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Research Article

Equalization principles in open subsystems, origins of information descriptors and state-continuity relations

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Abstract

The electronegativity-equalization at several hypothetical stages of chemical reactions is reexamined and phase-equalization in open substrates is explored. The equivalence of the energy and information reactivity criteria is stressed and local energy concept is shown to determine time-evolutions of wavefunction components. Independent sources of information content in electronic states are identified and the need for resultant entropy-information measures in quantum mechanics, combining information contributions due to the classical (probability) and nonclassical (phase/current) distributions, is reemphasized. Limitations for a simultaneous removal of uncertainties in the position and velocity distributions imposed by the Heisenberg indeterminacy principle, are discussed, continuities of the wavefunction modulus and phase components are examined, the convectional character of the local source of resultant gradient information is stressed, and a latent ("horizontal") probability currents in the stationary quantum states are discussed.

Abbreviations

A: Acid, electron acceptor; AIM: Atoms-in-Molecules; B: Base, electron donor; BO: Born-Oppenheimer approximation; CG: Contragradience criterion; CT: Charge Transfer; DFT: Density Functional Theory; EE: Electronegativity Equalization; ELF: Electron Localization Function; EO: Equidensity Orbitals; FF: Fukui Function; HZM: Harriman-Zumbach-Maschke construction; IT: Information Theory; MO: Molecular Orbitals; OCT: Orbital Communication Theory; QM: Quantum Mechanics; SE: Schrödinger Equation; SRL: Separated Reactant Limit

Introduction

In chemistry several intuitive concepts and rules still require more rigorous definitions within the molecular quantum mechanics (QM). Indeed, the semantics of chemical bonds, Atoms-in-Molecules (AIM), reactants or molecular fragments in general, the entangled quantum subsystems, still escapes the exact QM description, e.g. [1-4]. The interacting molecular pieces are described by the *mixed* quantum states, which require an ensemble description [5-10]. Chemical concepts and principles can be approached using modern Density Functional Theory (DFT) [11-16] and Information Theory (IT) [17-24], e.g., [1-4,25-34].

For example, IT provides a solid theoretical basis [1-4,25-34] for the intuitive stockholder AIM of Hirshfeld [35]. The Orbital Communication Theory (OCT) of the chemical bond [1-4,36-47] has provided an alternative IT interpretation of the bond pattern in a molecule, and of its covalent (communication-noise) and ionic (information-flow) composition. This approach has also identified the bridge chemical interactions between AIM [48-53], realized via cascade propagations in molecular information systems, through the orbital intermediates. The nonadditive gradient information of Fisher [17,18,34] has been linked [54] to the Electron Localization Function (ELF) [55-57] of DFT, and resulted in the Contragradience (CG) IT probe for localizing the chemical bonds [1-4,58].

The acquisition of information via the experimental removal of the position and velocity uncertainties in quantum states will be discussed and limitations for a simultaneous acquiring of the classical and nonclassical contributions to the resultant entropy/information descriptors, imposed by the Heisenberg indeterminacy principle, will be explored in some detail. A distinction between the classical (probability) and quantum (wavefunction) mappings will be examined and the

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need for generalized (resultant) measures of the entropy/information content in electronic states will be reemphasized. Such IT descriptors combine the wavefunction modulus (probability) and phase (current) contributions, and relate the overall gradient information to the state average kinetic energy of electrons.

It is the main purpose of the present analysis to reexamine the chemical potential (electronegativity) and phase equalizations in molecular an reactive systems. The classical (probability) and nonclassical (phase/current) origins of the quantum information content in molecular electronic states will be explored and relevant continuity relations will be summarized. These balance equations result from the fundamental Schrödinger equation (SE) of QM for the dynamics of quantum states. The effective velocity of the probability "fluid", measured by the current-per-particle, will be used to define fluxes of general physical and information properties, with the system electrons acting as carriers of the property densities. The probability acceleration and force concepts will be related to the phase-production, which identically vanishes in the stationary states.

