

# Quantum information descriptors and communications in molecules

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**Abstract** Several concepts of information theory (IT) are extended to cover the *complex* probability amplitudes (wave functions) of molecular quantum mechanics. The classical and *non*-classical aspects of the electronic structure are revealed by the electronic probability and phase distributions, respectively. The information terms due to the probability and current distributions are accounted for in the complementary Shannon and Fisher measures of the *resultant* information content of quantum states. Similar generalization of the information-distance descriptors is also established. The superposition principle (SP) of quantum mechanics, which introduces the conditional probabilities between quantum states, is used to generate a network of quantum communications in molecules, and to identify the *non*-additive contributions to physical and information quantities. The *phase*-relations in *two*-orbital model are explored. The *orbital communication theory* of the chemical bond introduces the entropic bond multiplicities and their partition into IT *covalent/ionic* components. The conditional probabilities between atomic orbitals, propagated *via* the network of the occupied molecular orbitals, which define the bond system and orbital communications in molecules, are generated from the *bond-projected* SP. In the *one*-determinantal representation of the molecular ground state the communication amplitudes are then related to elements of the *charge and bond-order* matrix. Molecular equilibria are reexamined and parallelism between the *vertical* (density-constrained) energy or entropy/information principles of IT and the corresponding thermodynamic criteria is emphasized.

**Keywords** Amplitude channels · Chemical bonds · Covalent/ionic composition · Direct/indirect communications · Entropic bond indices · Information theory · Fisher information · *Non*-additive quantities · Orbital communications · Probability/current

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distributions · Quantum information measures · Shannon entropy · Superposition principle

## 1 Introduction

Concepts and techniques of *information theory* (IT) [1–8] have been successfully applied to explore the molecular electron probabilities and the associated patterns of chemical bonds, e.g., [9–18]. In Schrödinger's quantum mechanics the electronic state is determined by the system wave function, the (complex) amplitude of the particle *probability*-distribution, which carries the resultant information content. 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*, ultimately contribute to the quantum information descriptors of molecular states. The former reveals the *classical* information term, while the latter determines its *non-classical* complement in the overall information measures [9, 10, 16, 17]. The phenomenological IT description of equilibria in molecular sub-systems has also been proposed [11, 19–22], which formally resembles the ordinary thermodynamics [23].

In the present analysis we shall emphasize the *non-classical*, (phase/current)-related contributions to *quantum* information measures of electronic states in molecules. It is the main purpose of this work to identify the *non-classical* supplements of the classical *cross* (relative) *entropy* (information-distance) descriptors within both the Fisher and Shannon measures of the information content, and to explore the the role of the phase dependence of scattering amplitudes in the *orbital communication theory* (OCT) [12, 13, 18, 24–27]. The information-cascade (bridge) propagation of electronic probabilities in molecular information systems, which generates the indirect bond contributions due to orbital intermediaries [13, 28–32], will be also examined.

Throughout the article the following tensor notation is used:  $A$  denotes a scalar quantity,  $\mathbf{A}$  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. In keeping with the custom in works on IT the logarithm taken to base 2 corresponds to the information measured in *bits* (binary digits), while selecting  $\log = \ln$  expresses the amount of information in *nats* (natural units): 1 nat = 1.44 bits.

## 2 Probability and current descriptors of electronic states

Consider the electron density  $\rho(\mathbf{r}) = Np(\mathbf{r})$ , or its shape (probability) factor  $p(\mathbf{r})$ , and the current density  $\mathbf{j}(\mathbf{r})$  in the quantum state  $\Psi(N)$  of  $N$  electrons,

$$\Psi(N) = R(N) \exp[i\Phi(N)] \equiv R(\mathbf{r}^N; \boldsymbol{\sigma}^N) \exp[i\Phi(\mathbf{r}^N; \boldsymbol{\sigma}^N)]. \quad (1)$$

Here  $R(N)$  and  $\Phi(N)$  stand for the wave-function *modulus* and (spatial) *phase* parts, respectively,  $\boldsymbol{\sigma}^N = (\sigma_1, \sigma_2, \dots, \sigma_N)$  groups the spin orientations of all  $N$  (indistinguishable) electrons and  $\mathbf{r}^N = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \equiv (\mathbf{r}_1, \mathbf{r}')$  combines their spatial

positions. These quantities are defined by the quantum-mechanical expectation values,

$$\rho(\mathbf{r}) = \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle \text{ and } \mathbf{j}(\mathbf{r}) = \langle \Psi | \hat{\mathbf{j}}(\mathbf{r}) | \Psi \rangle \equiv \sum_{k=1}^N \langle \Psi | \hat{\mathbf{j}}_k(\mathbf{r}) | \Psi \rangle = \sum_{k=1}^N \mathbf{j}_k(\mathbf{r}), \quad (2)$$

of the corresponding observables in the position representation,

$$\begin{aligned} \hat{\rho}(\mathbf{r}) &= \sum_{k=1}^N \delta(\mathbf{r}_k - \mathbf{r}) \equiv \sum_{k=1}^N \hat{\rho}_k(\mathbf{r}), \\ \hat{\mathbf{j}}(\mathbf{r}) &= \frac{1}{2m} \sum_{k=1}^N [\delta(\mathbf{r}_k - \mathbf{r}) \hat{\mathbf{p}}_k + \hat{\mathbf{p}}_k \delta(\mathbf{r}_k - \mathbf{r})] \\ &= \frac{\hbar}{2mi} \sum_{k=1}^N [\delta(\mathbf{r}_k - \mathbf{r}) \nabla_k + \nabla_k \delta(\mathbf{r}_k - \mathbf{r})] \equiv \sum_{k=1}^N \hat{\mathbf{j}}_k(\mathbf{r}), \end{aligned} \quad (3)$$

where  $m$  denotes the electronic mass and the momentum operator  $\hat{\mathbf{p}}_k = -i\hbar \nabla_k$ .

The modulus part of the wave function generates the state electron distribution,

$$\rho(\mathbf{r}) = N \sum_{\sigma} \int R^2(\mathbf{r}, \mathbf{r}'; \sigma^N) d\mathbf{r}' = Np(\mathbf{r}), \quad (4)$$

where the summation is over the admissible spin-orientations of all electrons,

$$\sigma \in \{\sigma_k \in (\text{spin-up}, \text{spin-down})\}, \quad (5)$$

and the integration covers the coordinates of positions  $\mathbf{r}' = (\mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)$  of all these indistinguishable fermions but the representative “first” electron in  $\mathbf{r}, \mathbf{r}_1 = \mathbf{r}$ , as enforced by the Dirac delta function. The probability current density is similarly shaped by the state phase gradient:

$$\mathbf{j}(\mathbf{r}) = \frac{\hbar}{m} N \sum_{\sigma} \int R^2(\mathbf{r}, \mathbf{r}'; \sigma^N) \nabla_{\mathbf{r}} \Phi(\mathbf{r}, \mathbf{r}'; \sigma^N) d\mathbf{r}'. \quad (6)$$

These expressions assume particularly simple forms in the MO approximation,

$$\Psi(N) = (1/\sqrt{N!}) \det(\psi_1, \psi_2, \dots, \psi_N) \equiv |\psi_1, \psi_2, \dots, \psi_N\rangle, \quad (7)$$

e.g., in the familiar Hartree–Fock (HF) or Kohn–Sham (KS) *self-consistent field* (SCF) theories, in which  $\Psi(N)$  is given by the antisymmetrized product (Slater determinant) of  $N$  *one-particle functions*, *spin molecular orbitals* (SMO),

$$\{\psi_k(\mathbf{q}) = \psi_k(\mathbf{r}; \sigma) \equiv \{R_k(\mathbf{r}) \exp[i\phi_k(\mathbf{r})] \zeta_k(\sigma) \equiv \varphi_k(\mathbf{r}) \zeta_k(\sigma), k = 1, 2, \dots, N\}, \quad (8)$$

each determined by a product of the associated *spatial* function (MO)  $\varphi_k(\mathbf{r})$  and the corresponding *spin*-state

$$\zeta_k(\sigma) \in \{\alpha(\sigma), \text{spin-up state } (\uparrow); \beta(\sigma), \text{spin-down state } (\downarrow)\}. \quad (9)$$

Indeed, since the observables of Eq. (2) combine *one*-electron operators their expectation values are given by the sum of the corresponding orbital expectation values:

$$\rho(\mathbf{r}) = \sum_{k=1}^N \langle \varphi_k | \hat{\rho}_k(\mathbf{r}) | \varphi_k \rangle = \sum_k |\varphi_k(\mathbf{r})|^2 = \sum_k R_k^2(\mathbf{r}) = \sum_k \rho_k(\mathbf{r}), \quad (10)$$

$$\mathbf{j}(\mathbf{r}) = \sum_{k=1}^N \langle \varphi_k | \hat{\mathbf{j}}_k(\mathbf{r}) | \varphi_k \rangle = \frac{\hbar}{m} \sum_k \rho_k(\mathbf{r}) \nabla \phi_k(\mathbf{r}) = \sum_k \mathbf{j}_k(\mathbf{r}), \quad (11)$$

where  $\{\rho_k(\mathbf{r})\}$  and  $\{\mathbf{j}_k(\mathbf{r})\}$  denote the orbital contributions to the system electron density and current distributions, respectively.

In the simplest case of a *single* ( $N = 1$ ) electron in a general state described by the complex MO,

$$\varphi(\mathbf{r}) = R(\mathbf{r}) \exp[i\phi(\mathbf{r})], \quad (12)$$

the modulus factor of this wave function determines the particle spatial probability/density distribution,

$$\begin{aligned} \rho(\mathbf{r}) &= \langle \varphi | \hat{\rho}(\mathbf{r}) | \varphi \rangle = \varphi^*(\mathbf{r})\varphi(\mathbf{r}) = R(\mathbf{r})^2 = p(\mathbf{r}), \\ \hat{\rho}(\mathbf{r}) &= \delta(\mathbf{r}' - \mathbf{r}), \quad \int p(\mathbf{r}) d\mathbf{r} = 1, \end{aligned} \quad (13)$$

while the gradient of its phase component generates the associated current density:

$$\begin{aligned} \mathbf{j}(\mathbf{r}) &= \langle \varphi | \hat{\mathbf{j}}(\mathbf{r}) | \varphi \rangle = \frac{\hbar}{2mi} [\varphi^*(\mathbf{r}) \nabla \varphi(\mathbf{r}) - \varphi(\mathbf{r}) \nabla \varphi^*(\mathbf{r})] = \frac{\hbar p(\mathbf{r})}{m} \nabla \phi(\mathbf{r}), \\ \hat{\mathbf{j}}(\mathbf{r}) &= \frac{\hbar}{2mi} [\delta(\mathbf{r}' - \mathbf{r}) \nabla_{\mathbf{r}'} + \nabla_{\mathbf{r}'} \delta(\mathbf{r}' - \mathbf{r})]. \end{aligned} \quad (14)$$

The phase gradient is thus proportional to the current-per-particle, “velocity” field  $\mathbf{V}(\mathbf{r}) = \mathbf{j}(\mathbf{r})/p(\mathbf{r})$ :

$$\nabla \phi(\mathbf{r}) = (m/\hbar) \mathbf{V}(\mathbf{r}). \quad (15)$$

The probability and current densities manifest the complementary facets of electron distributions in molecules. They respectively generate the classical and *non*-classical contributions to the generalized measures of the information content in quantum electronic states [9, 10, 16, 17, 33], which we shall briefly summarize in the next section.

### 3 Information measures

In Sects. 3–5 we provide a short overview of the pertinent concepts and techniques of IT, including the classical measures of the information content and their quantum generalizations capable of tackling the complex probability amplitudes (wave functions). As already remarked above, these generalized quantities have to be used in diagnosing the full, *quantum* information content of electronic states [9, 10], exploring molecular equilibria [16, 17], probing the chemical bond multiplicities due to orbital bridges, and in treating the associated multiple (cascade) communications in molecular information channels. Some rudiments of the classical communication systems and the associated *amplitude channels* will also be given and the entropic descriptors of the orbital networks will be linked to the chemical bond multiplicities and their covalent/ionic composition.

The key element of the IT approach to molecular electronic structure is an adequate definition of a generalized measure of the information content in the given (generally complex) quantum state of electrons in molecules. The system electron distribution, related to the wave-function *modulus*, reveals only the classical, *probability* aspect of the molecular information content [1–7], while the *phase (current)* component gives rise to the *non-classical* entropy/information terms [9, 10, 16, 17, 33]. The *resultant* quantum measure then allow one to monitor the full information content of the *non-equilibrium* (variational) quantum states, thus providing the complete information description of their evolution towards the final equilibrium.

In *density functional theory* (DFT) [34, 35] one often refers to the density-constrained principles [9, 10, 36] and states [37–40], which correspond to the fixed electronic probability distribution. They determine the so called *vertical* equilibria, which are determined solely by the *non-classical* (current related) entropy/information functionals [9, 10, 16, 17]. The density-unrestricted principles associated with the resultant information measure similarly determine the *horizontal* (unconstrained) equilibria in molecules [9–11].

