of the system AO conditional probabilities $\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \{\mathbf{P}(\boldsymbol{\chi}_\mathrm{Y}|\boldsymbol{\chi}_\mathrm{X})\}$, of the output AO events $\boldsymbol{b}$ given the input AO events $\boldsymbol{a}$, are then related to the corresponding blocks of the CBO matrix $\gamma = \{\langle\boldsymbol{\chi}_\mathrm{X}|\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}|\boldsymbol{\chi}_\mathrm{Y}\rangle\}$. The corresponding MO channel is similarly related to the (reactant-MO) transformed, molecular CBO matrix: $\gamma^\mathrm{MO} = \{\langle\boldsymbol{\varphi}_\mathrm{X}|\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}|\boldsymbol{\varphi}_\mathrm{Y}\rangle\}$. The respective molecular or promolecular input signals then give rise to the overall entropy/information descriptors of the IT bond multiplicities and their covalent/ionic components at these two resolution levels, which we have introduced in the preceding section: $(S^\mathrm{AO}, I^\mathrm{AO}, M^\mathrm{AO})$ or $(S^\mathrm{MO}, I^\mathrm{MO}, M^\mathrm{MO})$. It is also of interest to separately examine the diagonal (A→A and B→B) and off-diagonal (A→B and B→A) communications in these information channels for reactive systems. The intra-reactant communications are responsible for the valence-state promotion of the mutually non-bonded subsystems, while the inter-reactant communications generate descriptors of the true chemical bonds between reactants.

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