



# Role of electronic kinetic energy and resultant gradient information in chemical reactivity

Roman F. Nalewajski<sup>1</sup>

Received: 25 January 2019 / Accepted: 4 April 2019 / Published online: 16 August 2019  
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## Abstract

The role of resultant *gradient*-information concept, reflecting the kinetic energy of electrons, in shaping the molecular electronic structure and reactivity preferences of *open* reactants is examined. This *quantum*-information descriptor combines contributions due to both the modulus (probability) and phase (current) components of electronic wavefunctions. The importance of resultant entropy/information concepts for distinguishing the bonded (entangled) and nonbonded (disentangled) states of molecular fragments is emphasized and variational principle for the minimum of *ensemble*-average electronic energy is interpreted as a physically equivalent rule for the minimum of resultant *gradient*-information, and the information descriptors of charge-transfer (CT) phenomena are introduced. The in situ reactivity criteria, represented by the populational CT derivatives of the *ensemble*-average values of electronic energy or resultant information, are mutually related, giving rise to identical predictions of electron flows in the *acid*(A) — *base*(B), reactive systems. The virial theorem decomposition of electronic energy is used to reveal changes in the resultant information content due to the chemical bond formation, and to rationalize the Hammond postulate of reactivity theory. The complementarity principle of structural chemistry is confronted with the regional hard (soft) acid and bases (HSAB) rule by examining the polarizational and relaxational flows in such acceptor–donor reactive systems, responses to the external potential and CT displacements, respectively. The frontier-electron basis of the HSAB principle is reexamined and the intra- and inter-reactant communications in A—B systems are explored.

**Keywords** Chemical reactivity · Complementarity principle · Hammond postulate · HSAB rule · Information theory · Virial theorem

## Introduction

Thermodynamic principles for the minimum electronic energy in molecules can be interpreted as the variational rule for the minimum of the *ensemble*-average resultant *gradient*-information [1, 2], related to average kinetic energy of electrons in such (mixed) quantum states. In the *grand*-ensemble representation of the *externally* open molecular systems, they both determine the same set of the optimum probabilities of the system (pure) stationary states. This equivalence resembles identical predictions resulting from the minimum-energy and

maximum-entropy principles in ordinary thermodynamics [3]. The energy and resultant *gradient*-information rules thus represent physically equivalent sources of reactivity criteria. Such an information transcription of the familiar energy principle allows one to reinterpret criteria for the charge transfer (CT) in reactive systems, the populational derivatives of electronic energy, as the associated derivatives of the overall measure of the *quantum*-information in molecular states, which combines the “classical” (modulus, probability) and “nonclassical” (phase, current) aspects of molecular wavefunctions. The proportionality between the resultant *gradient*-information and the system kinetic energy then allows one to use the molecular virial theorem [4] in general reactivity considerations [1, 2].

The classical information theory (IT) of Fisher and Shannon [5–12] has been successfully applied to interpret in chemical terms the molecular probability distributions, e.g., [13–16]. Information principles have been explored [17–22] and density pieces attributed to atoms in molecules (AIM)

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This paper belongs to the Topical Collection Zdzislaw Latajka 70th Birthday Festschrift

✉ Roman F. Nalewajski  
nalewajs@chemia.uj.edu.pl

<sup>1</sup> Department of Theoretical Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Cracow, Poland

have been approached [13, 17, 21–25], providing the information basis for the intuitive (stockholder) division of Hirshfeld [26]. Patterns of chemical bonds have been extracted from molecular electronic communications [13–16, 27–37] and entropy/information distributions in molecules have been examined [13–16, 38, 39]. The nonadditive Fisher information [13–16, 40, 41] has been linked to electron localization function (ELF) [42–44] of modern density functional theory (DFT) [45–50]. This analysis has also formulated the contragradience (CG) probe for localizing chemical bonds [13–16, 51], and the orbital communication theory (OCT) of the chemical bond [27–37] has identified the *bridge*-bonds originating from the cascade propagations of information between AIM, which involve intermediate atomic orbitals [15, 16, 51–57].

In entropic theories of molecular electronic structure, one ultimately requires such quantum extensions of the complementary classical measures of Fisher [5, 6] and Shannon [7, 8], of the information/entropy content in probability distributions, which are appropriate for *complex* probability amplitudes (wavefunctions) of quantum mechanics (QM). The IT distinction between the *bonded* (entangled) and *nonbonded* (disentangled) states of molecular subsystems also calls for their generalized (resultant) information descriptors [16, 58–70], which combine the classical (probability) and nonclassical (current) contributions. Probability distributions generate the *classical* entropy/information descriptors of electronic states. These contributions reflect only the wavefunction modulus, while the wavefunction phase, or its gradient determining the current density, give rise to the corresponding nonclassical supplements in the *resultant* measure the overall information content in molecular electronic states [16, 58–60]. The variational principles of such generalized *entropy* concepts have been used to determine the *phase*-equilibria in molecules and their constituent fragments [16, 61–65].

Paraphrasing Prigogine [71], one could regard the molecular probability distribution as determining an instantaneous structure of “being”, while the system’s current pattern generates the associated structure of “becoming”. Both of these levels of the system electronic organization contribute to the state overall entropy/information content. In quantum information theory (QIT), the classical information term, conceptually rooted in DFT, probes the entropic content of the incoherent (disentangled) local “events”, while it is the nonclassical supplement that provides the information contribution due to coherence (entanglement) of such local events. For example, resultant measures combining the probability and phase/current contributions allow one to distinguish the information content of states generating the same electron density but differing in their phase/current distributions [47, 72, 73].

The resultant Fisher-type *gradient*-information in specified electronic state is proportional to the state average kinetic energy [1, 2, 13, 16, 18, 40]. This allows one to interpret the

variational principle for electronic energy as equivalent *quantum*-information rule. The latter forms a basis for the novel, *information*-treatment of reactivity phenomena [1, 2]. Various DFT-based approaches to classical issues in reactivity theory [74–80] use the *energy*-centered arguments in justifying the observed reaction paths and relative yields of their products. Qualitative considerations on preferences in chemical reactions usually emphasize changes in energies of both reactants and of the whole reactive system, which are induced by displacements (perturbations) in parameters describing the relevant (real or hypothetical) electronic states. In such treatments, usually covering also the linear responses to these primary shifts, one explores reactivity implications of the electronic equilibrium and stability criteria [13, 15, 74, 75, 79]. For example, in charge sensitivity analysis (CSA) [74, 75], the energy derivatives with respect to the system external potential ( $v$ ) and its overall number of electrons ( $N$ ) and the associated charge responses of both the whole reactive systems and their constituent subsystems have been explored as potential reactivity descriptors. In  $R = \text{acid}(A) \leftarrow \text{base}(B) \equiv A-B$  complexes, consisting of the coordinated electron-acceptor and electron-donor reactants, respectively, such responses can be subsequently combined into the corresponding in situ indices characterizing the  $B \rightarrow A$  CT [74, 75]. These difference characteristics of polarized subsystems can be expressed in terms of elementary (principal) charge sensitivities of reactants [74, 75, 78, 79]. The nonclassical IT descriptors of polarized subsystems can be similarly combined into the corresponding in situ properties describing the whole reactive system.

In this work, the role of resultant *gradient*-information/*kinetic*-energy in shaping the chemical reactivity preferences will be explored and variations of the kinetic energy of electrons in the bond-forming/bond-breaking processes will be examined. The continuities of the principal physical degrees-of-freedom of electronic states, the modulus/probability and phase/current distributions, respectively, will be summarized and the virial theorem will be used to interpret, in information terms, the bond-formation process. The theorem implications for the Hammond [81] postulate of reactivity theory will also be explored. The *frontier*-electron approximation to molecular interactions will be adopted to extract the information perspective on Pearson’s [82] hard (soft) acids and bases (HSAB) principle of structural chemistry (see also [83]), and physical equivalence of the energy and information reactivity descriptors in the *grand*-ensemble representation of molecular thermodynamic equilibria will be stressed. The populational derivatives of resultant *gradient*-information will be examined and advocated as alternative indices of chemical reactivity, adequate in predicting both the direction and magnitude of electron flows in reactive systems. The *phase*-description of hypothetical stages of reactants in chemical reactions will be explored, the activation (“promotion”) of molecular substrates will be examined, and the in situ populational derivatives of

resultant-information will be applied to determine the optimum amount of CT in donor–acceptor reactive systems.

### Classical and nonclassical sources of the structure-information in molecular states

Consider, for reasons of simplicity, a single electron moving in the external potential  $v(\mathbf{r})$  created by the fixed nuclei of the molecule. Its quantum state at time  $t$ ,  $|\psi(t)\rangle \equiv |\psi(t)\rangle$ , is then described by the generally complex wavefunction

$$\psi(\mathbf{r}, t) = \langle \mathbf{r} | \psi(t) \rangle = R(\mathbf{r}, t) \exp[i\phi(\mathbf{r}, t)], \tag{1}$$

where (real) functions  $R(\mathbf{r}, t) = p(\mathbf{r}, t)^{1/2} \geq 0$  and  $\phi(\mathbf{r}, t) \geq 0$  stand for its modulus and phase components, respectively. They generate the state two principal physical degrees-of-freedom: its instantaneous probability distribution,

$$p(\mathbf{r}, t) = \psi(\mathbf{r}, t) \psi(\mathbf{r}, t)^* = R(\mathbf{r}, t)^2, \tag{2}$$

and the current density

$$\mathbf{j}(\mathbf{r}, t) = [\hbar/(2mi)] [\psi(\mathbf{r}, t)^* \nabla \psi(\mathbf{r}, t) - \psi(\mathbf{r}, t) \nabla \psi(\mathbf{r}, t)^*] = (\hbar/m)p(\mathbf{r}, t) \nabla \phi(\mathbf{r}, t) \equiv p(\mathbf{r}, t) \mathbf{V}(\mathbf{r}, t), \tag{3}$$

where the current-per-particle  $\mathbf{V}(\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t)/p(\mathbf{r}, t)$  determines an effective velocity field  $d\mathbf{r}(t)/dt$  for the probability “fluid”. The probability descriptor of the (pure) molecular state thus measures a product of the conjugate states  $\psi$  and  $\psi^*$ , while the phase component reflects their ratio:

$$\phi(\mathbf{r}, t) = (2i)^{-1} \ln [\psi(\mathbf{r}, t)/\psi(\mathbf{r}, t)^*], \tag{4}$$

In the current definition of Eq. (3), the probability “velocity”

$$\mathbf{V}(\mathbf{r}, t) = \mathbf{V}[\mathbf{r}(t), t] = (\hbar/m) \nabla \phi(\mathbf{r}, t) \tag{5}$$

reflects the state *phase*-gradient  $\nabla \phi(\mathbf{r}, t)$ .

The physical descriptors  $p(\mathbf{r}, t)$  and  $\mathbf{j}(\mathbf{r}, t)$  of a complex quantum state constitute independent sources of an overall information content of the molecular electronic structure: the probability distribution alone generates its *classical* contribution while the current (velocity) density determines its *nonclassical* complement in the resultant measure [16, 58–60].