Of interest in the electronic structure theory also are the *cross* (or relative) *entropy* quantities, which measure the *information distance* between two probability distributions and reflect the information *similarity* between different states or molecules, as well as descriptors of the information propagation between bonded atoms and orbitals in the system chemical bonds. One also aims at formulating the adequate, consistent with the prevailing chemical intuition, measures of the chemical bond multiplicity in the system as a whole and its constituent fragments, as well as the entropy/information descriptors of the bond covalent/ionic composition.

The spread of information in molecular communication networks, among AIM or between AO they contribute to molecular bond system, is investigated in OCT in which molecular systems are regarded as the AO-resolved information channels. Their conditional-entropy (communication noise) and mutual-information (information-flow) descriptors [3, 7, 11–13] then provide a chemical resolution of the resulting IT bond multiplicities into the *covalent* and *ionic* bond components, respectively. One is also interested in mutual relations between analogous concepts developed within the SCF MO and IT approaches. Together they offer a deeper insight into the complex phenomenon called the chemical bonding.

The Shannon entropy [3] of the normalized probability vector  $\mathbf{p} = \{p_i\}$ ,  $\sum_i p_i = 1$ ,

$$S(\mathbf{p}) = - \sum_i p_i \log p_i, \quad (16)$$

where the summation extends over labels of the elementary events determining the *discrete* probability scheme in question, provides a measure of the average indeterminacy in the argument probability distribution. One similarly introduces the associated functional of the spatial probability distribution  $p(\mathbf{r}) = |\varphi(\mathbf{r})|^2$ , for the *continuous* labels of the electron locality events  $\{\mathbf{r}\}$ :

$$S^{\text{class.}}[\varphi] = S[p] = - \int p(\mathbf{r}) \log p(\mathbf{r}) \, d\mathbf{r} \equiv \int p(\mathbf{r}) S^{\text{class.}}(\mathbf{r}) \, d\mathbf{r} \equiv \int s^{\text{class.}}(\mathbf{r}) \, d\mathbf{r}. \quad (17)$$

These electron “uncertainty” quantities also measure the corresponding amounts of information,  $I^S(p) = S(p)$  or  $I^S[p] = S[p]$ , obtained when the distribution indeterminacy is removed by an appropriate measurement (experiment). This familiar (global) information measure is *classical* in character, being determined by probabilities alone. This property distinguishes it from the corresponding quantum concept of the *non-classical* entropy contribution due to the phase of the complex quantum state in question. As argued elsewhere [9, 10, 16, 17], for a *single* particle in the MO state of Eq. (12) the density of the *non-classical* entropy complement to the classical Shannon entropy of Eq. (17) is 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 local particle probability density providing the relevant weighting factor:

$$\begin{aligned} S^{\text{nclass.}}[\varphi] &= -2 \int p(\mathbf{r}) |\phi(\mathbf{r})| \, d\mathbf{r} \equiv S[p, \phi] \equiv \int p(\mathbf{r}) S^{\text{nclass.}}(\mathbf{r}) \, d\mathbf{r} \\ &\equiv \int s^{\text{nclass.}}(\mathbf{r}) \, d\mathbf{r} \equiv -2 \langle |\phi| \rangle. \end{aligned} \quad (18)$$

Therefore, for the given quantum state  $\varphi$  of an electron the two components  $S[p] = S^{\text{class.}}[\varphi]$  and  $S[p, \phi] = S^{\text{nclass.}}[\varphi]$  determine the *resultant* entropy descriptor:

$$S[\varphi] = S^{\text{class.}}[\varphi] + S^{\text{nclass.}}[\varphi] = S[p] + S[p, \phi]. \quad (19)$$

The classical Fisher information for locality events [1, 2], also called the *intrinsic accuracy*, historically predates the Shannon entropy by about 25 years, being proposed in about the same time, when the final form of the modern quantum mechanics was shaped. This classical gradient measure of the information content in the probability density  $p(\mathbf{r})$  reads:

$$I[p] = \int p(\mathbf{r}) [\nabla \ln p(\mathbf{r})]^2 \, d\mathbf{r} = \int [\nabla p(\mathbf{r})]^2 / p(\mathbf{r}) \, d\mathbf{r} = 4 \int [\nabla A(\mathbf{r})]^2 \, d\mathbf{r} \equiv I[A], \quad (20)$$

where  $A(\mathbf{r}) = \sqrt{p(\mathbf{r})}$  denotes the *classical* amplitude of this probability distribution.

This Fisher information is reminiscent of von Weizsäcker's [41] inhomogeneity correction to the electronic kinetic energy in the Thomas-Fermi theory. It characterizes the compactness of the probability density  $p(\mathbf{r})$ . For example, the Fisher information in the *normal distribution* measures the inverse of its variance, called the *invariance*, while the complementary Shannon entropy is proportional to the logarithm of variance, thus monotonically increasing with the spread of the Gaussian distribution. The Shannon entropy and intrinsic accuracy thus describe complementary facets of the probability density: the former reflects distribution's "spread" (delocalization, "disorder"), while the latter measures its "narrowness" (localization, "order").

This *classical* amplitude form of Eq. (20) is then naturally generalized into the domain of the *quantum* (complex) probability amplitudes, the wave functions of Schrödinger's quantum mechanics. For example, for the *one*-electron state of Eq. (12), when  $p(\mathbf{r}) = \varphi^*(\mathbf{r})\varphi(\mathbf{r}) = |\varphi(\mathbf{r})|^2 = [R(\mathbf{r})]^2$ , i.e.,  $A(\mathbf{r}) = R(\mathbf{r})$ , this generalized measure is given by the following MO functional related to the average kinetic energy  $T[\varphi]$ :

$$I[\varphi] = 4 \int |\nabla\varphi(\mathbf{r})|^2 d\mathbf{r} = \frac{8m}{\hbar^2} T[\varphi], \quad (21)$$

where from the spatial integration by parts,

$$T[\varphi] \equiv \langle \varphi | \hat{T} | \varphi \rangle = -\frac{\hbar^2}{2m} \int \varphi^*(\mathbf{r}) \Delta\varphi(\mathbf{r}) d\mathbf{r} = \frac{\hbar^2}{2m} \int |\nabla\varphi(\mathbf{r})|^2 d\mathbf{r}. \quad (22)$$

This quantum kinetic energy also consists of the classical Fisher contribution, depending solely upon the electron probability distribution  $p(\mathbf{r})$ ,

$$T^{class.}[\varphi] = T[p] = \frac{\hbar^2}{8m} \int \frac{|\nabla p(\mathbf{r})|^2}{p(\mathbf{r})} d\mathbf{r} = \frac{\hbar^2}{2m} \int (\nabla R(\mathbf{r}))^2 d\mathbf{r}, \quad (23)$$

and the *non*-classical, (phase/current)-related term,

$$T^{nclass.}[\varphi] = T[p, \mathbf{j}] = \frac{m}{2} \int (\mathbf{j}(\mathbf{r})/R(\mathbf{r}))^2 d\mathbf{r} = \frac{\hbar^2}{2m} \int R^2(\mathbf{r})(\nabla\phi(\mathbf{r}))^2 d\mathbf{r}, \quad (24)$$

$$T[\varphi] = T^{class.}[\varphi] + T^{nclass.}[\varphi] = T[p] + T[p, \mathbf{j}]. \quad (25)$$

Expressing the information functional of Eq. (21) in terms of the modulus and phase components of the argument MO state similarly gives:

$$\begin{aligned} I[\varphi] &= I[p] + 4 \int p(\mathbf{r})[\nabla\phi(\mathbf{r})]^2 d\mathbf{r} \equiv I[p] + I[p, \phi] \\ &= I[p] + 4 \left(\frac{m}{\hbar}\right)^2 \int \mathbf{j}^2(\mathbf{r})/p(\mathbf{r}) d\mathbf{r} = I[p] + I[p, \mathbf{j}] \equiv I^{class.}[\varphi] + I^{nclass.}[\varphi] \\ &\equiv \int p(\mathbf{r})[I^{class.}(\mathbf{r}) + I^{nclass.}(\mathbf{r})] d\mathbf{r} \equiv \int [f^{class.}(\mathbf{r}) + f^{nclass.}(\mathbf{r})] d\mathbf{r}. \end{aligned} \quad (26)$$

Here, the two information densities-per-electron read:

$$\begin{aligned}
 I^{class.}(\mathbf{r}) &= [\Delta p(\mathbf{r}) / p(\mathbf{r})]^2 = 4[\Delta R(\mathbf{r})]^2, \\
 I^{class.}(\mathbf{r}) &= 4[\Delta\phi(\mathbf{r})]^2 = 4(m/\hbar)^2 [j(\mathbf{r}) / p(\mathbf{r})]^2.
 \end{aligned}
 \tag{27}$$

The classical and *non*-classical densities-per-electron of these complementary measures of the information content are mutually related via the common-type dependence [9, 10]:

$$\begin{aligned}
 I^{class.}(\mathbf{r}) &= [\nabla \ln p(\mathbf{r})]^2 = [\nabla S^{class.}(\mathbf{r})]^2 \quad \text{and} \\
 I^{nclass.}(\mathbf{r}) &= \left( \frac{2m\mathbf{j}(\mathbf{r})}{\hbar p(\mathbf{r})} \right)^2 \equiv [\nabla S^{nclass.}(\mathbf{r})]^2.
 \end{aligned}
 \tag{28}$$

Thus, the square of the gradient of the local Shannon probe of the state quantum “indeterminicity” (disorder) generates the density of the corresponding Fisher measure of the state quantum “determinicity” (order). Notice, that the second of these relations determines the density  $S^{nclass.}(\mathbf{r})$  only up to its sign. Therefore, both positive and negative [see Eq. (18)] signs of this non-classical (phase-related) information density are admissible.

#### 4 Comparing probability distributions

An important generalization of Shannon’s entropy concept, called the *relative* (cross) *entropy*, also known as the *entropy deficiency*, *missing information* or *directed divergence*, has been proposed by Kullback and Leibler [5,6]. It measures the information “distance” between the two (normalized) probability distributions for the *same* set of events. For example, in the discrete probability scheme identified by events  $\mathbf{a} = \{a_i\}$  and their probabilities  $\mathbf{P}(\mathbf{a}) = \{P(a_i) = p_i\} = \mathbf{p}$ , this discrimination information in  $\mathbf{p}$  with respect to the reference distribution  $\mathbf{P}(\mathbf{a}^0) = \{P(a_i^0) = p_i^0\} = \mathbf{p}^0$  reads:

$$\Delta S(\mathbf{p}|\mathbf{p}^0) = \sum_i p_i \log(p_i/p_i^0) \geq 0.
 \tag{29}$$

This quantity provides a measure of the information resemblance between the two compared probability schemes. The more the two distributions differ from one another, the larger the information distance. For individual events the logarithm of probability ratio  $I_i = \log(p_i/p_i^0)$ , called the probability *surprisal*, provides a measure of the event information in  $\mathbf{p}$  relative to that in the reference distribution  $\mathbf{p}^0$ . Notice that the equality in the preceding equation takes place only for the vanishing surprisal for all events, i.e., when the two probability distributions are identical.

Similar classical concepts of the information distance can be advanced within the Fisher measure. The directed-divergence between the continuous probability density  $p(\mathbf{r}) = |\varphi|^2$  and the reference distribution  $p^0(\mathbf{r}) = |\varphi^0|^2$ , measuring the average



probability-surprisal  $I_p(\mathbf{r})$ ,

$$\Delta S[p|p^0] = \int p(\mathbf{r}) \log[p(\mathbf{r})/p^0(\mathbf{r})] d\mathbf{r} \equiv \int p(\mathbf{r}) I_p(\mathbf{r}) d\mathbf{r} \equiv \Delta S^{class.}[\varphi|\varphi^0], \quad (30)$$

has been generalized into its gradient analog [11,22]:

$$\begin{aligned} \Delta I[p|p^0] &= \int p(\mathbf{r}) [\nabla I_p(\mathbf{r})]^2 d\mathbf{r} \equiv \Delta I^{class.}[\varphi|\varphi^0] \\ &= \int p(\mathbf{r}) [p(\mathbf{r})^{-1} \nabla p(\mathbf{r}) - p^0(\mathbf{r})^{-1} \nabla p^0(\mathbf{r})]^2 d\mathbf{r} \geq 0. \end{aligned} \quad (31)$$

One can also introduce measures of the *non*-classical information distances, related to the phase/current degrees-of-freedom of the two quantum states  $\varphi$  and  $\varphi^0$ , which generate the associated (probability, phase, current) components,  $(p, \phi, \mathbf{j})$  and  $(p^0, \phi^0, \mathbf{j}^0)$ , respectively. The *non*-classical Shannon measure  $S[p, \phi]$  of Eq. (18) then generates the following information distance measuring the average *phase*-surprisal  $I_\phi(\mathbf{r})$ :

$$\Delta S[\phi|\phi^0] \equiv \Delta S^{nclass.}[\varphi|\varphi^0] = \int p(\mathbf{r}) \log|\phi(\mathbf{r})/\phi^0(\mathbf{r})| d\mathbf{r} \equiv \int p(\mathbf{r}) I_\phi(\mathbf{r}) d\mathbf{r}. \quad (32)$$