The electronegativity equalization will be described in the Equidensity Orbital (EO) representation and local-energy concept will be used to explore the phase equalization and dynamics of wavefunction components. The equivalence of the energy and information criteria of chemical reactivity will be emphasized. The limitations for a simultaneous removal of uncertainties in the position probability density and in local velocity distribution, imposed by the Heisenberg indeterminacy principle, will be discussed, continuities of the wavefunction modulus and phase components will be examined, and the *convection* character of the net source of resultant gradient information will be stressed.

Hypothetical stages of electronegativity equalization

The chemical concepts and principles can be approached using modern DFT and IT. The former constitutes the exact theory for determining reaction energetics, while the latter can be regarded as a supplementary interpretative tool for understanding the molecular structures and processes in *chemical* terms. Resultant entropy/information concepts have been applied to describe the molecular equilibria, current-activation of reaction substrates, and the bonded (entangled) and nonbonded (disentangled) states of general molecular fragments.

In chemical reactions one conventionally recognizes several hypothetical stages (Figures 1,2) of relaxing the electronic structure of the system constituent fragments [59-61]. The standard reference stage for the bond formation in the molecular system M(N, v), specified by its canonical parameters of the average number of electrons (N) and external potential due to nuclei (v), is the promolecular system $\mathrm{M}^{\mathrm{o}} = \mathrm{M}^{\mathrm{o}}(\{a_i^{\mathrm{o}}(Z_i, N_i^{\mathrm{o}})\}, v)$, $N = \sum_i N_i^{\mathrm{o}}$, consisting of the "frozen" constituent atoms or ions, $\{a_i^{\mathrm{o}}(Z_i, N_i^{\mathrm{o}})\}$, shifted to their molecular positions $\{R_i\}$: $v = v(\{Z_i, R_i\})$. The equilibrium states of the polarized AIM in M can be then viewed as electronically relaxed atoms of the promolecular system, after their mutual opening. The promolecular reference R$^{\mathrm{o}}$ of the reactive system R = R({α}) consisting of substrates {α} similarly represents the frozen (isolated) substrates {α$^{\mathrm{o}}$} shifted to their positions in the