The IT gradient descriptors extract the information contained in local inhomogeneities of these two principal physical distributions, reflected by their gradient and divergence, respectively. These gradient probes reflect the complementary facets of the state “structure” content:  $\nabla p = 2R \cdot \nabla R$  extracts the spatial inhomogeneity of the probability density, the structure of “being”, while  $\nabla \cdot \mathbf{j} = \nabla p \cdot \mathbf{V} = (\hbar/m) \nabla p \cdot \nabla \phi$  uncovers the current structure of “becoming”. We have used above a direct implication of the *probability*-continuity,

$$\begin{aligned} dp[\mathbf{r}(t), t]/dt &\equiv \sigma_p(\mathbf{r}, t) = \partial p(\mathbf{r}, t)/\partial t + \nabla \cdot \mathbf{j}(\mathbf{r}, t) \\ &= \partial p(\mathbf{r}, t)/\partial t + [\partial p(\mathbf{r}, t)/\partial \mathbf{r}] [d\mathbf{r}(t)/dt] \\ &= \partial p(\mathbf{r}, t)/\partial t + \nabla p(\mathbf{r}, t) \cdot \mathbf{V}(\mathbf{r}, t) = 0, \text{ or} \\ \partial p(\mathbf{r}, t)/\partial t &= -\nabla \cdot \mathbf{j}(\mathbf{r}, t) \\ &= -[\nabla p(\mathbf{r}, t) \cdot \mathbf{V}(\mathbf{r}, t) + p(\mathbf{r}, t) \nabla \cdot \mathbf{V}(\mathbf{r}, t)] \\ &= -\nabla p(\mathbf{r}, t) \cdot \mathbf{V}(\mathbf{r}, t), \end{aligned} \tag{6}$$

that divergence of the effective velocity field  $\mathbf{V}(\mathbf{r}, t)$ , determined by the state *phase*-Laplacian, identically vanishes:

$$\nabla \cdot \mathbf{V}(\mathbf{r}, t) = (\hbar/m) \Delta \phi(\mathbf{r}, t) = 0. \tag{7}$$

Here,  $dp/dt \equiv \sigma_p$  and  $\partial p/\partial t$  denote the *total* and *partial time*-derivatives of probability density  $p(\mathbf{r}, t) = p[\mathbf{r}(t), t]$ , respectively. The local probability “source” (“production”)  $\sigma_p$  is reflected by the total derivative  $dp/dt$ , which measures the time rate of change in an infinitesimal volume element of the probability fluid *flowing* with the probability current, while the partial derivative  $\partial p/\partial t$  represents the corresponding rate at the specified (*fixed*) point in space. One observes that the total time derivative of Eq. (6) expresses the sourceless continuity relation for electronic probability distribution:  $\sigma_p(\mathbf{r}, t) = 0$ .

In a molecular scenario, one envisages the system electrons moving in the external potential  $v(\mathbf{r})$  due to the “frozen” nuclei of the familiar Born–Oppenheimer (BO) approximation. The *mono*-electronic system is then described by the Hamiltonian

$$\hat{H}(\mathbf{r}) = -(\hbar^2/2m)\nabla^2 + v(\mathbf{r}) \equiv \hat{T}(\mathbf{r}) + v(\mathbf{r}) \tag{8}$$

where  $\hat{T}(\mathbf{r})$  stands for its kinetic part. The dynamics of electronic wavefunction  $\psi(\mathbf{r}, t)$  is determined by the Schrödinger equation (SE) of molecular quantum mechanics (QM),

$$i\hbar \partial \psi(\mathbf{r}, t)/\partial t = \hat{H}(\mathbf{r})\psi(\mathbf{r}, t), \tag{9}$$

which further implies specific temporal evolutions of  $p(\mathbf{r}, t)$  and  $\phi(\mathbf{r}, t)$ .

The *probability*-velocity descriptor should be also attributed to the current concept associated with the state *phase*-component:

$$\mathbf{J}(\mathbf{r}, t) = \phi(\mathbf{r}, t) \mathbf{V}(\mathbf{r}, t). \tag{10}$$

The phase field  $\phi(\mathbf{r}, t)$  and its current  $\mathbf{J}(\mathbf{r}, t)$  then determine a nonvanishing source term  $\sigma_\phi(\mathbf{r}, t)$  in the *phase*-continuity equation:

$$\begin{aligned} \sigma_\phi(\mathbf{r}, t) &\equiv d\phi(\mathbf{r}, t)/dt = \partial \phi(\mathbf{r}, t)/\partial t + \nabla \cdot \mathbf{J}(\mathbf{r}, t) \text{ or} \\ \partial \phi(\mathbf{r}, t)/\partial t &= -\nabla \cdot \mathbf{J}(\mathbf{r}, t) + \sigma_\phi(\mathbf{r}, t). \end{aligned} \tag{11}$$

Using Eq. (7) gives the following expression for this *phase*-source:

$$\begin{aligned} d\phi[\mathbf{r}(t), t]/dt &= \partial \phi[\mathbf{r}(t), t]/\partial t + d\mathbf{r}(t)/dt \cdot \partial \phi[\mathbf{r}(t), t]/\partial \mathbf{r} \\ &= \partial \phi(\mathbf{r}, t)/\partial t + \mathbf{V}(\mathbf{r}, t) \cdot \nabla \phi(\mathbf{r}, t) \\ &= \partial \phi(\mathbf{r}, t)/\partial t + (\hbar/m) [\nabla \phi(\mathbf{r}, t)]^2. \end{aligned} \tag{12}$$

The *phase*-dynamics from SE,

$$\partial\phi/\partial t = [\hbar/(2m)] \left[ R^{-1} \Delta R - (\nabla\phi)^2 \right] - v/\hbar, \quad (13)$$

ultimately identifies the state *phase*-production of Eq. (11):

$$\sigma_\phi = [\hbar/(2m)] \left[ R^{-1} \Delta R + (\nabla\phi)^2 \right] - v/\hbar. \quad (14)$$

To summarize, the classical continuity relation of QM expresses a sourceless character of the electron probability distribution, while its nonclassical companion introduces a non-vanishing *phase*-source combining both the classical (modulus) and nonclassical (phase) inputs.

## Resultant information and kinetic energy

Let us consider the fixed time  $t = t_0$  and for simplicity suppress this parameter in the list of state arguments. The average Fisher's measure [5, 6] of the *classical* gradient information for locality events contained in probability density  $p(\mathbf{r}) = R(\mathbf{r})^2$  is reminiscent of von Weizsäcker's [84] inhomogeneity correction to the *kinetic*-energy functional:

$$\begin{aligned} I[p] &= \int p(\mathbf{r}) [\nabla \ln p(\mathbf{r})]^2 d\mathbf{r} = \int [\nabla p(\mathbf{r})]^2 / p(\mathbf{r}) d\mathbf{r} \\ &\equiv \int p(\mathbf{r}) I_p(\mathbf{r}) d\mathbf{r} \equiv \int \mathcal{J}_p(\mathbf{r}) d\mathbf{r} \\ &= 4 \int [\nabla R(\mathbf{r})]^2 d\mathbf{r} \equiv I[R]. \end{aligned} \quad (15)$$

Here,  $\mathcal{J}_p(\mathbf{r}) = p(\mathbf{r}) I_p(\mathbf{r})$  denotes functional's overall density and  $I_p(\mathbf{r})$  stands for the associated density-per-electron. The amplitude form  $I[R]$  reveals that this classical descriptor reflects a magnitude of the state *modulus*-gradient. It characterizes an effective "narrowness" of the particle spatial probability distribution, i.e., a degree of *determinicity* in the particle position.

This *classical* functional of the gradient information in probability distribution generalizes into the corresponding *resultant* descriptor, functional of the quantum state  $|\psi(t)\rangle$  itself, which combines the modulus (probability) and phase (current) contributions [40]. It is defined by the quantum expectation value of the Hermitian operator of the overall gradient information [16, 40], related to the kinetic energy operator  $\hat{T}(\mathbf{r})$  of Eq. (8),

$$\hat{I}(\mathbf{r}) = -4\Delta = (2i\nabla)^2 = (8m/\hbar^2) \hat{T}(\mathbf{r}). \quad (16)$$

The integration by parts then gives the following expression for the state average (resultant) *gradient*-information

$$\begin{aligned} I[\psi] &= \langle \psi | \hat{I} | \psi \rangle = -4 \int \psi(\mathbf{r})^* \Delta \psi(\mathbf{r}) d\mathbf{r} = 4 \int |\nabla \psi(\mathbf{r})|^2 d\mathbf{r} \\ &\equiv \int p(\mathbf{r}) I_p(\mathbf{r}) d\mathbf{r} \equiv \int \mathcal{J}_p(\mathbf{r}) d\mathbf{r} \\ &= I[p] + 4 \int p(\mathbf{r}) |\nabla \phi(\mathbf{r})|^2 d\mathbf{r} \\ &\equiv \int p(\mathbf{r}) [I_p(\mathbf{r}) + I_\phi(\mathbf{r})] d\mathbf{r} \equiv I[p] + I[\phi] \equiv I[p, \phi] \\ &= I[p] + (2m/\hbar^2) \int p(\mathbf{r})^{-1} j(\mathbf{r})^2 d\mathbf{r} \equiv I[p] + I[j] \equiv I[p, j], \end{aligned} \quad (17)$$

with  $\mathcal{J}_p(\mathbf{r}) = p(\mathbf{r}) I_p(\mathbf{r})$  again denoting its overall density and  $I_p(\mathbf{r})$  standing for the corresponding density-per-electron. This *quantum*-information concept,  $I[\psi] = I[p, \phi] = I[p,$

$j]$ , is seen to combine the classical (probability) contribution  $I[p]$  of Fisher and the corresponding nonclassical (phase/current) supplement  $I[\phi] = I[j]$ . It also reflects the particle average (dimensionless) kinetic energy  $T[\psi]$ :

$$I[\psi] = (8m/\hbar^2) \langle \psi | \hat{I} | \psi \rangle \equiv (8m/\hbar^2) T[\psi] \equiv \sigma T[\psi]. \quad (18)$$

This *one*-electron development can be straightforwardly generalized into general  $N$ -electron systems in the corresponding quantum state  $|\Psi(N)\rangle$  exhibiting electron density  $\rho(\mathbf{r}) = Np(\mathbf{r})$ , where  $p(\mathbf{r})$  stands for its probability (shape) factor. The corresponding  $N$ -electron information operator then combines terms due to each particle,

$$\hat{I}(N) = \sum_{i=1}^N \hat{I}(\mathbf{r}_i) = (8m/\hbar^2) \sum_{i=1}^N \hat{T}(\mathbf{r}_i) \equiv (8m/\hbar^2) \hat{T}(N), \quad (19)$$

and determines the state overall *gradient*-information,

$$\begin{aligned} I(N) &= \langle \Psi(N) | \hat{I}(N) | \Psi(N) \rangle \\ &= (8m/\hbar^2) \langle \Psi(N) | \hat{T}(N) | \Psi(N) \rangle \\ &= (8m/\hbar^2) T(N), \end{aligned} \quad (20)$$

proportional to the associated expectation value  $T(N)$  of the system *kinetic*-energy operator  $\hat{T}(N)$ .

For example, in *one*-determinantal representation, of a *single* electron (orbital) configuration  $\Psi(N) = |\psi_1 \psi_2 \dots \psi_N\rangle$ , e.g., in the familiar Hartree–Fock of Kohn–Sham theories, these  $N$ -electron descriptors combine the additive contributions due to the (singly) occupied,  $\{n_s = 1\}$ , *spin* molecular orbitals (MO)  $\psi = (\psi_1, \psi_2, \dots, \psi_N) = \{\psi_s\}$ :

$$\begin{aligned} T(N) &= \sum_s n_s \langle \psi_s | \hat{T} | \psi_s \rangle \equiv \sum_s n_s T_s \\ &= (\hbar^2/8m) \sum_s n_s \langle \psi_s | \hat{I} | \psi_s \rangle \equiv (\hbar^2/8m) \sum_s n_s I_s. \end{aligned} \quad (21)$$

In the analytical LCAO MO representation, with the occupied MO expressed as linear combinations of (orthogonalized) atomic orbitals (AO)  $\chi = (\chi_1, \chi_2, \dots, \chi_k, \dots)$ ,

$$|\psi\rangle = |\chi\rangle \mathbf{C}, \quad \mathbf{C} = \langle \chi | \psi \rangle = \{C_{k,s} = \langle \chi_k | \psi_s \rangle\}, \quad (22)$$

the average gradient information in the orbital configuration  $\Psi(N)$ , for the unit matrix of MO occupations,  $\mathbf{n} = \{n_s \delta_{s,s'} = \delta_{s,s'}\}$ , reads:

$$\begin{aligned} I(N) &= \sum_s n_s \langle \psi_s | \hat{I} | \psi_s \rangle \\ &= \sum_k \sum_l \{ \sum_s C_{k,s} n_s C_{s,l}^* \} \langle \chi_l | \hat{I} | \chi_k \rangle \\ &\equiv \sum_k \sum_l \gamma_{k,l} I_{l,k} = \text{tr}(\boldsymbol{\gamma} \mathbf{I}). \end{aligned} \quad (23)$$

Here, the AO representation of the resultant *gradient*-information operator,

$$\mathbf{I} = \{I_{k,l} = \langle \chi_k | \hat{I} | \chi_l \rangle \propto \langle \chi_k | \hat{T} | \chi_l \rangle = T_{k,l}\}, \quad (24)$$

and the charge/bond-order (CBO) (density) matrix of LCAO MO theory,

$$\boldsymbol{\gamma} = \mathbf{CnC}^\dagger = \langle \chi | \psi \rangle \mathbf{n} \langle \psi | \chi \rangle \equiv \langle \chi | \hat{P}_\psi | \chi \rangle, \quad (25)$$

is seen to provide the AO-representation of the projection onto the occupied MO-subspace,

$$\begin{aligned} \hat{P}_\psi &= N[\sum_s |\psi_s\rangle \langle \psi_s|] (n_s/N) \langle \psi_s | \\ &\equiv N[\sum_s |\psi_s\rangle p_s \langle \psi_s|] \equiv N\hat{d}, \end{aligned} \quad (26)$$

proportional to the density operator  $\hat{d}$  of the configuration MO “ensemble”.