Two components of Eqs. (30) and (32) thus determine the following resultant entropy-deficiency between two complex wave functions:

$$\begin{aligned} \Delta S[\varphi|\varphi^0] &= \Delta S^{class.}[\varphi|\varphi^0] + \Delta S^{nclass.}[\varphi|\varphi^0] = \Delta S[p|p^0] + \Delta S[\phi|\phi^0] \\ &= \int p(\mathbf{r}) [I_p(\mathbf{r}) + I_\phi(\mathbf{r})] d\mathbf{r}. \end{aligned} \quad (33)$$

In a search for the *non*-classical Fisher-information distance,

$$\Delta I^{nclass.}[\varphi|\varphi^0] \equiv \int p(\mathbf{r}) \Delta I^{nclass.}(\mathbf{r}) d\mathbf{r}, \quad (34)$$

we use Eq. (28), which establishes a general relation between the complementary Shannon and Fisher information densities-per-electron. For comparing the two quantum states we thus propose

$$\begin{aligned} \Delta I^{nclass.}(\mathbf{r}) &= \{\nabla[\Delta S^{nclass.}(\mathbf{r})]\}^2 = [\nabla I_\phi(\mathbf{r})]^2 = [\nabla \ln|\phi(\mathbf{r})/\phi^0(\mathbf{r})|]^2 \\ &= \{\nabla \phi(\mathbf{r})/\phi(\mathbf{r}) - \nabla \phi^0(\mathbf{r})/\phi^0(\mathbf{r})\}^2, \end{aligned} \quad (35)$$

where we have used the gradient identity

$$\nabla|\phi(\mathbf{r})| = \nabla[\phi^2(\mathbf{r})]^{1/2} = [\phi(\mathbf{r})/|\phi(\mathbf{r})|]\nabla\phi(\mathbf{r}) = \text{sign}[\phi(\mathbf{r})]\nabla\phi(\mathbf{r}).$$

Since the phase gradients are related to the corresponding “velocities”, which measure the corresponding *currents-per-particle* [see Eq. (15)],

$$\mathbf{V} = \frac{\mathbf{j}}{p} = \frac{\hbar}{m} \nabla \phi \quad \text{and} \quad \mathbf{V}^0 = \frac{\mathbf{j}^0}{p^0} = \frac{\hbar}{m} \nabla \phi^0, \tag{36}$$

the resulting *non*-classical contribution to the Fisher measure of the quantum information distance between the two electronic states [Eq. (34)],

$$\begin{aligned} \Delta I^{n\text{class.}}[\varphi|\varphi^0] &= \int p(\mathbf{r}) [\nabla \log|\phi(\mathbf{r})/\phi^0(\mathbf{r})|^2] \, d\mathbf{r} \\ &= \int p(\mathbf{r}) [\nabla I_\phi(\mathbf{r})]^2 \, d\mathbf{r} \equiv \Delta I[\phi|\phi^0], \end{aligned} \tag{37}$$

represents the average value of the squared combination of currents (velocities) in the two states compared.

Together the two components of Eqs. (31) and (37) determine the resultant Fisher-information distance between the two complex wave functions:

$$\begin{aligned} \Delta I[\varphi|\varphi^0] &= \Delta I^{\text{class.}}[\varphi|\varphi^0] + \Delta I^{n\text{class.}}[\varphi|\varphi^0] = \Delta I[p|p^0] + \Delta I[\phi|\phi^0] \\ &= \int p(\mathbf{r}) \{[\nabla I_p(\mathbf{r})]^2 + [\nabla I_\phi(\mathbf{r})]^2\} \, d\mathbf{r}. \end{aligned} \tag{38}$$

The common amount of information in two dependent events  $a_i$  and  $b_j$ ,  $I(i : j)$ , measuring the information about  $a_i$  provided by the occurrence of  $b_j$  or the information about  $b_j$  provided by the occurrence of  $a_i$ , determines the *mutual information* in these two events,

$$\begin{aligned} I(i : j) &= \log[P(a_i \wedge b_j)/P(a_i) P(b_j)] = \log[\pi_{i,j}/(p_i q_j)] \\ &\equiv -\log p_i - \log q_j + \log \pi_{i,j} \equiv I(i) + I(j) - I(i \wedge j) \\ &\equiv \log[P(i|j)/p_i] = -\log p_i + \log P(i|j) = I(i) - I(i|j) \\ &\equiv \log[P(j|i)/q_j] = -\log q_j + \log P(j|i) = I(j) - I(j|i) = I(j : i); \end{aligned} \tag{39}$$

where  $P(a_i \wedge b_j) \equiv \pi_{i,j}$  stands for the probability of the *joint* event, of simultaneously observing  $a_i$  and  $b_j$ , while the quantity  $I(i|j) = -\log P(i|j)$  measures the *conditional entropy* in  $a_i$  given the occurrence of  $b_j$ , or the *self-information* in the conditional event of observing  $a_i$  given  $b_j$ . The mutual information  $I(i : j)$  may take on any real value, positive, negative, or zero: it vanishes, when both events are independent, i.e., when the occurrence of one event does not influence (or condition) the probability of the occurrence of the other event, and it is negative, when the occurrence of one event makes a *non*-occurrence of the other event more likely. It also follows from the preceding equation that the *self-information* of the joint event  $I(i \wedge j) = -\log \pi_{i,j}$  reads:

$$I(i \wedge j) = I(i) + I(j) - I(i : j). \tag{40}$$

Thus, the information in the joint occurrence of two events  $a_i$  and  $b_j$  is the information in the occurrence of  $a_i$  plus that in the occurrence of  $b_j$  minus the mutual information. Clearly, for independent events, when  $\pi_{i,j} = \pi_{i,j}^0 = p_i q_j$ ,  $I(i : j) = 0$  and hence  $I(i \wedge j) = I(i) + I(j)$ .

The mutual information of an event with itself defines its *self-information*:  $I(i : i) \equiv I(i) = \log[P(i|i)/p_i] = -\log p_i$ , since for a single event  $P(i|i) = 1$ . It vanishes for  $p_i = 1$ , i.e., when there is no uncertainty about the occurrence of  $a_i$ , so that the occurrence of this event removes no uncertainty, hence conveys no information. This quantity provides a measure of the uncertainty about the occurrence of the event itself, i.e., the information received when the event actually takes place.

Consider now two mutually dependent (discrete) probability vectors for *different* sets of events,  $\mathbf{P}(\mathbf{a}) = \{P(a_i) = p_i\} \equiv \mathbf{p}$  and  $\mathbf{P}(\mathbf{b}) = \{P(b_j) = q_j\} \equiv \mathbf{q}$  (see Fig. 1). One decomposes the joint probabilities of the simultaneous events  $\mathbf{a} \wedge \mathbf{b} = \{a_i \wedge b_j\}$  in these two schemes,  $\mathbf{P}(\mathbf{a} \wedge \mathbf{b}) = \{P(a_i \wedge b_j) = \pi_{i,j}\} \equiv \boldsymbol{\pi}$ , as products of the “marginal” probabilities of events in one set, say  $\mathbf{P}(\mathbf{a})$ , and the corresponding conditional probabilities  $\mathbf{P}(\mathbf{b}|\mathbf{a}) = \{P(j|i)\}$  of outcomes in the other set  $\mathbf{b}$ , given that events  $\mathbf{a}$  have already occurred [see Eq. (39)]:

$$\boldsymbol{\pi} = \{\pi_{i,j} = p_i P(j|i)\}. \quad (41)$$

The relevant normalization conditions for such joint and conditional probabilities read:

$$\sum_j \pi_{i,j} = p_i, \quad \sum_i \pi_{i,j} = q_j, \quad \sum_i \sum_j \pi_{i,j} = 1, \quad \sum_j P(j|i) = 1, \quad i = 1, 2, \dots \quad (42)$$

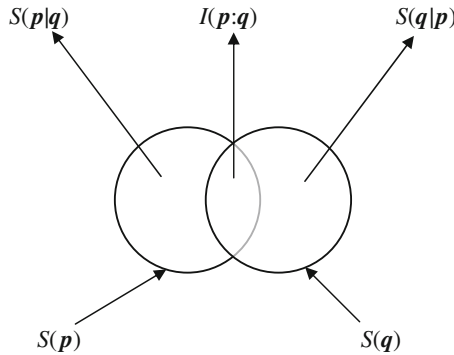
The Shannon entropy of the product distribution  $\boldsymbol{\pi}$ ,  $S(\boldsymbol{\pi}) = -\sum_i \sum_j \pi_{i,j} \log \pi_{i,j}$ ,

$$\begin{aligned} S(\boldsymbol{\pi}) &= -\sum_i \sum_j p_i P(j|i) [\log p_i + \log P(j|i)] \\ &= -\left[ \sum_j P(j|i) \right] \sum_i p_i \log p_i - \sum_i \sum_j \pi_{i,j} \log P(j|i) \\ &\equiv S(\mathbf{p}) + \sum_i p_i S(\mathbf{q}|i) \equiv S(\mathbf{p}) + S(\mathbf{q}|\mathbf{p}), \end{aligned} \quad (43)$$

can be thus expressed as the sum of the average entropy in the marginal probability distribution,  $S(\mathbf{p})$ , and the average *conditional entropy* in  $\mathbf{q}$  given  $\mathbf{p}$ ,

$$S(\mathbf{q}|\mathbf{p}) = -\sum_i \sum_j \pi_{i,j} \log P(j|i) = -\sum_i p_i \left[ \sum_j P(j|i) \log P(j|i) \right]. \quad (44)$$

The latter represents the extra amount of the uncertainty/information about the occurrence of events  $\mathbf{b}$ , given that the events  $\mathbf{a}$  are known to have occurred. In other words: the amount of information obtained as a result of simultaneously observing the events



**Fig. 1** Diagram of the conditional-entropy and mutual-information quantities for two dependent probability distributions  $\mathbf{p}$  and  $\mathbf{q}$ . Two circles enclose areas representing the entropies  $S(\mathbf{p})$  and  $S(\mathbf{q})$  of two separate probability vectors, while their common (overlap) area corresponds to the mutual information  $I(\mathbf{p} : \mathbf{q})$  in these two distributions. The remaining part of each circle represents the corresponding conditional entropy,  $S(\mathbf{p}|\mathbf{q})$  or  $S(\mathbf{q}|\mathbf{p})$ , measuring the residual uncertainty/information about events in one set of outcomes, when one has the full knowledge of the occurrence of events in the other set. The area enclosed by the circle envelope then represents the entropy of the “product” (joint) distribution:  $S(\boldsymbol{\pi}) = S(\mathbf{P}(\mathbf{a} \wedge \mathbf{b})) = S(\mathbf{p}) + S(\mathbf{q}) - I(\mathbf{p} : \mathbf{q}) = S(\mathbf{p}) + S(\mathbf{q}|\mathbf{p}) = S(\mathbf{q}) + S(\mathbf{p}|\mathbf{q})$

$\mathbf{a}$  and  $\mathbf{b}$  equals to the amount of information in one set, say  $\mathbf{a}$ , supplemented by the extra information provided by the occurrence of events in the other set  $\mathbf{b}$ , when  $\mathbf{a}$  are known to have occurred already (see Fig. 1).

The classical Shannon entropy [Eq. (16)] can be thus interpreted as the mean value of self-informations in all individual events:  $S(\mathbf{p}) = \sum_i p_i I(i)$ . One similarly defines the average mutual information in two probability distributions as the ( $\boldsymbol{\pi}$ -weighted) mean value of the mutual information quantities for individual joint events (see also Fig. 1):

$$\begin{aligned}
 I(\mathbf{p} : \mathbf{q}) &= \sum_i \sum_j \pi_{i,j} I(i : j) = \sum_i \sum_j \pi_{i,j} \log(\pi_{i,j} / \pi_{i,j}^0) \\
 &= S(\mathbf{p}) + S(\mathbf{q}) - S(\boldsymbol{\pi}) = S(\mathbf{p}) - S(\mathbf{p}|\mathbf{q}) = S(\mathbf{q}) - S(\mathbf{q}|\mathbf{p}) \geq 0. \quad (45)
 \end{aligned}$$

The equality holds only for independent distributions, when  $\pi_{i,j} = p_i q_j \equiv \pi_{i,j}^0$ . Indeed, the amount of uncertainty in  $\mathbf{q}$  can only decrease, when  $\mathbf{p}$  has been known beforehand,  $S(\mathbf{q}) \geq S(\mathbf{q}|\mathbf{p}) = S(\mathbf{q}) - I(\mathbf{p} : \mathbf{q})$ , with equality being observed only when the two sets of events are independent, thus giving non-overlapping entropy circles in Fig. 1.