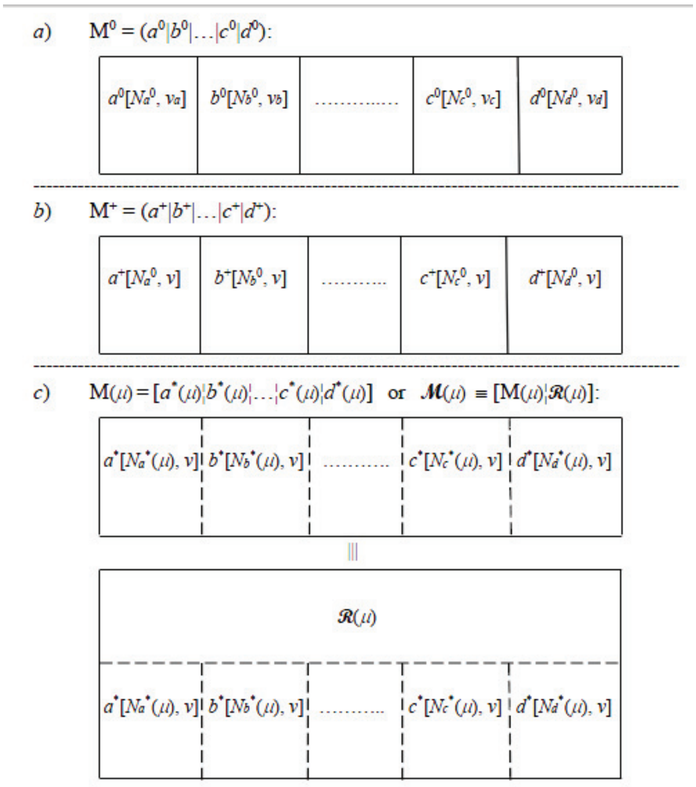

Figure 1: Hypothetical stages in relaxing the electronic structure of molecular fragments $\alpha \in \{a, b, \ldots, c, d\}$ from the isolated species $\{\alpha^0\}$ in promolecule $\mathrm{M}^0 = (a^0|b^0|\ldots|c^0|d^0)$ (Panel a), via the polarized subsystems $\{\alpha^+\}$ in $\mathrm{M}^+ = (a^+|b^+|\ldots|c^+|d^+)$ (Panel b), into the equilibrium (bonded) fragments $\{\alpha^*(\mu)\}$ in $\mathrm{M}(\mu) = [a^*(\mu)¦b^*(\mu)¦\ldots¦c^*(\mu)¦d^*(\mu)]$ (Panel c) for the specified level of (molecular) chemical potential $\mu = \mu_{\mathrm{M}}$. The latter can be equivalently viewed as molecular (internally open) composite molecular system M(μ) coupled to the macroscopic electron reservoir R(μ) in $\mathrm{M}(\mu) = [\mathrm{M}(\mu)¦\mathrm{R}(\mu)]$.

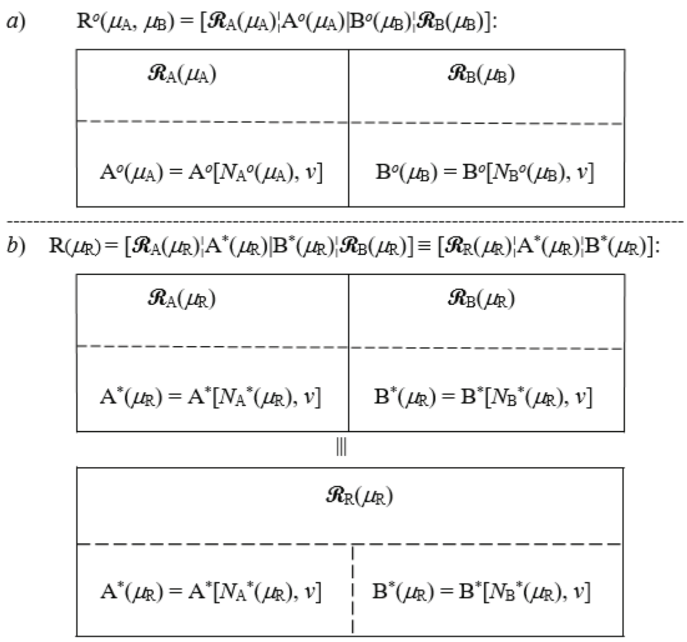

Figure 2: Externally open reactants of donor-acceptor systems $\mathrm{R}^o(\mu_A, \mu_B)$ (Panel *a*) and $\mathrm{R}(\mu_R)$ (Panel *b*) involving the separate and common electron reservoirs of subsystems, respectively. Panel *b* additionally illustrates that equalization of the chemical potentials of the separate reservoirs, $\mu_A = \mu_B = \mu_B$, effectively opens both reactants mutually.

molecular complex, while the equilibrium state in R as a whole, $\mathrm{R} = \mathrm{R}(\{\alpha^{*}\})$ reflects the bonded (open, entangled) reactants $\{\alpha^{*}\}$ at this stage of their mutual approach.

This electronic relaxation of *initial* (non-equilibrium) promolecular electronic structure to *final* (equilibrium) state of the system as a whole, for the fixed overall external potential due to the system nuclei in their fixed positions, goes through intermediate polarization (P) stage, $\mathrm{M}^{+} = \mathrm{M}^{+}(\{a_i^{+}\})$ or $\mathrm{R}^{+} = \mathrm{R}^{+}(\{\alpha^{+}\})$, involving *mutually*-closed atomic or reactant fragments, which are fully relaxed *internally* in the presence of remaining subsystems.