This average overall information thus assumes thermodynamic-like form, as the trace of the product of CBO matrix, the AO representation of the (occupation-weighted) MO projector, which establishes the configuration density operator, and the corresponding AO matrix of the Hermitian operator for the resultant gradient information, related to the system electronic kinetic energy. In this MO “ensemble”-averaging, the AO information matrix  $\mathbf{I}$  constitutes the *quantity*-matrix, while the CBO (density) matrix  $\boldsymbol{\gamma}$  provides the “geometrical” *weighting* factors in this MO “ensemble”, reflecting the system electronic state. It has been argued elsewhere [16, 27–37] that elements of the CBO matrix generate amplitudes of electronic communications between molecular AO “events”. This observation thus adds a new angle to interpreting this average-information expression: it is seen to represent the communication-weighted (dimensionless) kinetic energy of the system electrons.

The relevant separation of the *modulus*- and *phase*-components of general  $N$ -electron states calls for wavefunctions yielding the specified electron density [47]. It can be effected using the Harriman–Zumbach–Maschke (HZM) [83, 84] construction of DFT. It uses  $N$  (complex) *equidensity orbitals*, each generating the molecular probability distribution  $p(\mathbf{r})$  and exhibiting the density-dependent spatial phases, which safeguard the MO orthogonality.

### Bonded (entangled) and nonbonded (disentangled) states of reactants

The resultant entropy/information concepts of QIT have been applied to describe the substrate current activation and to distinguish the bonded and nonbonded states of molecular fragments [1, 2, 66–70]. In the course of a chemical reaction, one conventionally recognizes several of its hypothetical stages [1,

2, 13, 16, 72, 73] involving either the mutually *closed* [nonbonded ( $n$ ), disentangled] or *open* [bonded ( $b$ ), entangled] reactants, e.g., the electron *acceptor* and *donor* substrates in a bimolecular reactive system  $R = A \text{---} B$  involving the acidic (A) and basic (B) partners, respectively. The nonbonded status of such closed (polarized) subsystems in  $R^+ \equiv (A^+|B^+)$ , conserving the initial numbers of electrons of isolated reactants  $\{\alpha^0\}$ ,  $\{N_\alpha^+ = N_\alpha^0\}$ , and - at a finite separation - relaxed in a presence of the reaction partner,  $\{\rho_\alpha^+ \neq \rho_\alpha^0\}$ , is symbolized by the *solid* vertical line separating the two reactants at this polarization (+) stage. Only due to this mutual closure the identity of the two substrates remains a meaningful concept. The overall electron density of  $R^+$  as a whole then reads:

$$\begin{aligned} \rho_R^+ &= \rho_A^+ + \rho_B^+ \equiv N_A^+ p_A^+ + N_B^+ p_B^+ = N_R p_R^+, \\ p_\alpha^+ &= \rho_\alpha^+ / N_\alpha^+, N_\alpha^+ = \int \rho_\alpha^+ d\mathbf{r} = N_\alpha^0, \alpha = A, B, \end{aligned} \quad (27)$$

where

$$\begin{aligned} p_R^+ &= (N_A^+ / N_R) p_A^+ + (N_B^+ / N_R) p_B^+ \\ &\equiv P_A^+ p_A^+ + P_B^+ p_B^+ \end{aligned} \quad (28)$$

denotes the system global probability distribution, the *shape*-factor of  $\rho_R^+$ , and the condensed probabilities  $\{P_\alpha^+ = N_\alpha^+ / N_R = N_\alpha^0 / N_R = P_\alpha^0\}$  reflect reactant “shares” in the overall number of electrons:  $N_R^+ = \sum_\alpha N_\alpha^+ = \sum_\alpha N_\alpha^0 = N_R^0 \equiv N_R$ . These subsystems lose their “identity” in the bonded status, as mutually open parts of the externally closed (isoelectronic) reactive system  $R \equiv (A^*|B^*)$  conserving  $N_R$ , where the absence of a barrier for *internal* electron flows between the two substrates has been symbolically represented by the *broken* vertical line separating the two reactants. Indeed, in absence of the dividing “wall”, each “part” physically exhausts the whole reactive system.

However, one can also contemplate the *external* flows of electrons, between the *mutually* nonbonded reactants and their separate (external, macroscopic) reservoirs of electrons  $\{\mathcal{R}_\alpha\}$ . The formal *mutual*-closure then implies the relevancy of subsystem identities, while the *external*-openness in now macroscopic (composite) subsystems  $\{\mathcal{M}_\alpha = (\alpha^*|\mathcal{R}_\alpha)\}$  of the whole composite reactive system

$$\mathcal{M}_R = (\mathcal{R}_A|A^*|B^*|\mathcal{R}_B) = (\mathcal{M}_A|\mathcal{M}_B), \quad (29)$$

allows one to independently manipulate the chemical potentials of both parts,  $\{\mu_\alpha = \mu(\mathcal{R}_\alpha)\}$ , and hence also their ensemble-average electron densities  $\{\rho_\alpha^* = N_\alpha^* p_\alpha^*\}$  and populations  $N_\alpha^* = \int \rho_\alpha^* d\mathbf{r}$ . In particular, the substrate chemical potentials equalized at the molecular level in both composite subsystems,  $\{\mu_\alpha^* = \mu_R \equiv \mu_R(N_R)\}$ , thus conserving the overall (ensemble-average) electron number  $\langle N_R \rangle_{ens.} = N_R(\mu_R)$ , define the *equilibrium* macroscopic system

$$\mathcal{M}_R^* = \mathcal{M}_R(\mu_R) \equiv (\mathcal{M}_A^* | \mathcal{M}_B^*), \quad \{\mathcal{M}_\alpha^* = \mathcal{M}_\alpha(\mu_R)\}, \quad (30)$$

in which one observes the equilibrium reactant distributions  $\{\rho_\alpha^* = \rho_\alpha(\mu_R)\}$  and the associated populations  $\{N_\alpha^* = N_\alpha(\mu_R)\}$  of the “bonded” molecular fragments  $\{\alpha^*\}$  in  $(\mathcal{R}_A | A^* | B^* | \mathcal{R}_B)$ . They must also characterize the equilibrium “bonded” (entangled) substrates in a hypothetical reactive system  $R^* = (A^* | B^*) \equiv R$ , corresponding to the equalized fragment chemical potentials, at molecular level, and the conserved (*ensemble-average*) number of electrons:  $\langle N_R \rangle_{ens.} = N_R(\mu_R) = N_R$ . These effective electron populations thus exhibit the equilibrium amount of the *inter-reactant* CT:

$$N_{CT} = N_A^* - N_A^0 = N_B^0 - N_B^* > 0, \quad (31)$$

in the globally isoelectronic reaction:

$$\begin{aligned} N_R &\equiv N_A^* + N_B^* = N_A^+ + N_B^+ \equiv N_R^+ \\ &= N_A^0 + N_B^0 \equiv N_R^0 \end{aligned} \quad (32)$$

To summarize, the fragment identity can be retained only for the *mutually* closed (nonbonded) status of the acidic and basic reactants, e.g., in the *polarized* reactive system  $R_n^+$  or in the *equilibrium* composite system  $\mathcal{M}_R^*$ . The subsystem electron densities  $\{\rho_\alpha = N_\alpha p_\alpha\}$  can be either “frozen”, e.g., in the *promolecular* reference  $R^0 = (A^0 | B^0) \equiv R_n^0$  consisting of the *isolated-reactant* distributions shifted to their actual positions in the molecular reactive system  $R$ , or “polarized” in  $R^+$  or  $R$ , i.e., relaxed in presence of the reaction partner. The final equilibrium in  $R$  as a whole, combining the bonded subsystems  $\{\alpha^*\}$  after CT, accounts for the extra CT-induced polarization of reactants compared to  $R^+$ . As we have argued above, descriptors of this state, of the mutually bonded (formally open) reactants, can be inferred only indirectly, by examining the chemical potential equalization in the composite system  $\mathcal{M}_R$ . Similar external reservoirs are involved, when one examines the independent population displacements on reactants, e.g., in defining the fragment chemical potentials and their hardness tensor.

In this chain of hypothetical reaction “events”, the polarized system  $R^+$  appears as the launching stage for the subsequent CT and the accompanying *induced* polarization, after the hypothetical barrier for the flow of electrons between the two subsystems has been effectively lifted. This density polarization is also accompanied by the subsystem *current-promotion*, reflected by the modified electron flow patterns in both substrates, compared to promolecule  $R^0$ , in accordance with their current *equilibrium-phase* distributions [16, 66–69]. This *nonclassical* (current) activation of both subsystems complements the *classical* (probability) polarization of

reactants in presence of their reaction partners. The phase aspect is thus vital for accounting for the mutual coherence (entanglement) of reactants in the reactive system as a whole.

The fragment chemical potentials  $\mu_R^+ = \{\mu_\alpha^+\}$  and elements of the hardness matrix  $\eta_R^+ = \{\eta_{\alpha,\beta}\}$  of the polarized reactants represent the populational derivatives of the *ensemble-average* electronic energy  $\mathcal{E}_v(\{N_\beta\})$  in the reactant resolution, reflecting the *mutually* closed but *externally* open substrates  $\{\alpha(\mu_\alpha^+)\}$  in composite subsystems  $\{\mathcal{M}_\alpha^+ = \mathcal{M}_\alpha(\mu_\alpha^+) = (\alpha^+ | \mathcal{R}_\alpha^+)\}$  of the macroscopic polarized system

$$\mathcal{M}_R^+ = (\mathcal{R}_A | A^+ | B^+ | \mathcal{R}_B) \equiv (\mathcal{M}_A^+ | \mathcal{M}_B^+), \quad (33)$$

calculated for the fixed external potential of the whole system,  $v = v_A + v_B$ , reflecting the “frozen” molecular geometry in  $R^+$ :

$$\mu_\alpha \equiv \partial \mathcal{E}_v(\{N_\gamma\}) / \partial N_\alpha, \quad \eta_{\alpha,\beta} = \partial^2 \mathcal{E}_v(\{N_\gamma\}) / \partial N_\alpha \partial N_\beta = \partial \mu_\alpha / \partial N_\beta. \quad (34)$$

The associated global properties of  $R = (A^* | B^*)$  are defined by the corresponding derivatives with respect to the overall (*ensemble-average*) number of electrons  $N_R$  in the  $R$  fragment of the combined system

$$\begin{aligned} \mathcal{M}_R^* = (R | \mathcal{R}^*) &= (A^* | B^* | \mathcal{R}^*) = (\mathcal{R}^* | A^* | B^* | \mathcal{R}^*), \\ \mu_R &= \partial \mathcal{E}_v(N_R) / \partial N_R, \quad \eta_R = \partial^2 \mathcal{E}_v(N_R) / \partial N_R^2 = \partial \mu_R / \partial N_R. \end{aligned} \quad (35)$$