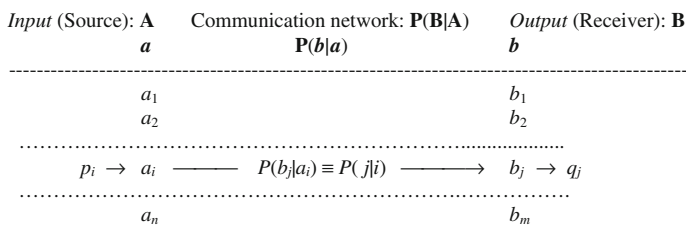
The average mutual information is an example of the entropy deficiency, measuring the missing information between the joint probabilities  $\mathbf{P}(\mathbf{a} \wedge \mathbf{b}) = \boldsymbol{\pi}$  of the dependent events  $\mathbf{a}$  and  $\mathbf{b}$ , and the joint probabilities  $\mathbf{P}^{ind.}(\mathbf{a}^0 \wedge \mathbf{b}^0) = \boldsymbol{\pi}^0 = \mathbf{p}^T \mathbf{q}$  for the independent events:  $I(\mathbf{p} : \mathbf{q}) = \Delta S(\boldsymbol{\pi}|\boldsymbol{\pi}^0)$ . The average mutual information thus reflects a dependence between events defining the two probability schemes. A similar information-distance interpretation can be attributed to the average conditional entropy:  $S(\mathbf{p}|\mathbf{q}) = S(\mathbf{p}) - \Delta S(\boldsymbol{\pi}|\boldsymbol{\pi}^0)$ .

## 5 Communication channels

We continue this short IT overview with the entropy/information descriptors of a transmission of the electron-assignment “signals” in molecular *communication systems* [11–13]. The *classical* orbital networks [3,6,11–13,18] propagate probabilities of electron assignments to basis functions of SCF MO calculations, while the *quantum* channels [13,33] scatter wave functions, i.e., (complex) probability amplitudes, between such elementary states. The former loose memory of the phase aspect of this information propagation, which becomes crucial in the *multi-stage* (cascade, bridge) propagations [28]. In determining the underlying conditional probabilities of the *output*-orbital events, given the *input*-orbital events, or the scattering amplitudes of the *emitting* (input) states among the *monitoring/receiving* (output) states, one uses the (bond-projected) *superposition principle* (SP) of quantum mechanics [42] (see also next section).

We begin with some rudiments on the classical information systems. The basic elements of such a “device” are shown in Fig. 2. The signal emitted from  $n$  “inputs”  $\mathbf{a} = (a_1, a_2, \dots, a_n)$  of the channel *source* **A** is characterized by the *a priori* probability distribution  $\mathbf{P}(\mathbf{a}) = \mathbf{p} = (p_1, p_2, \dots, p_n)$ , which describes the way the channel is exploited. It can be received at  $m$  “outputs”  $\mathbf{b} = (b_1, b_2, \dots, b_m)$  of the system *receiver* **B**. The transmission of signals in such communication network is randomly disturbed thus exhibiting a typical communication *noise*. Indeed, the signal sent at the given input can in general be received with a *non-zero* probability at several outputs. This feature of communication systems is described by the conditional probabilities of the outputs-given-inputs,  $\mathbf{P}(\mathbf{b}|\mathbf{a}) = \{P(b_j|a_i) = P(a_i \wedge b_j)/P(a_i) \equiv P(j|i)\}$ , where  $\{P(a_i \wedge b_j) \equiv \pi_{i,j}\} = \boldsymbol{\pi}$  stands for the probability of the joint occurrence of the specified pair of the input–output events. The latter define the simultaneous probability matrix  $\{P(a_i \wedge b_j) \equiv \pi_{i,j}\} = \boldsymbol{\pi}$ . The distribution of the output signal among the detection events  $\mathbf{b}$  is thus given by the *a posteriori* (output) probability distribution

$$\mathbf{P}(\mathbf{b}) = \mathbf{q} = (q_1, q_2, \dots, q_m) = \mathbf{p} \mathbf{P}(\mathbf{b}|\mathbf{a}).$$



**Fig. 2** Schematic diagram of the communication system characterized by two probability vectors:  $\mathbf{P}(\mathbf{a}) = \{P(a_i)\} = \mathbf{p} = (p_1, \dots, p_n)$ , of the channel “input” events  $\mathbf{a} = (a_1, \dots, a_n)$  in the system source **A**, and  $\mathbf{P}(\mathbf{b}) = \{P(b_j)\} = \mathbf{q} = (q_1, \dots, q_m)$ , of the “output” events  $\mathbf{b} = (b_1, \dots, b_m)$  in the system receiver **B**. The transmission of signals in this communication channel is described by the  $(n \times m)$ -matrix of the conditional probabilities  $\mathbf{P}(\mathbf{b}|\mathbf{a}) = \{P(b_j|a_i) \equiv P(j|i)\}$ , of observing different “outputs” (*columns*,  $j = 1, 2, \dots, m$ ), given the specified “inputs” (*rows*,  $i = 1, 2, \dots, n$ ). For clarity, only a single scattering  $a_i \rightarrow b_j$  is shown in the diagram

The input probabilities reflect the way the channel is used (probed). The Shannon entropy  $S(\mathbf{p})$  of the source probabilities  $\mathbf{p}$  determines the channel *a priori* entropy. The average *conditional entropy* of the outputs given inputs  $S(\mathbf{q}|\mathbf{p}) \equiv H(\mathbf{B}|\mathbf{A})$  is determined by the scattering probabilities  $\mathbf{P}(\mathbf{b}|\mathbf{a})$ . It measures the average noise in the  $\mathbf{a} \rightarrow \mathbf{b}$  transmission. The so called *a posteriori* entropy, of the input given output,  $H(\mathbf{A}|\mathbf{B}) \equiv S(\mathbf{p}|\mathbf{q})$ , is similarly defined by the conditional probabilities of the  $\mathbf{b} \rightarrow \mathbf{a}$  signals:  $\mathbf{P}(\mathbf{a}|\mathbf{b}) = \{P(a_i|b_j) = P(a_i \wedge b_j)/P(b_j) = P(i|j)\}$ . It reflects the residual indeterminacy about the input signal, when the output signal has already been received. The average conditional entropy  $S(\mathbf{p}|\mathbf{q})$  thus measures the indeterminacy of the source with respect to the receiver, while the conditional entropy  $S(\mathbf{q}|\mathbf{p})$  reflects the uncertainty of the receiver relative to the source. An observation of the output signal thus provides on average the amount of information given by the difference between the *a priori* and *a posteriori* uncertainties,  $S(\mathbf{p}) - S(\mathbf{p}|\mathbf{q}) = I(\mathbf{p} : \mathbf{q})$ , which defines the *mutual information* in the source and receiver. In other words, the mutual information measures the net amount of information transmitted through the communication channel, while the conditional entropy  $S(\mathbf{p}|\mathbf{q})$  reflects a fraction of  $S(\mathbf{p})$  transformed into “noise” as a result of the input signal being scattered in the information channel. Accordingly,  $S(\mathbf{q}|\mathbf{p})$  reflects the noise part of  $S(\mathbf{q}) = S(\mathbf{q}|\mathbf{p}) + I(\mathbf{p} : \mathbf{q})$  (see Fig. 1).

In OCT the orbital channels [3, 6, 11–13] propagate probabilities of electron assignments to basis functions of SCF MO calculations, e.g., *atomic orbitals* (AO)  $\chi = (\chi_1, \chi_2, \dots, \chi_m)$ . The underlying conditional probabilities of the *output* AO events, given the input AO events,  $\mathbf{P}(\chi'|\chi) = \{P(\chi_j|\chi_i) \equiv P(j|i) \equiv P_{i \rightarrow j} \equiv A(j|i)^2 \equiv (A_{i \rightarrow j})^2\}$ , or the associated scattering amplitudes  $\mathbf{A}(\chi'|\chi) = \{A(j|i) = A_{i \rightarrow j}\}$  of the *emitting* (input) states  $\mathbf{a} = |\chi\rangle = \{|\chi_i\rangle\}$  among the *monitoring/receiving* (output) states  $\mathbf{b} = |\chi'\rangle = \{|\chi_j\rangle\}$ , results from the (bond-projected) SP of quantum mechanics [42]. The local description (LCT) similarly invokes the basis functions  $\{|\mathbf{r}\rangle\}$  of the position representation, identified by the continuous labels of spatial coordinates determining the location  $\mathbf{r}$  of an electron. This complete basis set then determines both the input  $\mathbf{a} = \{|\mathbf{r}\rangle\}$  and output  $\mathbf{b} = \{|\mathbf{r}'\rangle\}$  events of the *local* molecular channel determined by the relevant kernel of conditional-probabilities:  $P(\mathbf{r}'|\mathbf{r}) = P_{\mathbf{r} \rightarrow \mathbf{r}'} = (A_{\mathbf{r} \rightarrow \mathbf{r}'})^2$  [43].

In OCT the entropy/information indices of the covalent/ionic components of the system chemical bonds respectively represent the complementary descriptors of the average communication *noise* and amount of information *flow* in the molecular channel. One observes that the *molecular* input  $\mathbf{P}(\mathbf{a}) \equiv \mathbf{p}$  generates the same distribution in the output of this network,  $\mathbf{q} = \mathbf{p} \mathbf{P}(\mathbf{b}|\mathbf{a}) = \{\sum_i p_i P(j|i) \equiv \sum_i P(i \wedge j) = p_j\} = \mathbf{p}$ , thus identifying  $\mathbf{p}$  as the *stationary* vector of AO-probabilities in the molecular ground state. 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:  $S(\mathbf{P}(\mathbf{b})|\mathbf{P}(\mathbf{a})) = S(\mathbf{q}|\mathbf{p}) \equiv S$ .

The AO channel with the *promolecular* input signal,  $\mathbf{P}(\mathbf{a}_0) = \mathbf{p}_0 = \{p_i^0\}$ , of AO in the system *free* constituent atoms, refers to the initial stage in the bond-formation process. It corresponds to the ground-state (fractional) occupations of the AO contributed by the system constituent atoms, before their mixing into MO. These input 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:

$$\begin{aligned} I(\mathbf{P}(a_0) : \mathbf{P}(b)) &= I(\mathbf{p}_0 : \mathbf{q}) = \sum_i \sum_j P(i, j) \log[p_i P(i, j)/(p_i q_j p_i^0)] \\ &= \sum_i \sum_j P(i, j) [-\log q_j + \log(p_i/p_i^0) + \log P(j|i)] \\ &= S(\mathbf{q}) + \Delta S(\mathbf{p}|\mathbf{p}_0) - S \equiv I_0. \end{aligned} \quad (46)$$

This amount of information reflects the fraction of the initial (promolecular) information content  $S(\mathbf{p}_0)$  which has not been dissipated as noise in the molecular communication system. In particular, for the molecular input, when  $\mathbf{p}_0 = \mathbf{p}$  and hence the vanishing information distance  $\Delta S(\mathbf{p}|\mathbf{p}_0)$ ,

$$I(\mathbf{p} : \mathbf{q}) = S(\mathbf{q}) - S \equiv I. \quad (47)$$

The sum of these two bond components, e.g.,

$$M(\mathbf{P}(a_0) ; \mathbf{P}(b)) = M(\mathbf{p}_0 ; \mathbf{q}) = S + I^0 = S(\mathbf{q}) + \Delta S(\mathbf{p}|\mathbf{p}_0) \equiv M_0, \quad (48)$$

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

$$M(\mathbf{p}; \mathbf{q}) = S(\mathbf{q}|\mathbf{p}) + I(\mathbf{p} : \mathbf{q}) = S(\mathbf{q}) \equiv M. \quad (49)$$

The *relative* index [43],

$$\Delta M = M - M_0 = \Delta S(\mathbf{p}|\mathbf{p}_0), \quad (50)$$

reflecting multiplicity changes due to the chemical bonds alone, is then interaction dependent. It correctly vanishes in the atomic dissociation limit of *separated atoms*, when  $\mathbf{p}_0$  and  $\mathbf{p}$  become identical. The entropy deficiency index  $S(\mathbf{p}|\mathbf{p}_0)$ , reflecting the information distance between the molecular electron density, generated by the constituent bonded atoms, thus represents the overall IT difference-index of the system chemical bonds.

## 6 Superposition principle, conditional probabilities and *non-additive* quantities

Let us recall SP of quantum mechanics [42]:

Any combination  $|\psi\rangle = \sum_k C_k |\psi_k\rangle$  of the admissible (orthonormal) quantum states  $\{|\psi_k\rangle\}$ , where the set  $\{C_k = \langle \psi_k | \psi \rangle\}$  denotes generally complex expansion coefficients, also represents a possible quantum state of the system under consideration. The projections determining the expansion coefficients represent quantum amplitudes  $\{C_k = A(\psi_k|\psi) = \langle \psi_k | \psi \rangle\}$  of the conditional probabilities

$$\begin{aligned}
 P(\psi_k|\psi) &= |A(\psi_k|\psi)|^2 = |C_k|^2 = \langle\psi_k|\psi\rangle\langle\psi|\psi_k\rangle \equiv \langle\psi_k|\hat{P}_\psi|\psi_k\rangle \\
 &= \langle\psi|\psi_k\rangle\langle\psi_k|\psi\rangle \equiv \langle\psi|\hat{P}_\psi|\psi\rangle,
 \end{aligned}
 \tag{51}$$

of observing  $|\psi_k\rangle$  given  $|\psi\rangle$ . For the complete (variable) set  $\{|\psi_k\rangle\}$ , when  $\sum_k |\psi_k\rangle\langle\psi_k| \equiv \sum_k \hat{P}_k = 1$ , these probabilities are normalized:

$$\sum_k P(\psi_k|\psi) = 1. \tag{52}$$

This axiom formally introduces the *conditional* probabilities between the specified quantum states, of observing the *variable* (monitoring) state  $|\psi_k\rangle$  given the *reference* (parameter) state  $|\psi\rangle$ , which define the associated molecular communications. They are given by the expectation value in the variable state of the projection operator onto the reference state.