In electronic structure and reactivity theories one examines the infinitesimal displacements $\{\delta N, \delta v\}$ in the system canonical state parameters, and explores the system responses to such perturbations [59-61]. The continuous variable N implies its *average* character, of the electron population in the molecular system coupled to an external (macroscopic) electron reservoir $\mathrm{R}(\mu)$ characterized by its chemical potential μ (Figures 1,2) or electronegativity $\chi = -\mu$. Such grand-ensemble interpretation [9,10,14,62,63] applies to all reactivity criteria involving populational derivatives of energy or information, e.g., the chemical potential [14,62-66], hardness/softness [14,67] and Fukui-Function (FF) [14,68] descriptors of molecular systems. The charge-transfer (CT) then emerges as a spontaneous response to the chemical-potential difference of the polarized subsystems. The mutually-closed subsystems of M^{+} or R^{+}, defining the relevant *in situ* CT "gradient" and "Hessian" descriptors, then determine the optimum amount of this electronic flow [59-61].

To summarize, the Electronegativity Equalization (EE) eventually establishes the system equilibrium distribution of electrons among its structural units. The probability flows also carry densities of general electronic descriptors of molecular systems. Such property currents constitute essential part of the associated continuity relations expressing the local balance of the quantity in question, which determines its source (net production) [9,10,69-71].

Consider the substrates $\alpha = (\mathrm{A}, \mathrm{B})$ in the specified donor-acceptor reactive system $\mathrm{R} = \mathrm{A}$----B (Figure 2). The isolated (separated) subsystems exhibit different global levels of the internally equalized chemical potentials, $\mu_{\mathrm{A}}^{o} < \mu_{\mathrm{B}}^{o}$,

$$\{\mu_{\alpha}^{o}(r) \equiv \delta E_{\alpha}[\rho_{\alpha}^{o}]/\delta\rho_{\alpha}^{o}(r) = \mu_{\alpha}[\rho_{\alpha}^{o}, v_{\alpha}] = \mu_{\alpha}^{o} \equiv \partial E(N_{\alpha}, v_{\alpha}\}/\partial N_{\alpha}|_{o}\}, \tag{1}$$

where $E_{\alpha}[\rho_{\alpha}^{o}[v_{\alpha}]] \equiv E[N_{\alpha}^{o}, v_{\alpha}]$ denotes the ground-state energy of α^{o}. Their nonbonded status, when they conserve the overall (integer) numbers of electrons $\{N_{\alpha} = N_{\alpha}^{o}\}$ in separated reactants $\{\alpha^{o}\}$, implies the vanishing exchanges of electrons with the reaction partner, i.e., their *mutual* closeness symbolized by the *solid* vertical line separating the two subsystems, or with the hypothetical (macroscopic) reservoir (*external* closeness) in the ensemble representation. All reaction stages below are assumed to be globally isoelectronic:

$$N \equiv N_{\mathrm{A}}^{o} + N_{\mathrm{B}}^{o} \equiv N_{\mathrm{R}}^{o} = N_{\mathrm{A}}^{+} + N_{\mathrm{B}}^{+} \equiv N^{+} = N_{\mathrm{A}}^{*} + N_{\mathrm{B}}^{*} \equiv N^{*}. \tag{2}$$

The initial, *promolecular* stage $\mathrm{R}^{o} \equiv (\mathrm{A}^{o}|\mathrm{B}^{o})$ signifies the "frozen" ground-state densities $\{\rho[N_{\alpha}^{o}, v_{\alpha}] = \rho_{\alpha}^{o} \equiv N_{\alpha}^{o} p_{\alpha}^{o}\}$ of isolated fragments $\{\alpha^{o}\}$ shifted to their "molecular" positions in R, for the specified mutual separation and orientation of these geometrically rigid fragments in the reactive system; here $p_{\alpha}^{o}(r)$ stands for the fragment probability distribution: $\int p_{\alpha}^{o}(r)dr = 1$. This initial (reference) stage of a chemical reaction generates a nonstationary "molecular" distribution of electrons, nonequilibrium for the *molecular* external potential $v = v_{\mathrm{A}} + v_{\mathrm{B}}$,

$$\rho^{o} = \rho_{\mathrm{A}}^{o} + \rho_{\mathrm{B}}^{o} \neq \rho[N, v], \tag{3}$$