The optimum amount of the (fractional) CT is then determined by the difference in chemical potentials of the (equilibrium) polarized reactants in  $R^+$ , the CT gradient

$$\mu_{CT} = \partial \mathcal{E}_v(N_{CT}) / \partial N_{CT} = \mu_A^+ - \mu_B^+ < 0, \quad (36)$$

and the effective in situ hardness ( $\eta_{CT}$ ) or softness ( $S_{CT}$ ) for this process,

$$\begin{aligned} \eta_{CT} &= \partial \mu_{CT} / \partial N_{CT} \\ &= (\eta_{A,A} - \eta_{A,B}) + (\eta_{B,B} - \eta_{B,A}) \\ &\equiv \eta_A^R + \eta_B^R = S_{CT}^{-1}, \end{aligned} \quad (37)$$

representing the CT Hessian and its inverse, respectively; here  $\eta_X^R$  denotes the effective chemical hardness of the “embedded” reactant  $X$  in  $R$  [72, 73]. The optimum amount of CT,

$$N_{CT} = -\mu_{CT} S_{CT}, \quad (38)$$

then generates the associated (second-order) stabilization energy:

$$E_{CT} = \mu_{CT} N_{CT}/2 = -\mu_{CT}^2 S_{CT}/2 < 0. \tag{39}$$

### Grand-ensemble principle for thermodynamic equilibrium

The populational derivatives of the average electronic energy or of the resultant *gradient*-information call for the *grand-ensemble* representation [1, 2, 85, 86]. Indeed, only the average overall number of electrons  $\langle N \rangle_{ens.} \equiv \mathcal{N}$  in the *externally* open molecular part  $\langle M(v) \rangle_{ens.}$ , identified by the system external potential  $v$ , of the equilibrium combined (macroscopic) system  $\mathcal{M} = (\langle M(v) \rangle_{ens.}, \mathcal{R})$  including the external electron reservoir  $\mathcal{R}$ ,

$$\mathcal{N} = \text{tr}(\hat{D}\hat{N}) = \sum_i N_i (\sum_j P_j^i) \equiv \sum_i N_i P^i, \quad \sum_i P^i = 1, \tag{40}$$

exhibits the continuous (fractional) spectrum of values, thus justifying the very concept of the populational ( $\mathcal{N}$ ) derivative itself. Here,

$$\hat{N} = \sum_i |\psi_i\rangle N_i \langle \psi_i| = \sum_i N_i \left[ \sum_j |\psi_j^i\rangle \langle \psi_j^i| \right]$$

stands for the particle-number operator in Fock’s space and the density operator

$$\hat{D} = \sum_i \sum_j |\psi_j^i\rangle P_j^i \langle \psi_j^i|$$

identifies the statistical mixture of the system (pure) states  $\{|\psi_i\rangle \equiv |\psi(N_i)\rangle = (\psi_j^i, j = 0, 1, \dots)\}$ , defined for different (integer) numbers of electrons  $\{N_i\}$ , which appear in the ensemble with the external (thermodynamic) probabilities  $\{P_j^i\}$ . Such  $\mathcal{N}$ -derivatives are involved in definitions of the system reactivity criteria, e.g., its chemical potential (negative electronegativity) [74, 75, 85–89] or the chemical hardness (softness) [74, 75, 90] and Fukui function (FF) [74, 75, 91] descriptors.

These  $\mathcal{N}$ -derivatives are thus definable only in the *mixed* electronic states, e.g., those corresponding to thermodynamic equilibria in the *externally* open molecule  $\langle M(v) \rangle_{ens.}$ . In the *grand-ensemble*, this state is determined by the equilibrium density operator specified by the corresponding thermodynamic (*externally* imposed) *intensive* parameters: the chemical potential of electron reservoir  $\mathcal{R}$ ,  $\mu = \mu_{\mathcal{R}}$ , and the absolute temperature  $T$  of heat bath  $\mathcal{B}$ :  $T = T_{\mathcal{B}}$ . These intensities ultimately determine the relevant Legendre-transform

$$\Omega = \mathcal{E} - (\partial \mathcal{E} / \partial \mathcal{N}) \mathcal{N} - (\partial \mathcal{E} / \partial \mathcal{S}) \mathcal{S} = \mathcal{E} - \mu \mathcal{N} - T \mathcal{S} \tag{41}$$

of the *ensemble*-average energy

$$\mathcal{E}[\hat{D}] \equiv \mathcal{E}(\mathcal{N}, \mathcal{S}; v) = \text{tr}(\hat{D}\hat{H}) = \sum_i \sum_j P_j^i E_j^i, \tag{42}$$

which minimizes at the optimum ensemble probabilities for these thermodynamic conditions,  $\{(P_j^i)^{opt.} = P_j^i(\mu, T; v)\}$ ,

$$\begin{aligned} \min_{\hat{D}} \Omega[\hat{D}] &= \Omega[\hat{D}(\mu, T; v)] = \mathcal{E}[\hat{D}_{eq.}] - \mu \mathcal{N}[\hat{D}_{eq.}] - T \mathcal{S}[\hat{D}_{eq.}] \equiv \Omega(\mu, T; v) \\ &\Rightarrow \{P_j^i(\mu, T; v)\}. \end{aligned} \tag{43}$$

The *grand*-potential corresponds to replacing the “extensive” state parameters of the particle number  $\mathcal{N} = \mathcal{N}[\hat{D}]$  and thermodynamic entropy [92].

$$\mathcal{S}[\hat{D}] = \text{tr}(\hat{D}\hat{S}) = -k_B \sum_i \sum_j P_j^i \ln P_j^i, \tag{44}$$

where  $k_B$  denotes the Boltzmann constant, by their “intensive” conjugates, the chemical potential  $\mu$  and absolute temperature  $T$ , respectively. The Legendre-transform (41) includes these “intensities” as Lagrange multipliers enforcing at the *grand*-potential minimum constraints of the specified values of the system *ensemble*-average values of the conjugate “extensive” parameters: the overall number of electrons,

$$\langle N \rangle_{ens.} = \mathcal{N}[\hat{D}_{eq.}] = \langle N(\mu, T) \rangle_{ens.} = \sum_i P^i(\mu, T; v) N_i = \mathcal{M}[\mu, T; v] \equiv \mathcal{N}, \tag{45}$$

and average thermodynamic (von Neumann’s [92]) entropy,

$$\begin{aligned} \langle \mathcal{S} \rangle_{ens.} &= \mathcal{S}[\hat{D}_{eq.}] = \langle \mathcal{S}(\mu, T) \rangle_{ens.} \\ &= -k_B \sum_i \sum_j P_j^i(\mu, T; v) \ln P_j^i(\mu, T; v) \\ &= \mathcal{S}[\mu, T; v] \equiv \mathcal{S}. \end{aligned} \tag{46}$$

This allows one to formally identify the (external) “intensive” parameters as partial derivatives of the average energy,

$$\mathcal{E}[\hat{D}_{eq.}] = \langle E(\mu, T) \rangle_{ens.} = \sum_i \sum_j P_j^i(\mu, T; v) E_j^i = \mathcal{E}[\mu, T; v], \tag{47}$$

with respect to the corresponding constraint-values:

$$\mu = \left( \frac{\partial \mathcal{E}}{\partial \mathcal{N}} \right)_{\mathcal{S}} \Big|_{\hat{D}_{eq.}} \quad \text{and} \quad T = \left( \frac{\partial \mathcal{E}}{\partial \mathcal{S}} \right)_{\mathcal{N}} \Big|_{\hat{D}_{eq.}}. \tag{48}$$

The *externally* imposed parameters  $\mu$  and  $T$  thus determine the associated optimum probabilities of the (pure) stationary states  $\{|\psi_j^i\rangle \equiv |\psi_j[N_i, v]\rangle\}$ , eigenstates of partial Hamiltonians,

$$\begin{aligned} \hat{H}(N_i, \nu) |\psi_j[N_i, \nu]\rangle &= E_j^i |\psi_j[N_i, \nu]\rangle, \\ P_j^i(\mu, T; \nu) &= \Xi^{-1} \exp \left[ \beta (\mu N_i - E_j^i) \right], \end{aligned} \quad (49)$$

which define the associated density operator of the (mixed) equilibrium state in the *grand-ensemble*:

$$\hat{D}(\mu, T; \nu) = \sum_i \sum_j |\psi_j^i\rangle P_j^i(\mu, T; \nu) \langle \psi_j^i| \equiv \hat{D}_{eq}. \quad (50)$$

Here,  $\Xi$  stands for the *grand-ensemble partition-function* and  $\beta = (k_B T)^{-1}$ . In the limit  $T \rightarrow 0$  such a mixture of molecular *ground-states*  $\{|\psi_i\rangle = \psi[N_i, \nu]\}$  corresponding to integer numbers of electrons  $\{N_i\}$  and energies

$$E_j^i = \langle \psi_j^i | \hat{H}(N_i, \nu) | \psi_j^i \rangle = E_j[N_i, \nu],$$

appearing in the *grand-ensemble* with probabilities  $\{P_j^i(\mu, T \rightarrow 0; \nu)\}$ , represents an *externally* open molecule  $\langle M(\mu, T \rightarrow 0; \nu) \rangle_{ens.}$  in these thermodynamic conditions.

## Information descriptors of chemical reactivity

The *ensemble-average* value of the resultant *gradient-information*, given by the weighted expression in terms of the equilibrium probabilities in this thermodynamic (mixed) state,

$$\begin{aligned} \langle I \rangle_{ens.} &\equiv \mathcal{J}[\hat{D}_{eq.}] = \text{tr}(\hat{D}_{eq.} \hat{I}) = \sum_i \sum_j P_j^i(\mu, T; \nu) \langle \psi_j^i | \hat{I} | \psi_j^i \rangle \equiv \sum_i \sum_j P_j^i(\mu, T; \nu) I_j^i, \\ I_j^i &= \sigma \langle \psi_j^i | \hat{I} | \psi_j^i \rangle \equiv \sigma T_j^i, \end{aligned} \quad (51)$$

is related to the *ensemble-average* kinetic energy  $\mathcal{J}$ :

$$\langle T \rangle_{ens.} \equiv \mathcal{J} = \text{tr}(\hat{D} \hat{T}) = \sum_i \sum_j P_j^i(\mu, T; \nu) \langle \psi_j^i | \hat{T} | \psi_j^i \rangle \equiv \sum_i \sum_j P_j^i(\mu, T; \nu) T_j^i = \sigma^{-1} \mathcal{J}. \quad (52)$$

Therefore, the thermodynamic rule of Eq. (43), for the minimum of the constrained average electronic energy, can be alternatively interpreted as the corresponding principle for the constrained average content of resultant *gradient-information*:

$$\begin{aligned} \sigma \min_{\hat{D}} \Omega[\hat{D}] &= \sigma \Omega[\hat{D}_{eq.}] \\ &= \mathcal{J}[\hat{D}_{eq.}] + \frac{8m}{\hbar^2} \{ \mathcal{W}[\hat{D}_{eq.}] - \mu \mathcal{N}[\hat{D}_{eq.}] - T \mathcal{S}[\hat{D}_{eq.}] \}. \end{aligned} \quad (53)$$

Here, the *ensemble-average* value of the system overall potential energy,

$$\mathcal{W}[\hat{D}_{eq.}] = \mathcal{V}[\hat{D}_{eq.}] + \mathcal{U}[\hat{D}_{eq.}], \quad (54)$$

combines contributions due to electron-nuclear attraction ( $\mathcal{V}[\hat{D}_{eq.}]$ ) as well as the electron and nuclear repulsions ( $\mathcal{U}[\hat{D}_{eq.}]$ ).

The information principle of Eq. (53) is seen to contain an additional constraint of the fixed overall potential energy,  $\langle \mathcal{W} \rangle_{ens.} = \mathcal{W}$ , multiplied by the Lagrange multiplier

$$\lambda_{\mathcal{W}} = -\sigma = \left( \frac{\partial \mathcal{J}}{\partial \mathcal{W}} \right)_{\mathcal{N}, \mathcal{S}} \Big|_{\hat{D}_{eq.}} \equiv \kappa. \quad (55)$$

It also includes the “scaled” intensities associated with the remaining constraints:

$$\text{information “potential”}: \quad \xi \equiv \sigma \mu = \left( \frac{\partial \mathcal{J}}{\partial \mathcal{N}} \right)_{\mathcal{W}, \mathcal{S}} \Big|_{\hat{D}_{eq.}} \quad (56)$$

$$\text{information “temperature”}: \quad \tau \equiv \sigma T = \left( \frac{\partial \mathcal{J}}{\partial \mathcal{S}} \right)_{\mathcal{W}, \mathcal{N}} \Big|_{\hat{D}_{eq.}}. \quad (57)$$

It should be stressed that the two conjugate thermodynamic principles, for the constrained minima of the *ensemble-average* energy

$$\delta(\mathcal{E}[\hat{D}] - \mu \mathcal{N}[\hat{D}] - T \mathcal{S}[\hat{D}])_{\hat{D}_{eq.}} = 0, \quad (58)$$

and overall *gradient-information*

$$\delta(\mathcal{J}[\hat{D}] - \kappa \mathcal{W}[\hat{D}] - \xi \mathcal{N}[\hat{D}] - \tau \mathcal{S}[\hat{D}])_{\hat{D}_{eq.}} = 0, \quad (59)$$

have the same *optimum-probability* solutions of Eq. (49). This manifests the physical equivalence of the energetic and entropic principles for determining the equilibrium states in thermodynamics [3].