Let us now examine the time evolution of the representative conditional probability of observing  $|\theta(t)\rangle$  given  $|\psi(t)\rangle$ ,  $P[\theta(t)|\psi(t)] = \langle\theta(t)|\hat{P}_\psi(t)|\theta(t)\rangle$ . In the Schrödinger picture of quantum mechanics the dynamics of quantum states is governed by the system energy operator  $\hat{H}$ :

$$i\hbar \partial|\psi(t)\rangle/\partial t = \hat{H}|\psi(t)\rangle. \tag{53}$$

This Schrödinger equation then gives the following expression for the time derivative of the conditional probability  $P[\theta(t)|\psi(t)]$  in question:

$$\begin{aligned}
 \partial P[\theta(t)|\psi(t)]/\partial t &= \{\langle\partial\theta(t)/\partial t|\hat{P}_\psi(t)|\theta(t)\rangle \\
 &\quad + \langle\theta(t)|\hat{P}_\psi(t)|\partial\theta(t)/\partial t\rangle + \langle\theta(t)|\partial\hat{P}_\psi(t)/\partial t|\theta(t)\rangle \\
 &= (i\hbar)^{-1} \langle\theta(t)|[\hat{P}_\psi(t), \hat{H}] + [\hat{H}, \hat{P}_\psi(t)]|\theta(t)\rangle = 0.
 \end{aligned}
 \tag{54}$$

Therefore, the conditional probabilities between general quantum states, which determine the associated information channels, remain conserved in time and so do their entropic descriptors of the bond multiplicity and composition.

The amplitude  $A(\psi_k|\psi)$  preserves the relative phase of the two states involved, which is responsible for the quantum-mechanical interference. As an illustration consider the two (complex, orthonormal) basis states:

$$\psi = \{\psi_k = R_k \exp(i\phi_k), \langle\psi_k|\psi_l\rangle = \delta_{k,l}; (k, l) \in (1, 2)\}, \tag{55}$$

in the combined molecular state

$$\psi = 2^{-1/2}(\psi_1 + \psi_2). \tag{56}$$

Expressing the probability density  $P = |\psi|^2$  in terms of probabilities  $\{p_k = |\psi_k|^2 = R_k^2 = p[\psi_k]\}$  and phases  $\{\phi_k\}$  of two individual states in this combination gives the familiar result:



$$p = \frac{1}{2}(p_1 + p_2) + \sqrt{p_1 p_2} \cos(\phi_1 - \phi_2) \equiv p_{\psi}^{add.} + p_{\psi}^{nadd.}. \quad (57)$$

It identifies the superposition term  $p_{\psi}^{nadd.}$ , depending upon the relative phase  $\phi_{rel.} = \phi_1 - \phi_2$  of two functions in the combined state, as the *non-additive* probability contribution,

$$p_{\psi}^{nadd.} = p_{\psi}^{total} - p_{\psi}^{add.}, \quad (58a)$$

expressed as the difference between the *total* probability in  $\psi$ -resolution,

$$p_{\psi}^{total} = p \equiv p[\psi], \quad (58b)$$

and its additive contribution given by the weighted average of probability distributions of individual states,

$$p_{\psi}^{add.} = P(\psi_1|\psi)p_1 + P(\psi_2|\psi)p_2 \equiv 1/2(p[\psi_1] + p[\psi_2]). \quad (58c)$$

In accordance with the SP, the probability “weights” in the preceding equation are provided by the squares of the combination coefficients, which define the relevant *conditional* probabilities  $P(\psi_1|\psi) = P(\psi_2|\psi) = 1/2$ :

$$\psi = \sqrt{P(\psi_1|\psi)}\psi_1 + \sqrt{P(\psi_2|\psi)}\psi_2 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2), \quad P(\psi_1|\psi) + P(\psi_2|\psi) = 1. \quad (59)$$

The probability interference term

$$p_{\psi}^{nadd.} = \sqrt{P(\psi_1|\psi)}\sqrt{P(\psi_2|\psi)}[\psi_1^*\psi_2 + \psi_2^*\psi_1] = \sqrt{p_1 p_2} \cos\phi_{rel.}, \quad (60)$$

is responsible for the direct chemical bond, say between two hydrogens, when the two (orthogonalized)  $1s$  AO's of constituent atoms are mixed into the symmetric (doubly occupied) bonding MO. Clearly, for the real AO case, when  $\phi_1 = \phi_2 = 0$ , this contribution reduces into the geometric average of probability densities of the two components:  $p_{\psi}^{nadd.} = \sqrt{p_1 p_2}$ . It should be also observed that the overall probability  $p$  determines the resultant modulus factor  $R = \sqrt{p}$  of  $\psi = R \exp(i\Phi)$ , while its resultant phase follows from equation:

$$\Phi = \arctg\{[R_1 \sin\phi_1 + R_2 \sin\phi_2]/[R_1 \cos\phi_1 + R_2 \cos\phi_2]\}. \quad (61)$$

Of interest also is the related partitioning of the probability-current density in this combined state, into the corresponding additive and *non-additive* contributions [33]:

$$\mathbf{j} = j[\psi] \equiv \mathbf{j}_{\psi}^{total} = \mathbf{j}_{\psi}^{add.} + \mathbf{j}_{\psi}^{nadd.}, \tag{62}$$

$$\mathbf{j}_{\psi}^{add.} \equiv P(\psi_1|\psi)\mathbf{j}_1 + P(\psi_2|\psi)\mathbf{j}_2 = \frac{1}{2}(\mathbf{j}_1 + \mathbf{j}_2),$$

$$\begin{aligned} \mathbf{j}_{\psi}^{nadd.} &= \sqrt{P(\psi_1|\psi)}\sqrt{P(\psi_2|\psi)}\frac{\hbar}{4mi}[(\psi_1^*\nabla\psi_2 - \psi_1\nabla\psi_2^*) + (\psi_2^*\nabla\psi_1 - \psi_2\nabla\psi_1^*)] \\ &= \frac{\hbar}{4mi}[(\psi_1^*\nabla\psi_2 - \psi_1\nabla\psi_2^*) + (\psi_2^*\nabla\psi_1 - \psi_2\nabla\psi_1^*)] \\ &= \frac{\hbar}{4mi}((\sqrt{p_2}\bar{\nabla}p_1 - \sqrt{p_1}\bar{\nabla}p_2)\sin\phi_{rel.} - i(\sqrt{p_2}\bar{\mathbf{j}}_1 - \sqrt{p_1}\bar{\mathbf{j}}_2)\cos\phi_{rel.}), \end{aligned} \tag{63}$$

where bars denote the reduced quantities:

$$\bar{\nabla}p_k = p_k^{-1/2}\nabla p_k \text{ and } \bar{\mathbf{j}}_k = [2m/(\hbar p_k^{1/2})]\mathbf{j}_k$$

This interference contribution to the resultant flow of probability density again depends on the relative phases of the two states combined. For real member functions, for which the relative phase and currents identically vanish, the above additive and *non*-additive flows of the electron probability are both seen to identically vanish.

In a similar way one partitions other physical quantities, which generally depend on both *p* and *j* (or  $\Phi$ ). Consider, e.g., the quantum extension of the gradient measure of the information content in state  $\psi$  [Eq. (21)]:

$$\begin{aligned} I[\psi] &= 4\int|\nabla\psi(\mathbf{r})|^2 d\mathbf{r} \equiv \int f(\mathbf{r}) d\mathbf{r} \\ &= \int[\nabla p(\mathbf{r})]^2/p(\mathbf{r}) d\mathbf{r} + 4\int p(\mathbf{r})[\nabla\Phi(\mathbf{r})]^2 d\mathbf{r} \\ &= I[p] + I[p, \Phi] = I[p] + 4(m/\hbar)^2 \int [j^2(\mathbf{r})/p(\mathbf{r})] d\mathbf{r} = I[p] + I[p, j] \\ &= I^{class.}[\psi] + I^{nclass.}[\psi], \end{aligned} \tag{64}$$

where the classical Fisher functional  $I^{class.}[\psi] = I[p]$  combines the contribution due to the probability distribution alone, while the *non*-classical functional  $I^{nclass.}[\psi] = I[p, j] = I[p, \Phi]$  carries the current(phase)-dependent information content.

Let us examine the superposition rule for the density  $f(\mathbf{r})$  of this quantum-generalized Fisher-information [32] in the combined state  $\psi$ ,

$$f \equiv f_{\psi}^{total} = f_{\psi}^{add.} + f_{\psi}^{nadd.}, \tag{65}$$

proportional to the squared modulus of the wave function gradient:

$$\begin{aligned} f \equiv f[\psi] &= 4\nabla\psi^* \cdot \nabla\psi = 4[(\nabla R)^2 + R^2(\nabla\Phi)^2] \\ &= (\nabla p)^2/p + \left(\frac{2m}{\hbar}\right)^2 \frac{j^2}{p} \equiv f[p] + f[p, j]. \end{aligned} \tag{66}$$

This information density defines the total local contribution in the adopted  $\psi$ -resolution,  $f_{\psi}^{total} \equiv f[\psi]$ , while the weighted sum of the information content of the two individual states determines its additive contribution:

$$f_{\psi}^{add.} \equiv P(\psi_1|\psi)f[\psi_1] + P(\psi_2|\psi)f[\psi_2] = 1/2(f_1 + f_2). \quad (67)$$

The information density  $f_k$  in the complex member-state  $\psi_k$  similarly reads:

$$\begin{aligned} f_k &= f[\psi_k] = 4\nabla\psi_k^* \cdot \nabla\psi_k = 4[(\nabla R_k)^2 + R_k^2(\nabla\phi_k)^2] \\ &= (\nabla p_k)^2/p_k + \frac{4m^2}{\hbar^2} \frac{\mathbf{j}_k^2}{p_k} \equiv f_k[p_k] + f_k[p_k, \mathbf{j}_k], \end{aligned} \quad (68)$$

where  $\mathbf{j}_k \equiv \mathbf{j}[\psi_k]$  denotes the probability-current density in  $\psi_k$ :

$$\mathbf{j}_k = \frac{\hbar}{2mi}(\psi_k^*\nabla\psi_k - \psi_k\nabla\psi_k^*) = \frac{\hbar}{m}\text{Im}(\psi_k^*\nabla\psi_k) = \frac{\hbar}{m}R_k^2\nabla\phi_k = p_k\nabla\left[\frac{\hbar\phi_k}{m}\right]. \quad (69)$$

The *non*-additive (interference) information density, determined by both the probability amplitudes and phases of the two combined states, now reads:

$$\begin{aligned} f_{\psi}^{nadd.} &= 4\sqrt{P(\psi_1|\psi)}\sqrt{P(\psi_2|\psi)}[\nabla\psi_1^* \cdot \nabla\psi_2 \\ &\quad + \nabla\psi_2^* \cdot \nabla\psi_1] = 2[\nabla\psi_1^* \cdot \nabla\psi_2 + \nabla\psi_2^* \cdot \nabla\psi_1] \\ &= 4[(\nabla R_1 \cdot \nabla R_2 + R_1 R_2 \nabla\phi_1 \cdot \nabla\phi_2) \cos \phi_{rel.} \\ &\quad + (R_2 \nabla R_1 \cdot \nabla\phi_2 - R_1 \nabla R_2 \cdot \nabla\phi_1) \sin \phi_{rel.}]. \end{aligned} \quad (70)$$

It again depends on the relative phase of two constituent states. This expression somewhat simplifies, when formulated in terms of the probability and current descriptors  $\{p_k, \mathbf{j}_k\}$  of individual states. More specifically, eliminating  $\nabla\psi_k = \psi_k\nabla\psi_k^* + \psi_k^*\nabla\psi_k$  and Eq. (69),

$$\nabla\psi_k = \frac{\psi_k}{2p_k} \left( \nabla p_k + \frac{2mi}{\hbar} \mathbf{j}_k \right), \quad k = 1, 2, \quad (71)$$

gives:

$$\begin{aligned} f_{\psi}^{nadd.} &= \frac{1}{\sqrt{p_1 p_2}} \left[ \left( \nabla p_1 \cdot \nabla p_2 + \frac{4m^2}{\hbar^2} \mathbf{j}_1 \cdot \mathbf{j}_2 \right) \cos \phi_{rel.} \right. \\ &\quad \left. + \frac{2m}{\hbar} (\nabla p_1 \cdot \mathbf{j}_2 - \nabla p_2 \cdot \mathbf{j}_1) \sin \phi_{rel.} \right] \\ &\equiv (\bar{\nabla} p_1 \cdot \bar{\nabla} p_2 + \bar{\mathbf{j}}_1 \cdot \bar{\mathbf{j}}_2) \cos \phi_{rel.} + (\bar{\nabla} p_1 \cdot \bar{\mathbf{j}}_2 - \bar{\nabla} p_2 \cdot \bar{\mathbf{j}}_1) \sin \phi_{rel.}. \end{aligned} \quad (72)$$

This equation expresses the change in the quantum Fisher information density, relative to the reference level of the additive contribution of Eq. (67), which accompanies the

quantum-mechanical superposition of two individual states in the combination of Eq. (56).