Different from the equilibrium (ground-state) density $\rho[N, v]$ for the specified overall electron number $N_{\mathrm{R}} = N_{\mathrm{A}} + N_{\mathrm{B}}$ and the "molecular" external potential v. The promolecular state thus implies the nonequalized local chemical potentials in both subsystems, determined by functional derivatives $\{\mu_{\alpha}^{o}(r) \equiv \delta E[\{\rho_{\gamma}\}]/\delta\rho_{\alpha}(r)|_{o}\}$ of the density bifunctional $E[\rho_{\mathrm{A}}, \rho_{\mathrm{B}}; v]$ for the electronic energy in R, calculated for the "frozen" densities $\{\rho_{\alpha}^{o}\}$ of isolated subsystems:

$$\mu_{\mathrm{A}}^{o}[v; r] \neq \mu_{\mathrm{A}}^{o}[v; r'] \ldots \text{ and } \mu_{\mathrm{B}}^{o}[v; r] \neq \mu_{\mathrm{B}}^{o}[v; r'] \ldots \tag{4}$$

The intermediate, *polarized* reactive system $\mathrm{R}^{+} \equiv (\mathrm{A}^{+}|\mathrm{B}^{+})$ similarly combines densities $\{\rho_{\alpha}^{+} = \rho_{\alpha}[N_{\mathrm{A}}^{o}, N_{\mathrm{B}}^{o}; v] \equiv N_{\alpha}^{+} p_{\alpha}^{+}\}$ of the mutually-closed subsystems $\{\alpha^{+}\}$ in their internal equilibria, separated in R^{+} by the *solid* vertical line symbolizing preservation of electron numbers in subsystems, $\{N_{\alpha}^{+} = N_{\alpha}^{o}\}$, thus exhibiting different levels of their (internally-equalized) chemical potentials:

$$\mu_{\mathrm{A}}^{+} \equiv \mu_{\mathrm{A}}[\rho_{\mathrm{A}}^{+}, \rho_{\mathrm{B}}^{+}; v] = \mu_{\mathrm{A}}^{+}[v; r] = \mu_{\mathrm{A}}^{+}[v; r'] = \ldots$$

$$< \mu_{\mathrm{B}}^{+} \equiv \mu_{\mathrm{B}}[\rho_{\mathrm{A}}^{+}, \rho_{\mathrm{B}}^{+}; v] = \mu_{\mathrm{B}}^{+}[v; r] = \mu_{\mathrm{B}}^{+}[v; r'] = \ldots \tag{5}$$

The implicit barrier for the flow of electrons between polarized reactants is eventually lifted in the final *equilibrium* stage of a "molecular" reactive system $\mathrm{R} \equiv (\mathrm{A}^{*} ¦ \mathrm{B}^{*})$, after the optimum $\mathrm{B}^{+} \rightarrow \mathrm{A}^{+}$ CT between the initially polarized reactants (Figure 2). This freedom to exchange electrons has been symbolized above by the *broken* line separating the bonded subsystems $\{\alpha^{*}\}$, which exhibit the ensemble-average densities

$$\{\rho_{\alpha}^{*}(r) \equiv N_{\alpha}^{*} p_{\alpha}^{*}(r) = \rho_{\alpha}[N_{\mathrm{A}}^{*}, N_{\mathrm{B}}^{*}, v; r] \equiv \rho_{\alpha}^{*}[\rho; r]\},$$

$$\{N_{\alpha}^{*} = \int \rho_{\alpha}^{*}(r)\, dr = N_{\alpha}^{*}[N; v]\}. \tag{6}$$

For the lack of the separating boundary in R its mutually-open subsystems must explore the electron probability distribution of the whole reactive system:

$$p_{\mathrm{A}}^{*}(r) = p_{\mathrm{B}}^{*}(r) = p(r) = \rho(r)/N_{\mathrm{R}}. \tag{7}$$