Several  $\mathcal{N}$ -derivatives of the *ensemble-average* electronic energy or resultant *gradient-information* define useful reactivity criteria [74, 75]. The physical equivalence of the energy and information principles in molecular thermodynamics indicates that such concepts are mutually related, being both capable of describing the CT phenomena in donor–acceptor systems [1, 2]. The ensemble interpretation also applies to diagonal and mixed *second* derivatives of the electronic energy, which involve the differentiation with respect to electron population variable  $\mathcal{N}$ . For example, in the electronic energy representation the *chemical hardness* reflects  $\mathcal{N}$ -derivative of the chemical potential,

$$\eta = \left( \frac{\partial^2 \mathcal{E}}{\partial \mathcal{N}^2} \right)_{\mathcal{S}} \Big|_{\hat{D}_{eq.}} = \left( \frac{\partial \mu}{\partial \mathcal{N}} \right)_{\mathcal{S}} \Big|_{\hat{D}_{eq.}} > 0, \quad (60)$$



while the information “hardness” measures the  $\mathcal{N}$ -derivative of information “potential”:

$$\omega = \left( \frac{\partial^2 \mathcal{J}}{\partial \mathcal{N}^2} \right)_{w,s} \Big|_{\hat{\delta}_{eq}} = \left( \frac{\partial \xi}{\partial \mathcal{N}} \right)_{w,s} \Big|_{\hat{\delta}_{eq}} = \sigma \eta > 0. \tag{61}$$

The positive signs of these “diagonal” populational derivatives assure the external stability of  $\langle M(v) \rangle_{ens}$  with respect to hypothetical electron flows between the molecular system and its reservoir [74, 75]. Indeed, they imply an increase (a decrease) of the global energetic and information “intensities” ( $\mu$  and  $\xi$ ), which are coupled to  $\mathcal{N}$ , in response to the perturbation created by the primary electron inflow (outflow). This is in accordance with the familiar Le Châtelier and Le Châtelier-Braun principles of thermodynamics [3] that spontaneous responses in system intensities to the initial population displacements diminish effects of such primary perturbations.

By the Maxwell cross-differentiation relation the mixed second derivative of the system ensemble-average energy,

$$f(\mathbf{r}) = \left( \frac{\partial^2 \mathcal{E}}{\partial \mathcal{N} \partial v(\mathbf{r})} \right)_{s} \Big|_{\hat{\delta}_{eq}} = \left( \frac{\partial \mu}{\partial v(\mathbf{r})} \right)_{s} \Big|_{\hat{\delta}_{eq}} = \left( \frac{\partial \rho(\mathbf{r})}{\partial \mathcal{N}} \right)_{s} \Big|_{\hat{\delta}_{eq}}, \tag{62}$$

measuring its global FF [91], can be alternatively interpreted as either the density response per unit populational displacement or the response in global chemical potential per unit displacement in the external potential. The associated mixed derivative of the average resultant gradient information then reads:

$$\varphi(\mathbf{r}) = \left( \frac{\partial^2 \mathcal{J}}{\partial \mathcal{N} \partial v(\mathbf{r})} \right)_{w,s} \Big|_{\hat{\delta}_{eq}} = \left( \frac{\partial \xi}{\partial v(\mathbf{r})} \right)_{w,s} \Big|_{\hat{\delta}_{eq}} = \sigma f(\mathbf{r}). \tag{63}$$

### Use of virial-theorem partitioning

It is of interest to examine the ground-state variations of the electronic resultant gradient-information in specific geometrical displacements  $\Delta \mathbf{Q}$  of the molecular or reactive systems. Its proportionality to the system kinetic-energy component calls for using the virial theorem [4] in the BO approximation of molecular QM,

$$2\Delta T(\mathbf{Q}) + \Delta W(\mathbf{Q}) + \mathbf{Q} \cdot [\partial \Delta E(\mathbf{Q}) / \partial \mathbf{Q}] = 0, \tag{64}$$

$$\Delta E(\mathbf{Q}) = \Delta T(\mathbf{Q}) + \Delta W(\mathbf{Q}),$$

which allows one to extract changes in the kinetic,  $\Delta T(\mathbf{Q})$ ,

and potential,  $\Delta W(\mathbf{Q})$ , components of the overall electronic energy  $\Delta E(\mathbf{Q})$  for the system current geometrical structure  $\mathbf{Q}$ :

$$\Delta T(\mathbf{Q}) = -\Delta E(\mathbf{Q}) - \mathbf{Q} \cdot [\partial \Delta E(\mathbf{Q}) / \partial \mathbf{Q}] \text{ and} \tag{65}$$

$$\Delta W(\mathbf{Q}) = 2\Delta E(\mathbf{Q}) + \mathbf{Q} \cdot [\partial \Delta E(\mathbf{Q}) / \partial \mathbf{Q}].$$

These virial relations assume a particularly simple form in diatomics, for which the internuclear distance  $R$  uniquely specifies the molecular geometry,

$$\Delta E(R) = \Delta T(R) + \Delta W(R),$$

$$2\Delta T(R) + \Delta W(R) + R[d\Delta E(R)/dR] = 0,$$

or

$$\Delta T(R) = -\Delta E(R) - R[d\Delta E(R)/dR] = -d[R\Delta E(R)]/dR \text{ and}$$

$$\Delta W(R) = 2\Delta E(R) + R[d\Delta E(R)/dR] = R^{-1}d[R^2\Delta E(R)]/dR. \tag{66}$$

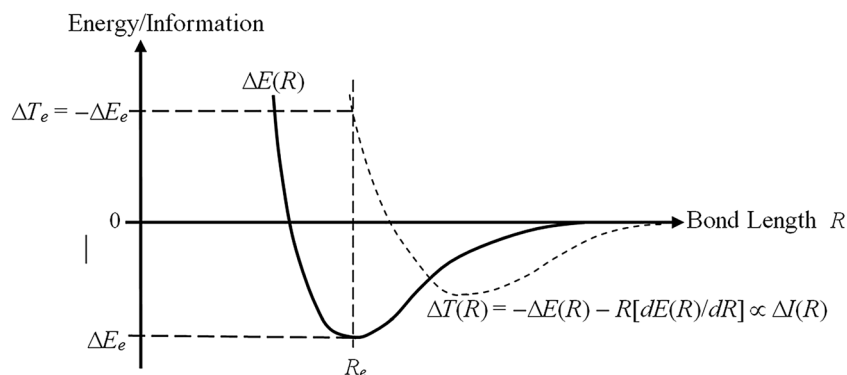
Figure 1 presents qualitative plots for a diatomic molecule: of the BO potential  $\Delta E(R)$  and its kinetic-energy component  $\Delta T(R)$ , which also reflects the ground-state resultant gradient-information  $\Delta I(R)$ . It follows from the figure that during a mutual approach by both atoms the kinetic-energy/gradient-information is first diminished relative to the separated-atom limit (SAL), due to the longitudinal Cartesian component of the kinetic energy associated with the “z” direction along the bond axis [93–96]. At the equilibrium distance  $R_e$  the resultant information rises above the SAL value, due to an increase in transverse components of the kinetic energy, corresponding to “x” and “y” directions perpendicular to the bond axis. Therefore, at the equilibrium separation  $R_e$ , for which  $\Delta T(R_e) = -\Delta E(R_e)$ , the bond-formation results in a net increase of the molecular resultant gradient-information relative to SAL, due to generally more compact electron distribution in the field of both nuclei.

Another interesting case of variations in molecular geometry is the (intrinsic) reaction coordinate  $\mathbf{R}_c$ , or the associated progress variable  $P$  of the arc-length along this trajectory, for which the virial relations also assume the diatomic-like form [4]. Let us examine the virial theorem decomposition of the energy profile along  $\mathbf{R}_c$  in typical bimolecular reaction



where  $R^\ddagger$  denotes the transition-state (TS) complex, to which the qualitative Hammond postulate [81] of the chemical reactivity theory applies (see Fig. 2). The virial-theorem application to extract qualitative plots of the resultant gradient-information from energy profiles in the endo- and exo-ergic reactions (upper panel), and in the energy-neutral chemical processes on symmetric potential energy surfaces (PES) (lower panel) has been reported elsewhere [1, 2, 4]. These analyses have shown that this qualitative rule of chemical reactivity is fully explained by the sign of the  $P$ -derivative of the overall gradient-information measure at TS complex.

**Fig. 1** Qualitative diagram of variations in electronic energy  $\Delta E(R)$  (solid line) with the internuclear distance  $R$  in a diatomic molecule, and of its kinetic energy component  $\Delta T(R) = -d/dR[R\Delta E(R)]$  (broken line) reflecting also the state resultant gradient-information  $\Delta I(R) \propto \Delta T(R)$



The qualitative Hammond postulate emphasizes a relative resemblance of the reaction TS complex  $R^\ddagger$  to its substrates (products) in the *exo*-ergic (*endo*-ergic) reactions, while for the vanishing reaction energy the position of TS complex is predicted to be located symmetrically between substrates and products. The activation barrier thus appears “early” in *exo*-ergic reactions, e.g.,  $H_2 + F \rightarrow H + HF$ , with the reaction *substrates* being only slightly modified in TS,  $R^\ddagger \approx [A-B]$ , both electronically and geometrically. Accordingly, in *endo*-ergic bond-breaking-bond-forming process, e.g.,  $H + HF \rightarrow H_2 + F$ , the barrier is “late” along the reaction-progress coordinate  $P$  and the activated complex resembles more the reaction *products*:  $R^\ddagger \approx [C-D]$ . This qualitative statement has been subsequently given several more quantitative formulations and theoretical explanations using both the energetic and entropic arguments [20, 97–103].

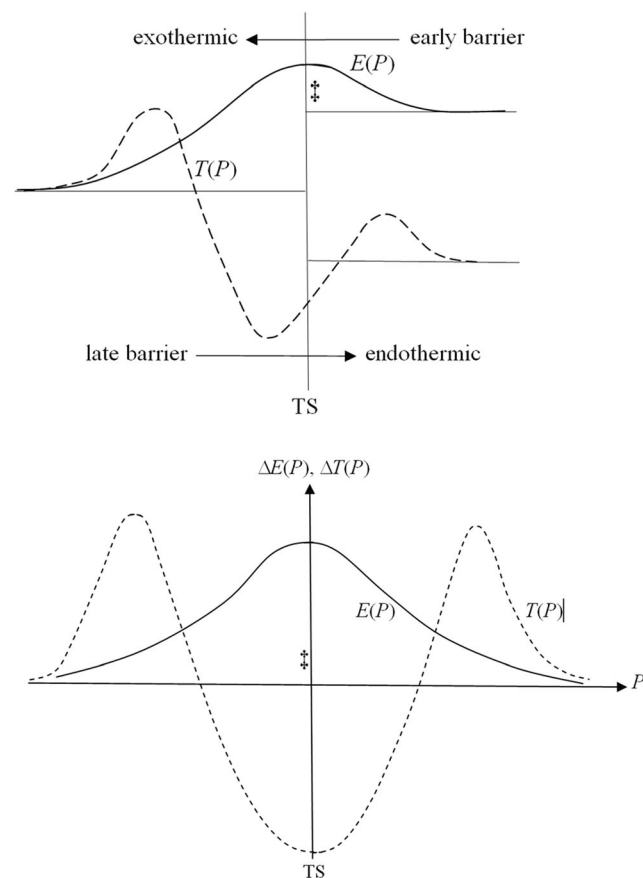
The energy profile along the reaction “progress” coordinate  $P$ ,  $\Delta E(P) = E(P) - E(P_{sub.})$  is directly “translated” by the virial theorem into the associated displacement  $\Delta T(P) = T(P) - T(P_{sub.})$  in its kinetic-energy contribution, proportional to the corresponding change  $\Delta I(P) = I(P) - I(P_{sub.})$  in the system resultant *gradient-information*,  $\Delta I(P) = \sigma \Delta T(P)$ ,

$$\begin{aligned} \Delta T(P) &= -\Delta E(P) - P [d\Delta E(P)/dP] \\ &= -d[P\Delta E(P)]/dP \end{aligned} \quad (68)$$