For the stationary member states, when the current-dependent contributions identically vanish, e.g., when combining two real AO into MO, this information contribution is seen to be solely determined by the product of the reduced gradients of the particle probability distributions in the combined state. It is then related to the *non-additive* kinetic energy in AO resolution [11–13,44], which has been successfully employed as an efficient CG criterion for localizing chemical bonds in molecular systems [44]. The related quantity in MO resolution [45] generates the key concept of ELF [46–48].

## 7 Phase relations in two-orbital model

In order to examine the phase aspect of orbital superposition and orbital communications in a more detail we examine the 2-AO model of the preceding section, with each of the *complex* basis functions  $\boldsymbol{\psi}(\mathbf{r}) = [\psi_1(\mathbf{r}), \psi_2(\mathbf{r})]$  of the *promolecular* reference again contributing a single electron to this model *two*-electron system. These complex AO give rise to two MO: bonding,

$$\varphi_b(\mathbf{r}) = \psi_1(\mathbf{r}) U_{1,b} + \psi_2(\mathbf{r}) U_{2,b} \equiv \boldsymbol{\psi}(\mathbf{r}) \mathbf{U}_b, \quad (73)$$

and *anti*-bonding,

$$\varphi_a(\mathbf{r}) = \psi_1(\mathbf{r}) U_{1,a} + \psi_2(\mathbf{r}) U_{2,a} \equiv \boldsymbol{\psi}(\mathbf{r}) \mathbf{U}_a. \quad (74)$$

In a more compact, matrix notation, with  $\boldsymbol{\varphi}(\mathbf{r}) = [\varphi_b(\mathbf{r}), \varphi_a(\mathbf{r})]$  grouping the orthonormal MO combinations, the preceding equations jointly read:

$$\boldsymbol{\varphi}(\mathbf{r}) = \boldsymbol{\psi}(\mathbf{r}) [\mathbf{U}_b | \mathbf{U}_a] \equiv \boldsymbol{\psi}(\mathbf{r}) \mathbf{U}. \quad (75)$$

These MO now combine the complex AO,

$$\boldsymbol{\psi}(\mathbf{r}) = \{\psi_k(\mathbf{r}) = R_k(\mathbf{r}) \exp[i\phi_k(\mathbf{r})], \quad k = 1, 2\},$$

where we again assume their spatial orthonormality:

$$\langle \psi_k | \psi_l \rangle = \int R_k(\mathbf{r}) R_l(\mathbf{r}) \exp(i[\phi_l(\mathbf{r}) - \phi_k(\mathbf{r})]) d\mathbf{r} = \delta_{k,l} \quad \text{or} \quad \langle \boldsymbol{\psi} | \boldsymbol{\psi} \rangle = \mathbf{I}. \quad (76)$$

Hence, MO-orthonormality condition implies the unitary character of the (complex) transformation matrix  $\mathbf{U}$ :

$$\langle \boldsymbol{\varphi} | \boldsymbol{\varphi} \rangle = \mathbf{U}^\dagger \langle \boldsymbol{\psi} | \boldsymbol{\psi} \rangle \mathbf{U} = \mathbf{U}^\dagger \mathbf{U} = \mathbf{I}. \quad (77)$$

The MO combinations can be similarly expressed in terms of their *resultant* moduli and phases:

$$\begin{aligned}\varphi_s(\mathbf{r}) &= \psi_1(\mathbf{r})U_{1,s} + \psi_2(\mathbf{r})U_{2,s} \equiv R_s(\mathbf{r}) \exp[i\Phi_s(\mathbf{r})], \\ U_{k,s} &= \langle \psi_k | \varphi_s \rangle \equiv z_{k,s} \exp(ik_s), \\ |U_{1,s}|^2 + |U_{2,s}|^2 &= (z_{1,s})^2 + (z_{2,s})^2 \equiv P + Q = 1, \quad s = b, a.\end{aligned}\quad (78)$$

The complementary *conditional* probabilities,

$$P = P(\psi_1|\varphi_b) = P(\psi_2|\varphi_a) \quad \text{and} \quad Q = P(\psi_2|\varphi_b) = P(\psi_1|\varphi_a) = 1 - P, \quad (79)$$

determining weights of AO in MO, also reflect the bond polarization, when two spin-paired electrons occupy  $\varphi_b$ .

In terms of these resultant components the MO-orthonormality condition reads:

$$\langle \varphi_s | \varphi_{s'} \rangle = \int R_s(\mathbf{r}) R_{s'}(\mathbf{r}) \exp[i[\Phi_{s'}(\mathbf{r}) - \Phi_s(\mathbf{r})]] d\mathbf{r} = \delta_{s,s'}. \quad (80)$$

The two diagonal (*normalization*) requirements are seen to be automatically satisfied by the normalization of the complementary conditional probabilities of Eq. (79):

$$P(\psi_1|\varphi_b) + P(\psi_2|\varphi_b) = P(\psi_1|\varphi_a) + P(\psi_2|\varphi_a) = P + Q = 1. \quad (81)$$

In order to satisfy the MO-orthogonality equation, e.g.,  $\langle \varphi_a | \varphi_b \rangle = 0$ , the resultant MO phases have to obey the *off*-diagonal constraint

$$\langle \varphi_a | \varphi_b \rangle = \langle \varphi_b | \varphi_a \rangle^* = \left( \mathbf{U}^\dagger \mathbf{U} \right)_{a,b} = U_{1,a}^* U_{1,b} + U_{2,a}^* U_{2,b} \equiv Z \exp(iF) = 0. \quad (82)$$

This equation is automatically fulfilled for the vanishing modulus  $Z$  of this scalar product or its square

$$\begin{aligned}[Z^{(1)}]^2 &= (z_{1,a})^2 (z_{1,b})^2 + (z_{2,a})^2 (z_{2,b})^2 \\ &\quad - 2z_{1,a} z_{1,b} z_{2,a} z_{2,b} \cos\{\pi - [(f_{2,b} - f_{2,a}) - (f_{1,b} - f_{1,a})]\} \\ &= 2PQ\{1 + \cos[(f_{2,b} - f_{2,a}) - (f_{1,b} - f_{1,a})]\} = 0.\end{aligned}\quad (83)$$

Hence, the MO-orthogonality constraint imposes the following requirement to be satisfied by phases  $\mathbf{f} = \{f_{k,s}\}$  of the complex LCAO MO coefficients  $\mathbf{U}$  [Eq. (78)]:

$$[f_{2,b} - f_{2,a}] - [f_{1,b} - f_{1,a}] \equiv \theta_2 - \theta_1 = \pi. \quad (84)$$

In other words, the differences between phases of the expansion coefficients multiplying the two basis functions in the bonding and *anti*-bonding MO combinations, respectively, determine the opposite directions in the complex plane. The preceding

equation can be also interpreted in terms of the opposite directions corresponding to differences between phases of the expansion coefficients in the same MO:

$$(f_{2,b} - f_{1,b}) - (f_{2,a} - f_{1,a}) \equiv \varepsilon_b - \varepsilon_a = \pi. \quad (85)$$

Yet another interpretation of this phase relation involves the *cross*-phase sums,  $\vartheta_{2,1} \equiv f_{2,b} + f_{1,a}$  and  $\vartheta_{1,2} \equiv f_{1,b} + f_{2,a}$ ,

$$\vartheta_{2,1} - \vartheta_{1,2} = \pi. \quad (86)$$

For example, in the real AO case, for  $\psi = \chi$ , the LCAO MO coefficients

$$\mathbf{U} = \mathbf{C} = \begin{bmatrix} \sqrt{P} & -\sqrt{Q} \\ \sqrt{Q} & \sqrt{P} \end{bmatrix} \equiv [\mathbf{C}_b | \mathbf{C}_a] \quad (87)$$

correspond to the following modulus and phase parts of Eq. (78):

$$\mathbf{z} = \{z_{k,s}\} \equiv \begin{bmatrix} \sqrt{P} & \sqrt{Q} \\ \sqrt{Q} & \sqrt{P} \end{bmatrix} \quad \text{and} \quad \mathbf{f} = \{f_{k,s}\} \begin{bmatrix} 0 & \pi \\ 0 & 0 \end{bmatrix} \equiv [f_b | f_a]. \quad (88)$$

In accordance with Eqs. (84)–(86) they determine the opposite phase differences:

$$\begin{aligned} \theta_1 = -\pi, \quad \theta_2 = 0; \quad \varepsilon_b = 0, \quad \varepsilon_a = -\pi; \\ \theta_{1,2} \equiv f_{1,b} - f_{2,a} = 0, \quad \theta_{2,1} \equiv f_{2,b} - f_{1,a} = -\pi, \quad \theta_{1,2} - \theta_{2,1} = \pi, \end{aligned} \quad (89)$$

and sums:

$$\vartheta_{1,2} = 0, \quad \vartheta_{2,1} = \pi, \quad \vartheta_{2,1} - \vartheta_{1,2} = \pi. \quad (90)$$

## 8 Molecular communications

Let us now turn to the conditional probabilities between AO events in molecules. For simplicity we focus on the probability and amplitude channels in a single electron configuration; for the *multi*-configuration extension the reader is referred to refs. [33,43]. An exploration of the chemical bond system in the given ground-state of a molecule indeed calls for the AO resolution determined by the basis functions  $\chi = (\chi_1, \chi_2, \dots, \chi_m)$  of typical (HF or KS) SCF calculations. They express the bonding subspace of the *singly* occupied SMO,

$$\psi = \chi \mathbf{C} = \{\psi_k(\mathbf{q}) = \psi_k(\mathbf{r}; \sigma) = \varphi_k(\mathbf{r}) \zeta_k(\sigma), \quad k = 1, 2, \dots, N\},$$

which define the molecular ground-state  $\Psi(N)$  given by the Slater determinant consisting of  $N$ -lowest SMO:

$$\Psi(N) = \det[\psi] \equiv |\psi_1, \psi_2, \dots, \psi_N|.$$

Here  $\varphi_k(\mathbf{r})$  denotes the *spatial* function (MO) and  $\zeta_k = \{\alpha(\text{spin-up}) \text{ or } \beta(\text{spin-down})\}$  stands for one of the two admissible spin states of an electron [see Eq. (9)].

In this simplest orbital approximation one thus takes into account only the *physical* (bond) subspace  $\varphi$  of the configuration occupied MO, which defines the associated MO projector  $\hat{P}_\varphi \equiv |\varphi\rangle\langle\varphi|$ . It gives rise to the (idempotent) *charge and bond-order* (CBO) *one*-electron density matrix in AO representation,

$$\begin{aligned} \boldsymbol{\gamma} &= \{\gamma_{i,j}\} = \langle\chi|\varphi\rangle\langle\varphi|\chi\rangle \equiv \langle\chi|\hat{P}_\varphi|\chi\rangle = \mathbf{C}\mathbf{C}^\dagger, \\ \boldsymbol{\gamma}^2 &= \langle\chi|\hat{P}_\varphi|\chi\rangle\langle\chi|\hat{P}_\varphi|\chi\rangle = \langle\chi|\hat{P}_\varphi\hat{P}_\varphi\hat{P}_\varphi|\chi\rangle = \mathbf{C}(\mathbf{C}^\dagger\mathbf{C})\mathbf{C}^\dagger = \mathbf{C}\mathbf{C}^\dagger = \boldsymbol{\gamma}, \end{aligned} \quad (91)$$

where we have used the AO orthonormality,  $\langle\chi|\chi\rangle = \mathbf{I}_m$ , and that of the occupied MO expanded in this basis,  $\langle\varphi|\chi\rangle\langle\chi|\chi\rangle\langle\chi|\varphi\rangle = \mathbf{C}^\dagger\mathbf{C} = \mathbf{I}_N$ , which further implies

$$\hat{P}_\varphi\hat{P}_\chi\hat{P}_\varphi = |\varphi\rangle(\mathbf{C}^\dagger\mathbf{C})\langle\varphi| = \hat{P}_\varphi. \quad (92)$$

The molecular joint probabilities of the given pair of the *input–output* AO in the bond system determined by  $\varphi$  are then proportional to the square of the corresponding CBO matrix element:

$$\begin{aligned} P(\chi_i \wedge \chi_j) &= P(i \wedge j) = \gamma_{i,j}\gamma_{j,i}/N = (\gamma_{i,j})^2/N, \\ \sum_j P(i \wedge j) &= N^{-1} \sum_j \gamma_{i,j}\gamma_{j,i} = \gamma_{i,i}/N = p_i. \end{aligned} \quad (93)$$

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

$$\{P(j|i) \equiv P_{i \rightarrow j} = |A_{i \rightarrow j}|^2 = N_i |\langle\chi_i|\hat{P}_\varphi|\chi_j\rangle|^2 = |\gamma_{i,j}|^2/\gamma_{i,i}\}, \quad (94)$$

reflect the electron delocalization in this MO system and identify the associated scattering amplitudes  $\mathbf{A}(\chi'| \chi) = \{A(j|i) = A_{i \rightarrow j}\}$ :

$$A_{i \rightarrow j} = \gamma_{i,j}/[\gamma_{i,i}]^{1/2} \equiv [N_i]^{1/2} \gamma_{i,j}. \quad (95)$$

These amplitudes for the ground-state probability propagation are thus related to the corresponding elements of the CBO matrix  $\boldsymbol{\gamma} = \langle\chi|\hat{P}_\varphi|\chi\rangle$ , the AO representation of the ground-state occupied SMO projector  $\hat{P}_\varphi$ .