The energy profile  $\Delta E(P)$  in the *endo*- or *exo*-direction, for the positive and negative reaction energy  $\Delta E_r = E(P_{prod.}) - E(P_{sub.})$ , respectively, thus uniquely determines the associated profiles of the kinetic-energy or resultant-information:  $\Delta T(P) \propto \Delta I(P)$ . A reference to qualitative plots in Fig. 2 shows that the latter distinguishes these two directions by the sign of its derivative at TS:

$$\begin{aligned} \text{endo-direction} &: (dI/dP)^\ddagger > 0 \text{ and } (dT/dP)^\ddagger > 0, \Delta E_r > 0; \\ \text{energy-neutral} &: (dI/dP)^\ddagger = 0 \text{ and } (dT/dP)^\ddagger = 0, \Delta E_r = 0; \\ \text{exo-direction} &: (dI/dP)^\ddagger < 0 \text{ and } (dT/dP)^\ddagger < 0, \Delta E_r < 0. \end{aligned} \quad (69)$$

This observation demonstrates that RC derivative of the resultant *gradient-information* at TS complex,  $dI/dP|^\ddagger$ , proportional to  $dT/dP|^\ddagger$ , can serve as an alternative detector of the reaction energetic character: its positive/negative values respectively identify the *endo/exo*-ergic reactions exhibiting the late/early activation energy barriers, with the neutral case ( $\Delta E_r = 0$  or  $dT/dP|^\ddagger = 0$ ) exhibiting an equidistant position of TS between the reaction substrates and products on a



**Fig. 2** Variations of the electronic total ( $E$ ) and kinetic ( $T$ ) energies in the *exo*-ergic ( $\Delta E_r < 0$ ) and *endo*-ergic ( $\Delta E_r > 0$ ) reactions (upper panel). The lower panel provides qualitative plots for the symmetrical PES ( $\Delta E_r = 0$ )

symmetrical potential energy surface, e.g., in the hydrogen exchange reaction  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ .

The reaction energy  $\Delta E_r$  determines the corresponding change in the resultant *gradient*-information,  $\Delta I_r = I(P_{prod.}) - I(P_{sub.})$ , proportional to  $\Delta T_r = T(P_{prod.}) - T(P_{sub.}) = -\Delta E_r$ . The virial theorem thus implies a net decrease of the resultant gradient information in *endo*-ergic processes,  $\Delta I_r(endo) < 0$ , its increase in *exo*-ergic reactions,  $\Delta I_r(exo) > 0$ , and a conservation of the overall *gradient*-information in the energy-neutral chemical rearrangements:  $\Delta I_r(neutral) = 0$ . One also recalls that the classical part of this information displacement probes an average spatial inhomogeneity of the electronic density. Therefore, the *endo*-ergic processes, requiring a net supply of energy to R, give rise to relatively less compact electron distributions in the reaction products, compared with the substrates. Accordingly, the *exo*-ergic transitions, which net release the energy from R, generate a relatively more concentrated electron distributions in products, compared to substrates, and no such an average change is predicted for the energy-neutral case.

### Regional HSAB versus complementary coordinations

Some subtle preferences in chemical reactivity result from the induced (polarizational or relaxational) electron-flows in reactive systems, reflecting responses to the primary or induced displacements in the electronic structure of the reaction complex, e.g., [16, 104]. Such flow patterns can be diagnosed, estimated, and compared by using either the energetical or information reactivity criteria defined above. One such still-problematic issue is the best mutual arrangement of the acidic and basic parts of molecular reactants in the donor-acceptor systems [16, 104, 105].

Consider the reactive complex A—B consisting of the basic reactant  $B = (a_B | \dots | b_B) \equiv (a_B | b_B)$  and the acidic substrate  $A = (a_A | \dots | b_A) \equiv (a_A | b_A)$ , where  $a_X$  and  $b_X$  denote the acidic and basic parts of subsystem X, respectively. The acidic (electron acceptor) part is relatively harder, i.e., less responsive to external perturbation, exhibiting lower values of the fragment FF descriptor, while the basic (electron donor) fragment is relatively softer, more polarizable, as reflected by its higher density/population responses. The *acidic* part  $a_X$  exerts an *electron-accepting* (stabilizing) influence on the neighboring part of the other reactant Y, while the basic fragment  $b_X$  produces an *electron-donor* (destabilizing) effect on a fragment of Y in its vicinity.

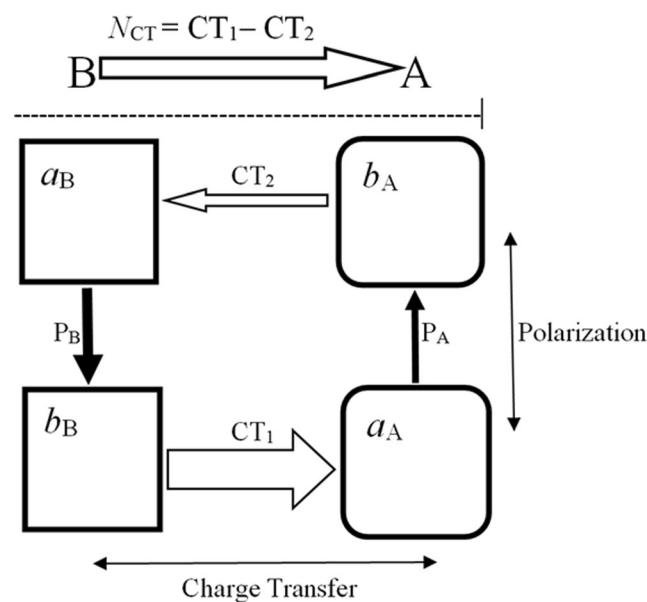
There are two ways in which both reactants can mutually coordinate in the corresponding reactive complexes [16, 104, 105]. In the *complementary* (c) arrangement of Fig. 3,

$$R_c \equiv \begin{bmatrix} a_A - b_B \\ b_A - a_B \end{bmatrix} \quad (70)$$

the reactants orient themselves in such a way that geometrically accessible *a*-fragment of one reactant faces the geometrically accessible *b*-fragment of the other substrate. This pattern follows from the *maximum complementarity* (MC) rule [104] of chemical reactivity, which reflects a simple *electrostatic* preference that *electron-rich* (repulsive, basic) fragment of one reactant prefers to face the *electron-deficient* (attractive, acidic) part of the reaction partner. In the alternative regional HSAB-type structure of Fig. 4, the acidic (basic) fragment of one reactant faces the like-fragment of the other substrate:

$$R_{HSAB} \equiv \begin{bmatrix} a_A - a_B \\ b_A - b_B \end{bmatrix} \quad (71)$$

The complementary complex, in which the “excessive” electrons of  $b_X$  are in the attractive field generated by the electron



**Fig. 3** Polarizational  $\{P_\alpha = (a_\alpha \rightarrow b_\alpha)\}$ ,  $(\alpha, \beta) \in \{A, B\}$ , and charge-transfer,  $CT_1 = (b_B \rightarrow a_A)$  and  $CT_2 = (b_A \rightarrow a_B)$ , electron flows involving the acidic  $A = (a_A | b_A)$  and basic  $B = (a_B | b_B)$  reactants in the complementary arrangement  $R_c$  of their acidic (*a*) and basic (*b*) parts, with the chemically “hard” (acidic) fragment of one substrate facing the chemically “soft” (basic) fragment of its reaction partner. The polarizational flows  $\{P_\alpha\}$  (black arrows) in the mutually *closed* substrates, relative to the substrate “promolecular” references, preserve the overall numbers of electrons in *isolated* reactants  $\{\alpha^0\}$ , while the two partial CT fluxes (white arrows), from the basic fragment of one reactant to the acidic part of the other reactant, generate a substantial *resultant*  $B \rightarrow A$  transfer of  $N_{CT} = CT_1 - CT_2$  electrons between the mutually *open* reactants. These electron flows in the “complementary complex” are seen to produce an effective *concerted* (“circular”) flux of electrons between the four fragments invoked in this regional “functional” partition, which precludes an exaggerated depletion or concentration of electrons on any fragment of this reactive system

“deficiency” of  $a_Y$ , is expected to be electrostatically preferred since the other arrangement produces the regional repulsion either between two acidic or two basic sites of both reactants.

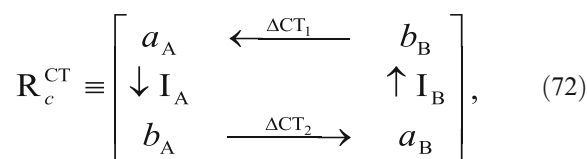
An additional rationale for this complementary preference over the regional HSAB alignment of reactants comes from examining the charge flows created by the dominating shifts in the site chemical potential due to the presence of the (“frozen”) coordinated site of the nearby part of the reaction partner. At finite separations between the two subsystems, these displacements trigger the polarizational flows  $\{P_X\}$  shown in Figs. 3 and 4, which restore the internal equilibria in both subsystems, initially displaced by the presence of the other reactant.

In  $R_c$ , the harder (acidic) site  $a_Y$  initially lowers the chemical potential of the softer (basic) site  $b_X$ , while  $b_Y$  rises the chemical potential level of  $a_X$ . These shifts trigger the internal (polarizational) flows  $\{a_X \rightarrow b_X\}$ , which enhance the acceptor capacity of  $a_X$  and donor ability of  $b_X$ , thus creating more favorable conditions for the subsequent *inter-reactant* CT of Fig. 3. A similar analysis of  $R_{HSAB}$  (Fig. 4) predicts the  $b_X \rightarrow a_X$  polarizational flows, which lowers the acceptor capacity of  $a_X$  and donor ability of  $b_X$ , i.e., the electron accumulation on

$a_X$  and electron depletion on  $b_X$ , thus creating less favorable conditions for the subsequent *inter-reactant* CT.

The complementary preference also follows from the electronic *stability* considerations, in spirit of the familiar Le Châtelier-Braun principle of the ordinary thermodynamics [3]. In contrast to analysis of Figs. 3 and 4, where the CT responses follow the internal polarizations of reactants, the equilibrium responses to displacements  $\{\Delta v_X = v_Y\}$  in the external potential on subsystems, one now assumes the *primary* (*inter-reactant*) CT displacements  $\{\Delta CT_1, \Delta CT_2\}$  of Figs. 3 and 4, in the *internally* closed but *externally* open reactants, and then examines the induced (*secondary*) relaxational responses  $\{I_X\}$  to these perturbations.

Let us first examine the CT-displaced complementary complex  $R_c$  of Fig. 3,



defined by the initial populational shifts:

$$\begin{aligned} [\Delta(CT_1) = \Delta N(a_A) = -\Delta N(b_B)] \\ > [\Delta(CT_2) = \Delta N(a_B) = -\Delta N(b_A)]. \end{aligned} \quad (73)$$

In accordance with the Le Châtelier stability principle [3], an inflow (outflow) of electrons from the given site  $c$  increases (decreases) the site chemical potential, as indeed reflected by the positive value of the site (diagonal) hardness descriptor

$$\eta_{c,c} = \partial \mu_c / \partial N_c \equiv \eta_c > 0. \quad (74)$$

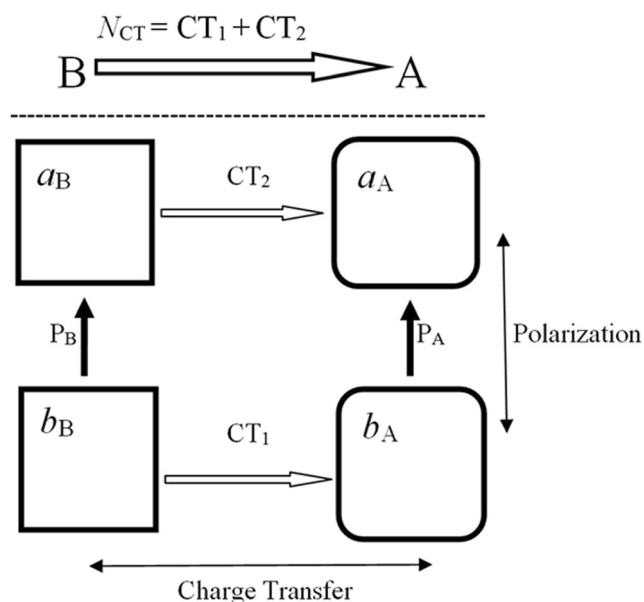
The initial CT flows  $\{\Delta CT_k\}$  thus create the following shifts in the site chemical potentials, compared to the equalized levels in isolated reactants  $A^0 = (a_A^0 | b_A^0)$  and  $B^0 = (a_B^0 | b_B^0)$ ,

$$\begin{aligned} [\Delta \mu_{a_A}(CT_1) > 0] > [\Delta \mu_{b_A}(CT_2) < 0] \text{ and} \\ [\Delta \mu_{a_B}(CT_2) > 0] > [\Delta \mu_{b_B}(CT_1) < 0]. \end{aligned} \quad (75)$$

These CT-induced shifts in the fragment electronegativities thus trigger the following secondary, induced flows  $\{I_X\}$  in  $R_c^{CT}$ :

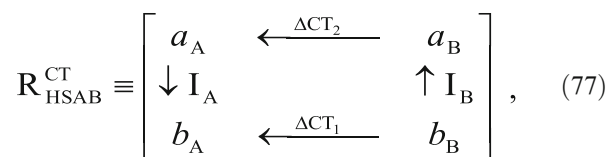


which diminish effects of the initial CT perturbations by reducing the extra charge accumulations/depletions created by these primary CT displacements.



**Fig. 4** Polarizational  $\{P_\alpha = (b_\alpha \rightarrow a_\alpha)\}$ ,  $(\alpha, \beta) \in \{A, B\}$ , and charge-transfer,  $CT_1 = (b_B \rightarrow b_A)$  and  $CT_2 = (a_B \rightarrow a_A)$ , electron flows involving the acidic  $A = (a_A | b_A)$  and basic  $B = (a_B | b_B)$  reactants in the HSAB complex  $R_{HSAB}$ , in which the chemically hard (acidic) and soft (basic) fragments of one reactant coordinate to the like-fragments of the other substrate. The two partial CT fluxes (*white arrows*) now generate a moderate overall  $B \rightarrow A$  transfer of  $N_{CT} = CT_1 + CT_2$  electrons between the mutually *open* reactants. These electron flows in the *regional*-HSAB complex are seen to produce a *disconcerted* pattern of four elementary fluxes, producing an exaggerated outflow of electrons from  $b_B$  and their accentuated inflow to  $a_A$ . This electron removal/accumulation pattern of the charge reconstruction is predicted to be energetically less favorable compared to the concerted-flow model of Fig. 3

In the CT-displaced HSAB complex  $R_{HSAB}$  of Fig. 4,



the primary CT perturbations,

$$[\Delta(CT_1) = \Delta N(b_A) = -\Delta N(b_B)] < [\Delta(CT_2) = \Delta N(a_A) = -\Delta N(a_B)], \quad (78)$$

where the inequality sign reflects magnitudes of the associated in situ chemical potentials,

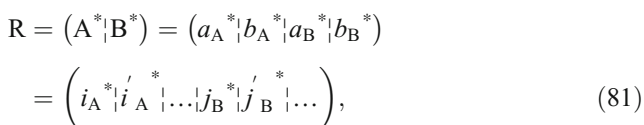
$$[|\mu(CT_1)| = \mu(b_B) - \mu(b_A)] < [|\mu(CT_2)| = \mu(a_B) - \mu(a_A)], \quad (79)$$

induce the internal relaxations in reactants,



which further exaggerate the charge depletions/accumulations created by the primary perturbation, thus giving rise to a less stable reactive complex compared to  $R_c^{CT}$ .

The global CT equilibrium in the reactive complex as a whole is reached when reactants are both *internally* and *mutually* open, as a result of the hypothetical barrier for *inter-subsystem* flows of electrons being lifted,



as symbolized by the broken vertical lines separating the two reactants and their constituent parts. This global equilibrium marks the chemical potential equalization throughout R:

$$\begin{aligned} \mu_A^* &= \partial E(R) / \partial N_A^* = \{ \mu_i^*(R) = \partial E(R) / \partial N_i^* \} \\ &= \mu_B^* = \partial E(R) / \partial N_B^* = \{ \mu_j^*(R) = \partial E(R) / \partial N_j^* \} \\ &= \mu_R = \partial E(R) / \partial N_R. \end{aligned} \quad (82)$$

The final electron densities  $\{\rho_X^*\}$  of reactants, marking the equilibrium distributions in the reactive system as a whole, then account for the extra, CT-induced substrate polarizations  $\{\Delta\rho_X^{CT} = \rho_X^* - \rho_X^+\}$  in the resultant displacements  $\{\Delta\rho_X^* = \rho_X^* - \rho_X^0 = \Delta\rho_X^+ + \Delta\rho_X^{CT}\}$  relative to isolated reactants  $\{X^0\}$ . They integrate to fractional, CT-displaced changes in electron populations of reactants  $\{\Delta N_X^* = N_X^* - N_X^0\}$ . Here,  $\Delta\rho_X^+ = \rho_X^+ - \rho_X^0$  stands for the density shift of  $X^+$  due to the substrate internal polarization, in the polarized complex  $R^+ = (A^+|B^+)$  consisting of the *internally* open but *externally* closed reactants.

The two partial CT-responses in  $R_c$  generate the overall CT between reactants,

$$\begin{aligned} N_{CT} &= CT_1 - CT_2 \\ &= N_A^* - N_A^0 \equiv \Delta N_A \\ &= N_B^0 - N_B^* \equiv -\Delta N_B > 0, \end{aligned} \quad (83)$$

where  $\{N_X^* = N_X^0 + \Delta N_X\}$  stand for the equilibrium electron populations in the molecular complex  $R = (A^*|B^*) = (a_A^*|b_A^*|a_B^*|b_B^*)$  consisting of the mutually open reactants  $\{X^*\}$  and their constituent parts  $\{a_X^*$  and  $b_X^*\}$ . Its magnitude is determined by in situ chemical potential of this reactive system, measured by the difference of chemical potentials of the *mutually* closed (*internally* polarized) acidic and basic reactants in  $R^+ = (A^+|B^+) = (a_A^+|b_A^+|a_B^+|b_B^+)$  [see Eq. (36)]:

$$\Delta\mu_{R^+} = \mu_{A^+} - \mu_{B^+} \equiv \mu_{CT} < 0, \quad (84)$$

and the reactant-resolved hardness tensor of the polarized reactive system  $R^+$ ,

$$\eta_{R^+} = \{ \eta_{X,Y} = \partial\mu_X / \partial N_Y; \quad X, Y \in (A, B) \}, \quad (85)$$

which generates the in situ hardness ( $\eta_{CT}$ ) and softness ( $S_{CT}$ ) descriptors [74, 75] for this CT process [see Eq. (37)]:

$$\begin{aligned} \eta_{CT} &= \partial\mu_{CT} / \partial N_{CT} \\ &= (\eta_{A,A} - \eta_{A,B}) + (\eta_{B,B} - \eta_{B,A}) \\ &\equiv \eta_{A^+} + \eta_{B^+} = S_{CT}^{-1} > 0. \end{aligned} \quad (86)$$

The resultant CT,

$$N_{CT} = -\mu_{CT} / \eta_{CT} = -\mu_{CT} S_{CT} > 0, \quad (87)$$

then generates the associated (second-order) CT stabilization energy of Eq. (39):

$$E_{CT} = \mu_{CT} N_{CT} / 2 = -(\mu_{CT})^2 S_{CT} / 2 < 0. \quad (88)$$

### Frontier-electron and communication outlooks on HSAB principle

The physical equivalence of reactivity concepts formulated in the energy and resultant *gradient*-information representations has also direct implications [1, 2] for the *communication theory of the chemical bond* (CTCB) [13–16, 27–37]. In OCT, the theory orbital realization, one treats a molecule as an information channel propagating signals of the AO origins of electrons in the bond system determined by the system occupied MO. It has been argued elsewhere [14–16] that elements of the CBO matrix  $\gamma = \{\gamma_{k,l}\}$  [Eq. (25)], the weighting factors

in expression of Eq. (23) for the average resultant gradient-information, determine amplitudes of conditional probabilities defining the *direct* communications between AO. Entropic descriptors of this channel then generate the information bond orders and their covalent/ionic components, which ultimately facilitate an IT understanding of molecular electronic structure in chemical terms.

The *communication noise* (orbital indeterminicity) in this network, measured by the channel conditional entropy, is due to the electron delocalization in the bond system of a molecule. It represents the overall bond “covalency”, while the channel *information capacity* (orbital determinicity), reflected by the mutual information of this communication network, measures the resultant bond “ionicity”. Therefore, the more scattering (indeterminate) the molecular information system, the higher its *covalent* character. Accordingly, a less noisy (more deterministic) channel represents a more *ionic* molecular system [13–16, 27–37].

In chemistry the bond covalency, a common possession of electrons by interacting atoms, is indeed synonymous with the electron delocalization generating the communication noise. A classical example is provided by bonds connecting identical atoms, e.g., hydrogens in H<sub>2</sub> or carbons in ethylene, when the interacting AO in the familiar MO diagrams of chemistry exhibit the same levels of AO energies. The bond *ionicity* accompanies large differences in atomic electronegativities generating a substantial CT. Such bonds correspond to a wide separation of the interacting AO energies in the familiar MO diagrams of chemistry. The ionic bond component introduces more determinicity (less noise) into molecular AO communications, thus representing a bond mechanism competitive with bond covalency [29, 106–110].

One of the celebrated (qualitative) rules of chemistry deals with stability preferences in molecular coordinations. The HSAB principle of Pearson [82] predicts that chemically hard (H) acids (A) prefer to coordinate hard bases (B) in the [HH]-complexes, and soft (S) acids prefer to coordinate soft bases in [SS]-complexes, whereas the “mixed” [HS]- or [SH]-complexes, of hard acids with soft bases or of soft acids with hard bases, respectively, are relatively unstable [83, 90]. As we have emphasized in the preceding section, this *global* preference is no longer valid *regionally*, between fragments of reactants, where the *complementarity* principle [104, 105] dictates the preferred arrangement between the acidic and basic sites of both reactants.

Little is known about the communication implications of the HSAB principle [1, 2]. The following questions arise in the reactivity context:

How does the [HH] or [SS] preference shape the *intra*- and *inter*-reactant communications in the whole reactive complex?

How is the H or S character of a substrate reflected by its internal communications?

How does the HSAB preference influence the *inter*-reactant propagations of information?

In the communication perspective on reactive systems [16, 111], the H and S reactants correspond to the *internally* ionic (deterministic) and covalent (noisy) reactant channels, respectively. The former involves *localized* orbital communications between chemically bonded atoms, while the latter corresponds to strongly *delocalized* information scatterings between AO basis states. A natural question then arises: what is the overall character of communications responsible for the mutual interaction between reactants? Do the S-substrates in [SS]-complex predominantly interact “covalently”, and H substrates of the [HH]-complex “ionically”?

In the frontier electron (FE) approach [112–114] to molecular interactions and CT phenomena, the orbital energy of the substrate highest occupied MO (HOMO) determines its donor (basic) level of the chemical potential, while the lowest unoccupied MO (LUMO) energy establishes its acceptor (acidic) capacity (see Fig. 5). The HOMO-LUMO energy gap then reflects the molecular hardness. One also recalls that the interaction between the reactant MO of comparable orbital energies is predominantly *covalent* (chemically “soft”) in character, while that between the subsystem MO of distinctly different energies becomes mostly *ionic* (chemically “hard”). A qualitative diagram of Fig. 5 summarizes the alternative, relative positions of the donor (HOMO) levels of the basic reactant, relative to the acceptor (LUMO) levels of its acidic partner, for all admissible hardness combinations in the R = A—B reactive system. In view of the proportionality relations between the energetic and information reactivity criteria, these relative MO energy levels also reflect the corresponding information potential and hardness quantities of subsystems, including the in situ derivatives driving the information transfer between reactants.