In the *closed*-shell state, when the occupied spatial MO accommodate two spin-paired electrons each, the ground state is generated by the  $N/2$  lowest MO,  $\varphi^o = (\varphi_1, \varphi_2, \dots, \varphi_{N/2}) = \chi\mathbf{C}^o$ ,

$$\Psi(N) = |\varphi_1\alpha, \varphi_1\beta, \dots, \varphi_{N/2}\alpha, \varphi_{N/2}\beta\rangle, \quad (96)$$

and  $\hat{P}_\varphi = |\varphi\rangle\langle\varphi| = 2|\varphi^o\rangle\langle\varphi^o| \equiv 2\hat{P}_\varphi^o$ ; hence, the SMO idempotency then implies  $(\hat{P}_\varphi)^2 = [2|\varphi^o\rangle\langle\varphi^o|]^2 = 4|\varphi^o\rangle\langle\varphi^o| = 2\hat{P}_\varphi$  and [see Eqs. (91) and (92)]

$$\begin{aligned} \gamma &= \langle\chi|\varphi\rangle\langle\varphi|\chi\rangle \\ &= 2\langle\chi|\varphi^o\rangle\langle\varphi^o|\chi\rangle \equiv 2\langle\chi|\hat{P}_\varphi^o|\chi\rangle = 2\mathbf{C}^o\mathbf{C}^{o\dagger} = 2\gamma^o, \\ (\gamma^o)^2 = \gamma^o &= \left\{\gamma_{i,j}^o\right\}, \quad \gamma^2 = 4(\gamma^o)^2 = 4\gamma^o = 2\gamma. \end{aligned} \tag{97}$$

For such molecular states the representative conditional probability of the molecular AO channel reads [12, 13]:

$$\begin{aligned} P(j|i) &\equiv P_{i\rightarrow j} = |A_{i\rightarrow j}|^2 = \gamma_{i,j}\gamma_{j,i}/[2\gamma_{i,i}] = \gamma_{i,j}^o\gamma_{j,i}^o/\gamma_{i,i}^o \\ &= N_i^o\langle\chi_i|\hat{P}_\varphi^o|\chi_j\rangle\langle\chi_j|\hat{P}_\varphi^o|\chi_i\rangle \equiv N_i^o\langle\chi_i|\hat{P}_\varphi^o\hat{P}_j\hat{P}_\varphi^o|\chi_i\rangle \equiv N_i^o\langle\chi_i|\hat{\tilde{P}}_j|\chi_i\rangle, \\ A(j|i) &\equiv A_{i\rightarrow j} = \gamma_{i,j}/(2\gamma_{i,i})^{1/2} = \gamma_{i,j}^o/(\gamma_{i,i}^o)^{1/2} \equiv (N_i^o)^{1/2}\gamma_{i,j}^o. \end{aligned} \tag{98}$$

Here,  $N_i^o = (\gamma_{i,i}^o)^{-1}$  stands for the multiplicative constant required to satisfy the appropriate normalization condition:

$$\sum_j P(j|i) = \sum_j \gamma_{i,j}^o\gamma_{j,i}^o/\gamma_{i,i}^o = \sum_j \gamma_{i,j}\gamma_{j,i}/(2\gamma_{i,i}) = 1, \tag{99}$$

where we have used the assumed *closed-shell* idempotency of Eq. (97). In Eq. (98) the  $i \rightarrow j$  probability scattering has been expressed as the expectation value in the *input* AO  $\chi_i$  of the *communication operator* to the specified *output* AO  $\chi_j$ ,  $\hat{\tilde{P}}_j^o \equiv \hat{P}_\varphi^o\hat{P}_j\hat{P}_\varphi^o$ .

It should be again stressed that the classical, *probability-channel* determined by the conditional probabilities of the output AO-events  $\chi'$  given the input AO-events  $\chi$ ,  $\mathbf{P}(\chi'|\chi) = \{P(j|i) = P_{i\rightarrow j}\}$ , which in short notation reads

$$\chi \text{---}\mathbf{P}(\chi'|\chi)\text{---}\chi', \tag{100}$$

losses memory about phases of the scattering amplitudes  $\{A_{i\rightarrow j}\}$ , which are preserved in the associated *amplitude-channel* defined by the *direct* communications  $\mathbf{A}(\chi'|\chi) = \{A(j|i) = A_{i\rightarrow j}\}$ :

$$|\chi\rangle\text{---}\mathbf{A}(\chi'|\chi)\text{---}|\chi'\rangle. \tag{101}$$

This observation also applies to the sequential (product) arrangements of several such (*direct*) channels, called “cascades”, for the *indirect* (bridge) communications between orbitals in molecules, since the modulus of the product of complex functions is given by the product of the moduli of its factors. For example, the *single*-AO intermediates  $\chi''$  in the sequential *three*-orbital scatterings  $\chi \rightarrow \chi'' \rightarrow \chi'$  define the following probability and amplitude cascades:



$$\begin{aligned} \chi - [\mathbf{P}(\chi''|\chi) \rightarrow \chi'' - \mathbf{P}(\chi'|\chi'')] \rightarrow \chi' \Rightarrow \chi - \mathbf{P}[(\chi'|\chi); \chi''] \rightarrow \chi', \\ |\chi\rangle - [\mathbf{A}(\chi''|\chi) \rightarrow |\chi''\rangle - \mathbf{A}(\chi'|\chi'')] \rightarrow |\chi'\rangle \Rightarrow |\chi\rangle - \mathbf{A}[(\chi'|\chi); \chi''] \rightarrow |\chi'\rangle. \end{aligned} \quad (102)$$

The associated (*indirect*) conditional probabilities between AO-events and their amplitudes are then given by products of the corresponding elementary *two-orbital* communications in each (*direct*) *sub-channel*:

$$P[(j|i); k] \equiv P_{i \rightarrow j; k} = P_{i \rightarrow k} P_{k \rightarrow j} \quad \text{and} \quad A[(j|i); k] \equiv A_{i \rightarrow j; k} = A_{i \rightarrow k} A_{k \rightarrow j}. \quad (103)$$

Therefore, such *bridge* probabilities can be straightforwardly derived from the *direct* probability and amplitude channels. They satisfy the relevant *bridge-normalization sum-rules* over the final and intermediate output AO events:

$$\sum_k \left( \sum_j P_{i \rightarrow j; k} \right) = \sum_k P_{i \rightarrow k} = 1. \quad (104)$$

This *single-cascade* development can be straightforwardly generalized to any bridge order. Consider the sequential *t-cascade* involving all basis functions at each propagation stage. Let us examine the resultant amplitudes,  $\mathbf{A}[(\chi'|\chi); t - \chi] = \{A_{i \rightarrow j}^{(t)}\}$ , and probabilities,  $\mathbf{P}[(\chi'|\chi); t - \chi] = \{|A_{i \rightarrow j}^{(t)}|^2\}$ , of the multiple scatterings in the *t-stage bridge* involving sequential cascades *via t-AO intermediates* (orbital bridges) ( $k, l, \dots, m, n$ ), e.g., in the amplitude channel [31]:

$$\begin{aligned} |\chi\rangle - [\mathbf{A}(\chi^{(1)}|\chi) \longrightarrow |\chi^{(1)}\rangle - \mathbf{A}(\chi^{(2)}|\chi^{(1)}) \longrightarrow |\chi^{(2)}\rangle \\ - \dots \rightarrow |\chi^{(t)}\rangle - \mathbf{A}(\chi'|\chi^{(t)})] \longrightarrow |\chi'\rangle \\ \Rightarrow |\chi\rangle - \mathbf{A}[(\chi'|\chi); t - \chi] \longrightarrow |\chi'\rangle. \end{aligned} \quad (105)$$

Such *t-cascade* amplitudes  $\mathbf{A}[(\chi'|\chi); t - \chi] = \{A_{i \rightarrow j; k, l, \dots, m, n} \equiv A_{i \rightarrow j}^{(t)}\}$  are proportional to the corresponding matrix element of the  $(t + 1)$ -power of the (idempotent) projector onto the occupied SMO subspace,

$$A_{i \rightarrow j}^{(t)} = \left( N_{i \rightarrow j}^{(t)} \right)^{1/2} \langle \chi_i | (\hat{\mathbf{P}}_\psi)^{t+1} | \chi_j \rangle = (N_i)^{1/2} \langle \chi_i | \hat{\mathbf{P}}_\psi | \chi_j \rangle = A_{i \rightarrow j}, \quad (106)$$

where we have again used the idempotency property of the SMO projector  $\hat{\mathbf{P}}_\psi$  :  $(\hat{\mathbf{P}}_\psi)^n = \hat{\mathbf{P}}_\psi$ .

Hence, the amplitude  $A_{i \rightarrow j}^{(t)}$  for the *complete* consecutive *t-cascade* preserves the *direct-scattering* probabilities,

$$\mathbf{P}[(\chi'|\chi); t - \chi] = \left\{ \left| A_{i \rightarrow j}^{(t)} \right|^2 = |A_{i \rightarrow j}|^2 = P_{i \rightarrow j} \right\} = \mathbf{P}(\chi'|\chi), \quad (107)$$

thus satisfying the important consistency requirement of the *stationary* molecular channel [30,31]. It also obeys the relevant *bridge*-normalization *sum*-rules:

$$\begin{aligned} \sum_k \sum_l \dots \sum_m \sum_n \left[ \sum_j P_{i \rightarrow j}; k, l, \dots, m, n \right] &= \sum_k \sum_l \dots \sum_m \left[ \sum_n P_{i \rightarrow n}; k, l, \dots, m \right] \\ &= \sum_k \sum_l \dots \left[ \sum_m P_{i \rightarrow m}; k, l, \dots \right] = \dots = \sum_k \left[ \sum_l P_{i \rightarrow l}; k \right] = \sum_k P_{i \rightarrow k} = 1. \end{aligned} \quad (108)$$

For the specified pair of the “terminal” AO, say  $\chi_i \in \chi$  and  $\chi_j \in \chi'$ , one can similarly examine the *indirect* scatterings in the molecular bond system, *via* the *incomplete* cascades consisting of the remaining (“bridge”) functions  $\chi^b = \{\chi_{k \neq (i,j)}\}$ , with the two terminal AO being then excluded from the set of admissible intermediate scatterers. The associated *bridge*-communications give rise to the indirect (through-*bridge*) components of bond multiplicities [28–32], which complement the familiar direct (through-*space*) chemical “bond-orders” [49–59] and provide a novel IT perspective on chemical interactions between more distant AIM, alternative to the fluctuational *charge-shift* mechanism [60].

## 9 Vertical equilibrium principles

The IT (entropic) representation in the theory of molecular electronic structure provides a thermodynamic-like outlook on molecular equilibria [16,17]. A generally complex probability amplitudes in the molecular quantum mechanics, the system electronic wave functions, require generalized information measures of Sect. 3, which combine the classical and *non*-classical contributions, due to the particle probability and current (or phase) distributions, respectively. Let us briefly comment on the density-constrained (“vertical”) variational principles for these quantum information functionals [17], which closely resemble their familiar entropy and energy analogs in the ordinary thermodynamics [23]. By the Hohenberg–Kohn (HK) [35] theorem, the conserved values of the system ground-state energy or classical entropy in these searches, are exactly determined by the corresponding DFT functionals of the system ground-state electron density  $\rho_0(\mathbf{r}) = Np_0(\mathbf{r})$ . It also fixes other *classical* measures of the state information content. Therefore, these “vertical” principles for determining molecular equilibria, for the fixed ground-state distribution of electrons, involve only displacements in the *non*-classical entropy/information complements, functionals of the system current/phase.

In Sect. 3 the *non*-classical information contributions for the constrained probability density  $p_0(\mathbf{r})$ , in a trial state of a single particle [Eq. (12)], were shown to be given by the following functionals of the *spatial* phase function  $\phi(\mathbf{r})$ :

$$\begin{aligned} S[p_0, \phi] &= -2 \int p_0(\mathbf{r}) [\phi^2(\mathbf{r})]^{1/2} d\mathbf{r} \quad \text{and} \\ I[p_0, \phi] &= 4 \int p_0(\mathbf{r}) [\nabla \phi(\mathbf{r})]^2 d\mathbf{r} = 4(m/\hbar)^2 \int \mathbf{j}_0[\phi; \mathbf{r}]^2 / p_0(\mathbf{r}) d\mathbf{r} \equiv I[p_0, \mathbf{j}_0[\phi]], \end{aligned} \quad (109)$$

where  $j_0[\phi] \equiv j[p_0, \phi]$ . The sign of the *non*-classical entropy term has been chosen to guarantee the *maximum* value  $S[p_0, \phi = 0]$  at the exact ground-state solution, when the spatial phase vanishes, for which the complementary *non*-classical Fisher information reaches its *minimum* value  $I[p_0, \phi = 0] = 0$ .

The combined classical and *non*-classical contributions determine the associated resultant entropy/information content of general (variational) quantum states:

$$S[p_0, \phi] = S[p_0] + S[p_0, \phi] \quad \text{and} \quad I[p_0, \phi] = I[p_0] + I[p_0, \phi]. \quad (110)$$

The ground-state equilibrium of a molecule then alternatively results either from the entropy-constrained principle for the system *minimum-energy*, or from the energy-constrained searches for the *maximum* of the *non*-classical Shannon entropy or the *minimum* of the *non*-classical Fisher information [16, 17].

It should be realized that general (*trial*) states of such entropic rules generally imply *non*-vanishing contributions from both the classical (probability) and *non*-classical (*phase-current*) functionals of the entropy/information content. Only in the final, exact (stationary) ground-state, which exhibits purely *time*-dependent phase, the state information is measured by the corresponding classical measure, since then the *space*-dependent part of the wave-function phase, responsible for the current distribution, exactly vanishes.

As an illustration consider again a single particle moving in an external potential  $v(\mathbf{r})$  due to the fixed nuclei (Born–Oppenheimer approximation), described by the Hamiltonian

$$\hat{H}(\mathbf{r}) = -\left(\hbar^2/2m\right)\nabla^2 + v(\mathbf{r}), \quad (111)$$

in the complex variational state  $\varphi(\mathbf{r}) = R(\mathbf{r}) \exp[i\phi(\mathbf{r})]$ . In the *non*-degenerate ground state the lowest-energy amplitude eigenfunction of the Hamiltonian is then described solely by the modulus factor:  $\varphi_0 = R_0$ . It specifies the equilibrium probability distribution  $p_0 = R_0^2$ , while the exactly vanishing spatial phase  $\phi_0 = 0$  implies the vanishing current density in this stationary molecular state:  $j_0(\mathbf{r}) = (\hbar/m)p_0\nabla\phi_0 = \mathbf{0}$ .

Let us examine the modulus-constrained (*vertical*) search for the unknown phase function in the trial state  $\varphi^0(\mathbf{r}) = R_0(\mathbf{r}) \exp[i\phi(\mathbf{r})]$ , where  $R_0(\mathbf{r}) = [p_0(\mathbf{r})]^{1/2}$ , for the conserved classical (*phase-independent*) entropy  $S^{class.}[\psi_0] = S[p_0]$  in the system exact ground-state, which also marks the vanishing spatial phase,  $\phi = \phi_0 = 0$ . The corresponding expression for the expectation value of the system energy in this probability-constrained state reads:

$$E_v[\varphi^0] = \langle \varphi^0 | \hat{H} | \varphi^0 \rangle = (\hbar^2/2m) \int [(\nabla R_0)^2 + R_0^2(\nabla\phi)^2] d\mathbf{r} + \int R_0^2 v d\mathbf{r} \equiv E_v[R_0, \phi]. \quad (112)$$

Its *phase*-minimum principle recovers the familiar (classical) DFT energy expression:

$$\begin{aligned} \min_{\phi} E_v[R_0, \phi] &= \langle \varphi_0 | \hat{H} | \varphi_0 \rangle = (\hbar^2/2m) \int (\nabla R_0)^2 d\mathbf{r} + \int R_0^2 v d\mathbf{r} \equiv E_v[R_0, \phi_0] \\ &= \left( \frac{\hbar^2}{8m} \right) \int \frac{(\nabla p_0)^2}{p_0} d\mathbf{r} + \int p_0 v d\mathbf{r} = E_v[p_0]. \end{aligned} \tag{113}$$

The optimum solution  $\phi_0 = 0$  marks the *maximum* of the quantum entropy,  $S[p_0, \phi_0] = 0$ , and the minimum of the associated (density-constrained) *non*-classical Fisher information  $I[p_0, \phi_0] = 0$ . This eigenstate solution indeed corresponds exclusively to the classical measures of the entropy/information content:  $S[\varphi_0] = S[p_0]$  and  $I[\varphi_0] = I[p_0]$ .

This optimum solution of the *maximum* quantum entropy also implies the *minimum* of the associated (density-constrained) quantum Fisher information:

$$\min_{\phi} I[\varphi^0] = I[\rho_0] + \min_{\phi} I[\rho_0, \phi] = I[\rho_0]. \tag{114}$$

Therefore, the phase component, vital for identifying the trial (*vertical*) functions, identically vanishes for the exact phase  $\phi_0 = 0$  of the ground state. Notice, that only then the classical DFT functionals of the system electron density can be used to predict the state average energy and the information content of this stationary electron distribution.

We have thus arrived at a remarkable parallelism with the ordinary thermodynamics [23]: the ground-state equilibrium results from the equivalent *vertical* (density-constrained) variational principles: either for the system *minimum energy*, at the constrained ground-state entropy  $S[p_0]$  or the classical information  $I[p_0]$ , or—alternatively—for the *extremum entropy/information*, at the constrained ground-state energy  $E_v[p_0]$ . One has to use the *quantum* measures of the system information content, in order to distinguish the phase/current composition of the trial (*vertical*) states. The evolution of such entropic search is then properly described by the current shape of the phase function, which ultimately vanishes in the optimum ground-state solution.

Consider next a general case of a trial quantum state of  $N$  electrons,  $\Psi(N)$ , corresponding to the fixed ground-state electron density  $\rho = \rho_0 = Np_0$ . The energy variational principle now involves a search for the optimum (normalized) wave function, which minimizes the expectation value of the electronic Hamiltonian

$$\hat{H}(N) = \hat{V}_{ne}(N) + [\hat{T}(N) + \hat{V}_{ee}(N)] \equiv \sum_{i=1}^N v(i) + \hat{F}(N), \tag{115}$$

where  $\hat{F}(N)$  combines the electron kinetic  $[\hat{T}(N)]$  and repulsion  $[\hat{V}_{ee}(N)]$  energy operators of  $N$  electrons. One recalls that the “entropic” interpretation has been also attributed previously [11, 13], to the density-constrained principles of the modern DFT, in searches performed for the specified electron density  $\rho$ . For example, in Levy’s [36] constrained-search one defines the universal part of the density functional for the system electronic-energy, which admits *non*–( $v$ -representable) densities, by the following (*vertical*) variational principle,

$$F[\rho] = T[\rho] + V_{ee}[\rho] = \inf_{\Psi \rightarrow \rho} \langle \Psi | \hat{F} | \Psi \rangle \equiv \langle \Psi[\rho] | \hat{F} | \Psi[\rho] \rangle; \quad (116)$$

here, one searches over wave functions which yield the given electron density  $\rho$ , symbolically denoted by  $\Psi \rightarrow \rho$ , and calculates the universal ( $v$ -independent) part  $F[\rho]$  of the density functional for the system electronic energy,

$$E_v[\rho] = F[\rho] + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}, \quad (117)$$

as the lowest value (*infimum*) of the quantum expectation value of  $\hat{F}(N)$ . When this search is performed for the fixed *ground-state* density,  $\rho = \rho_0$ , it also implies the fixed DFT value of the system electronic energy, by the first HK theorem [35]. This feature is thus reminiscent of the thermodynamic criterion for determining the equilibrium state formulated in the entropy representation. By analogy to the maximum-entropy principle for constant internal energy in the phenomenological thermodynamics, this DFT construction can be thus regarded as being also “entropic” in character [11].

It should be emphasized that the variational principle for determining the ground-state wave function, involving the constrained search for the minimum of the system energy, can be also interpreted as the DFT optimization over all admissible densities, in accordance with the second HK theorem [35]. It combines the external (“horizontal”) search, over trial electron densities, and the internal (vertical) search, over wave functions of  $N$  fermions that yield the current density of the external search:

$$\begin{aligned} \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle &= \min_{\rho} E_v[\rho] = \min_{\rho} \left\{ \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right. \\ &\quad \left. + \inf_{\Psi \rightarrow \rho} \langle \Psi | \hat{F} | \Psi \rangle \right\} = E_v[\rho_0]. \end{aligned} \quad (118)$$

Let us focus on the *vertical* (internal) optimization in the preceding equation. It corresponds to the fixed ground-state electron density, say,  $\rho = \rho_0 = \rho[v]$ , identified in the (external) *horizontal* search. The internal, quantum-entropy rule thus involves the energy-constrained search over  $\Psi \rightarrow \rho_0$  for the optimum wave function  $\Psi[\rho_0]$  corresponding to the fixed, matching external potential  $v = v[\rho_0]$  due to the “frozen” nuclei:

$$\begin{aligned} E_v[\rho_0] &= \int v(\mathbf{r}) \rho_0(\mathbf{r}) d\mathbf{r} + \inf_{\Psi \rightarrow \rho_0} \langle \Psi | \hat{F} | \Psi \rangle = V_{ne}[\rho_0] + V_{ee}[\rho_0] + \inf_{\Psi \rightarrow \rho_0} \langle \Psi | \hat{T} | \Psi \rangle \\ &= V_{ne}[\rho_0] + V_{ee}[\rho_0] + T[\rho_0] = V_{ne}[\rho_0] + V_{ee}[\rho_0] + \left( \frac{\hbar^2}{8m} \right) I[\rho_0]. \end{aligned} \quad (119)$$

One observes the presence of Levy’s functional  $F[\rho_0]$  as the crucial (entropic) part of this extremum principle of the system physical information. Notice, that the external potential and electron-repulsion energies are fixed by the frozen-density constraint so that the optimum state also marks the infimum  $I[\rho_0] = I[\varphi_0]$  of the quantum Fisher measure of the information in the trial (vertical) wave functions, related to the system average kinetic energy  $T[\rho_0]$ .

## 10 Conclusion

The quantum-generalized information measures and their vertical variation principles have been examined. This analysis of molecular equilibria has stressed the need for using the resultant information measures, which take into account both the *classical* and *quantum* contributions, due to the electronic probability and current (phase) distributions, respectively. The *non*-classical generalization of the gradient (Fisher) information introduces the information contribution due to the probability current. The proposed *quantum*-generalized Shannon entropy includes the additive contribution due to the average magnitude of the state phase. This extension has been accomplished by requesting that the relation between the classical Shannon and Fisher information densities-per-electron extends into their *non*-classical (quantum) analogs. A similar generalization of the information-distance (entropy-deficiency) concept for comparing spatial probability/current distributions has also been proposed in both the Shannon cross-entropy and Fisher missing-information representations.

These quantum-information terms complement the classical Fisher and Shannon measures, functionals of the particle probability distribution alone. The resultant quantum measures are thus capable to extract the *full* information content of the complex probability amplitudes (wave functions), due to both the probability and current distributions. Elsewhere, the associated continuity equations have been examined, the *non*-classical information sources, linked to the wave function phase or the probability-current densities, have been identified and the *phase*-current density has been introduced, which complements the familiar *probability*-current concept in quantum mechanics [10–13].

As in the ordinary thermodynamics, the equilibrium ground state of a molecule was shown to alternatively result either from the (entropy/information)-constrained principle for the system *minimum energy*, or from the energy-constrained search for the *extremum of the information content*: either the *maximum* of the *non*-classical *Shannon entropy* or the *minimum* of the quantum *Fisher information*. By the HK theorem the ground-state values of the density/probability functionals for the system energy and its entropy/information content uniquely identify the equilibrium distribution of electrons. Therefore, in *vertical* searches carried for this fixed electron density, the vanishing spatial phase and probability current in the *non*-degenerate ground-state, are both determined by the variational principles of the *non*-classical entropy/information contributions, for the fixed values of the corresponding classical terms. The *spatial*-phase aspect identifies the trial function in this density-constrained (*vertical*) searches, and it ultimately vanishes in the final *non*-degenerate ground-state solution.

The SP of quantum mechanics introduces the conditional probabilities between quantum states, which generate a network of molecular communications. The *non*-additive contributions to probability/current distributions and information densities have been identified and the phase relations in *two*-orbital model have been examined. The OCT of the chemical bond introduces the molecular information system transmitting “signals” of electron allocations to AO states, which define the set of elementary electronic events. The conditional probabilities between these basis functions, propagated *via* the network of the occupied molecular orbitals, determine the

orbital communications in molecules, which are generated by the bond-projected SP. In the SCF MO theory their amplitudes are related to the corresponding elements of the CBO matrix. The standard conditional-entropy and mutual-information descriptors of this orbital network provide useful indices of the IT covalency and ionicity.

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