A magnitude of the *ionic* (CT) stabilization energy in A—B systems is then determined by the corresponding in situ populational derivatives in R,

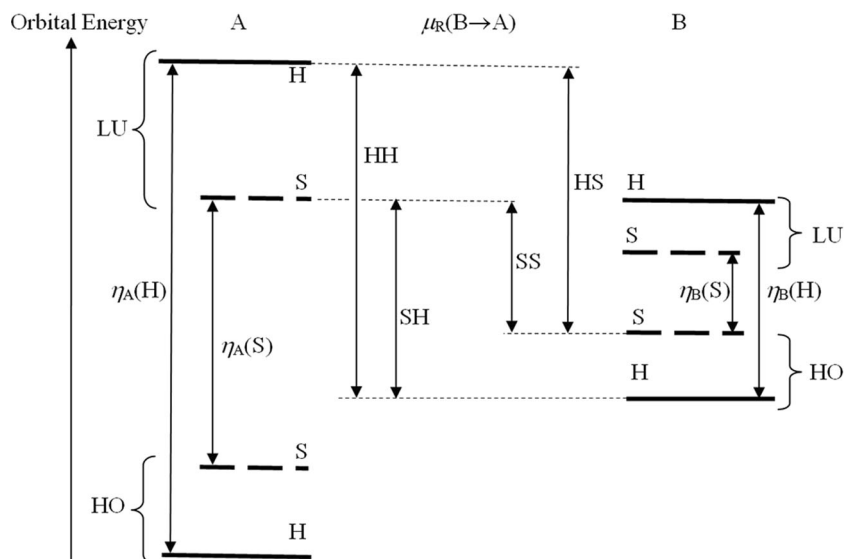
$$\Delta\varepsilon_{ion.} = |E_{CT}| = \mu_{CT}^2 / (2\eta_{CT}), \quad (88)$$

where  $\mu_{CT}$  and  $\eta_{CT}$  stand for the effective chemical potential and hardness descriptors of R involving the relevant FE of reactants. Since the donor/acceptor properties of reactants are already implied by their (known) relative acidic or basic character, one applies the biased estimate of the CT chemical potential.

In this FE approximation the chemical potential difference  $\mu_{CT}$  for the effective internal B → A CT thus reads (see Fig. 5):

$$\begin{aligned} \mu_{CT}(B \rightarrow A) &= \mu_A^{(-)} - \mu_B^{(+)} \\ &= \varepsilon_A(\text{LUMO}) - \varepsilon_B(\text{HOMO}) \approx I_{B-A_A} > 0. \end{aligned} \quad (89)$$

**Fig. 5** Schematic diagram of the in situ chemical potentials  $\mu_{CT}(B \rightarrow A) \equiv \mu_R(B \rightarrow A)$ , determining the effective internal CT from the basic (B) reactant to its acidic (A) partner in  $R = [A \text{---} B]$  complex, for their alternative hard (H) and soft (S) combinations. The subsystem hardnesses, measured by the HOMO-LUMO gaps in their MO energies, are also indicated



It determines the associated first-order energy change for this electron-transfer process:

$$\Delta E_{B \rightarrow A}(N_{CT}) = \mu_{CT}(B \rightarrow A) N_{CT} < 0. \tag{90}$$

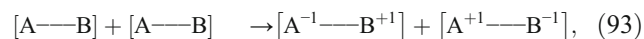
The CT chemical potential of Eq. (89) combines the electron-removal potential of the basic reactant, i.e., its negative ionization potential  $I_B = E(B^{+1}) - E(B^0) > 0$ ,

$$\mu_B^{(+)} = \varepsilon_B(\text{HOMO}) \approx -I_B, \tag{91}$$

and the electron-insertion potential of the acidic substrate, i.e., its negative electron affinity  $A_A = E(A^0) - E(A^{-1}) > 0$ ,

$$\mu_A^{(-)} = \varepsilon_A(\text{LUMO}) \approx -A_A. \tag{92}$$

The energy of the CT disproportionation process,



then generates the (unbiased) finite-difference measure of the effective hardness descriptor for this implicit CT [48, 74, 75]:

$$\begin{aligned} \eta_{CT} &= (I_A - A_A) + (I_B - A_B) \\ &\approx [\varepsilon_A(\text{LUMO}) - \varepsilon_A(\text{LUMO})] + [\varepsilon_B(\text{LUMO}) - \varepsilon_B(\text{HOMO})] \\ &= \eta_A + \eta_B > 0. \end{aligned} \tag{94}$$

These in situ populational derivatives ultimately determine a magnitude of the CT stabilization energy of Eq. (88), the ionic part of the overall interaction energy,

$$\begin{aligned} \Delta \varepsilon_{ion.} &= \mu_{CT}^2 / (2\eta_{CT}) \\ &= [\varepsilon_A(\text{LUMO}) - \varepsilon_B(\text{HOMO})]^2 / [2(\eta_A + \eta_B)]. \end{aligned} \tag{95}$$

In the FE framework of Fig. 5, the CT (ionic) interaction energy is thus proportional to the squared gap between the LUMO orbital energy of the acidic reactant and the HOMO

level of the basic substrate. This ionic interaction is thus predicted to be strongest in the [HH] pair of subsystems and weakest in the [SS]-arrangement, with the mixed [HS]- and [SH]-combinations representing the intermediate magnitudes of the ionic-stabilization effect [83].

It should be realized, however, that the ionic and covalent energy contributions complement each other in the resultant bond energy. Therefore, the [SS]-complex, for which the energy gap between the interacting orbitals,  $\varepsilon_A(\text{LUMO}) - \varepsilon_B(\text{HOMO})$ , reaches the minimum value, implies the strongest covalent-stabilization of the reactive complex. Indeed, the lowest (bonding) energy level  $\varepsilon_b$  of this FE interaction, corresponding to the bonding combination of the (positively overlapping),  $S = \langle \varphi_A(\text{LUMO}) | \varphi_B(\text{HOMO}) \rangle > 0$ , frontier MO of subsystems,

$$\varphi_b = N_b [\varphi_B(\text{HOMO}) + \lambda \varphi_A(\text{LUMO})], \tag{96}$$

then exhibits the maximum bonding energy due to covalent effect:

$$\Delta \varepsilon_{cov.} = \varepsilon_B(\text{HOMO}) - \varepsilon_b > 0. \tag{97}$$

It follows from the familiar secular equations of the Ritz method that this covalent energy can be approximated by the limiting MO expression

$$\Delta \varepsilon_{cov.} \cong (\beta - \varepsilon_b S)^2 / [\varepsilon_A(\text{LUMO}) - \varepsilon_B(\text{HOMO})], \tag{98}$$

where the coupling matrix element of the system electronic Hamiltonian,

$$\beta = \langle \varphi_A(\text{LUMO}) | \hat{H} | \varphi_B(\text{HOMO}) \rangle, \tag{99}$$

is expected to be proportional to the overlap integral  $S$  between the frontier MO.

It follows from Eq. (97) that the maximum covalent component of the *inter*-reactant chemical bond is expected in interactions between soft, *strongly* overlapping reactants [83], since then the numerator assumes the highest value while the denominator reaches its minimum. For the same reason one predicts the smallest covalent stabilization in interactions between the hard, *weakly* overlapping substrates, with the mixed hardness combinations giving rise to intermediate bond covalencies.

To summarize, the [HH]-complex exhibits the maximum *ionic*-stabilization, the [SS]-complex the maximum *covalent*-stabilization, while the mixed combinations of reactant hardnesses in [HS]- and [SH]-coordinations exhibit a mixture of moderate covalent and ionic interactions between the acidic and basic subsystems [83]. Therefore, communications representing the *inter*-reactant bonds between the chemically soft (covalent) reactants are also expected to be predominantly “soft” (delocalized, indeterministic) in character, while those between the chemically hard (ionic) subsystems are predicted to be dominated by the “hard” (localized, deterministic) propagations in the communication system for R as a whole [1, 2].

The electron communications between reactants  $\{\alpha = A, B\}$  in the acceptor–donor reactive system  $R = A\text{---}B$  are determined by the corresponding matrix of conditional probabilities in AO-resolution (or of their amplitudes), which can be partitioned into the corresponding *intra*-reactant (diagonal) parts, combining *internal* communications within individual substrates, and the *inter*-reactant (*off*-diagonal) blocks of *external* communications, between different subsystems,

$$[R \rightarrow R] = \{[\alpha \rightarrow \beta]\} = \{[\alpha \rightarrow \alpha]\delta_{\alpha,\beta}\} + \{[\alpha \rightarrow \beta](1 - \delta_{\alpha,\beta})\} \quad (100) \\ = \{intra\} + \{inter\}$$

The [SS] complexes combining the “soft” (noisy), delocalized (internal) blocks of such probability propagations imply similar covalent character of the external blocks of electron AO communications between reactants, i.e., strongly indeterministic scatterings between subsystems:

$$\{intra\text{-S}\} \Rightarrow \{inter\text{-S}\}$$

The “hard” (ionic) internal channels are similarly associated with the ionic (localized) external communications:

$$\{intra\text{-H}\} \Rightarrow \{inter\text{-H}\}$$

This observation adds a communication angle to the classical HSAB principle of chemistry.

## Conclusions

In this work, we have attempted the QIT description of the bimolecular donor–acceptor reactive system, including all hypothetical processes that accompany the bond-breaking/bond-forming processes of chemical reactions. The present (resultant) information analysis of reactivity phenomena complements earlier (classical) DFT-IT approaches, e.g., [115–121]. It should be emphasized, however, that the present *resultant*-information analysis has followed the standard thermodynamic approach to open microscopic systems, which does not imply any new “thermodynamic” transcription of DFT, see, e.g., [120, 121]. The continuities of the classical (modulus/probability) and nonclassical (phase/current) state parameters have been examined and contributions, that these molecular degrees-of-freedom generate in the resultant *gradient*-information descriptor of a quantum state, have been identified. The need for nonclassical (phase/current) complements of the classical (probability) measures of the information content in molecular electronic states has been reemphasized. It has been argued that the electron density alone reflects only the structure of “being”, missing the structure of “becoming” contained in the current distribution. Both of these manifestations of the molecular “organization” ultimately contribute to the overall information content in generally complex electronic wavefunctions, reflected by the *resultant* QIT concepts. Their importance in describing the mutual bonding and nonbonding status of reactants has been stressed and the *in situ* populational derivatives in the energy and information representations have been examined.

The DFT-based theory of chemical reactivity distinguishes several intuitive, hypothetical stages involving either the mutually bonded (entangled) or nonbonded (disentangled) states of reactants for the same electron distribution in constituent subsystems. These two categories are discerned only by the *phase* aspect of the quantum entanglement between molecular fragments. The equilibrium phases and currents of reactants can be related to the relevant electron densities using the entropic principles of QIT. This generalized approach deepens our understanding of the molecular promotions of constituent fragments and provides a more precise framework for monitoring the reaction progress.

The *grand*-ensemble description of thermodynamic equilibria in *externally* open molecular systems has been used to demonstrate the physical equivalence of the energy and resultant *gradient*-information principles. The populational derivatives of the resultant *gradient*-information, related to the system average kinetic energy, have been suggested as reliable reactivity criteria. They were shown to predict both the direction and magnitude of the electron flows in reactive systems. The *grand*-ensemble description of thermodynamic equilibria in the *externally* open molecular systems has been outlined and the physical equivalence of variational principles for the



electronic energy and resultant *gradient*-information has been emphasized. The virial theorem has been used to explain the qualitative Hammond postulate of the theory of chemical reactivity, and the information production in chemical reactions has been addressed. The ionic and covalent interactions between frontier MO of the acidic and basic reactants have been examined to justify the HSAB principle of chemistry and to provide the communication perspective on interaction between reactants. It has been argued that the internally soft and hard reactants prefer to externally communicate in the like manner, consistent with their internal communications. This preference should be also reflected by the predicted character of the *inter*-reactant bonds/communications in stable coordinations: covalent in [SS] and ionic in [HH] complexes.

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