Indeed, the density additivity implies

$$\rho(r) = \rho[N_{\mathrm{R}}, v; r] \equiv Np(r) = (N_{\mathrm{A}}^{*} + N_{\mathrm{B}}^{*})\, p(r)$$

$$= \rho_{\mathrm{A}}^{*}(r) + \rho_{\mathrm{B}}^{*}(r) = N_{\mathrm{A}}^{*} p_{\mathrm{A}}^{*}(r) + N_{\mathrm{B}}^{*} p_{\mathrm{B}}^{*}(r) \tag{8}$$

and hence:

$$p_{\alpha}^{*}(r) = p(r) \text{ and } \rho_{\alpha}^{*}(r)/\rho(r) = N_{\alpha}^{*}/N \equiv P_{\alpha}^{*}, \textstyle\sum_{\alpha} P_{\alpha}^{*} = 1. \tag{9}$$

The effective mutual-openess of both substrates signifies the bonded character of these reaction partners and hence also the equalization of their chemical potentials at the "molecular" level characterizing R as a whole:

$$\mu_\alpha^{\,*} \equiv \mu[\rho_\mathrm{A}^{\,*}, \rho_\mathrm{B}^{\,*}; v] \equiv \mu_\alpha[N; v] = \mu[N, v] \equiv \mu[\rho, v],\ \alpha = \mathrm{A, B}. \tag{10}$$

These bonded fragments generally exhibit fractional values of the average numbers of electrons, due to a finite amount $N_\mathrm{CT} > 0$ of the $\mathrm{B}^* \rightarrow \mathrm{A}^*$ CT:

$$N_\mathrm{A}^{\,*} = \int \rho_\mathrm{A}^{\,*} dr = N_\mathrm{A}^{\,0} + N_\mathrm{CT} > N_\mathrm{A}^{\,0},\ N_\mathrm{B}^{\,*} = \int \rho_\mathrm{B}^{\,*} dr = N_\mathrm{A}^{\,0} - N_\mathrm{CT} < N_\mathrm{B}^{\,0}. \tag{11}$$

Such mutually-open fragments call for an ensemble description of their average densities and electron populations. Their identity is properly defined only when they represent the mutually-closed fragments of the macroscopic subsystems composed a the reactant fragments coupled to their own (separate) electron reservoirs. The substrate identity indeed represents a meaningful concept only when both subsystems remain mutually closed.

Indeed, the fragment properties in the final, equilibrium reactive system R combining the bonded fragments can be inferred only indirectly, by externally opening the mutually closed subsystems of R^+, with respect to their separate (macroscopic) electron reservoirs $\{\mathrm{R}^+\}$ in the polarized composite system (Figure 2*a*):

$$\mathrm{M}^+ = [\mathrm{R}_\mathrm{A}^{\,+}(\mu_\mathrm{A}^{\,+}) \mathrel{\text{¦}} \mathrm{A}^+(\mu_\mathrm{A}^{\,+}) | \mathrm{B}^+(\mu_\mathrm{A}^{\,+}) \mathrel{\text{¦}} \mathrm{R}_\mathrm{B}^{\,+}(\mu_\mathrm{B}^{\,+})] \equiv [\mathrm{M}_\mathrm{A}^{\,+}(\mu_\mathrm{A}^{\,+}) | \mathrm{M}_\mathrm{B}^{\,+}(\mu_\mathrm{B}^{\,+})]. \tag{12}$$

The independent chemical potentials of such mutually-closed composite subsystems can be subsequently equalized at the "molecular" level (Figure 2b),

$$\mu_\mathrm{A}^{\,+} \equiv \mu_\mathrm{A}^{\,*} = \mu_\mathrm{B}^{\,+} \equiv \mu_\mathrm{B}^{\,*} = \mu_\mathrm{R}[N_\mathrm{R}, v], \tag{13}$$

of the chemical potential of R as a whole. Such a composite system M thus effectively involves a *common* electron reservoir $\mathrm{R}_\mathrm{A}^{\,*}(\mu_\mathrm{R}) = \mathrm{R}_\mathrm{B}^{\,*}(\mu_\mathrm{R}) = \mathrm{R}(\mu_\mathrm{R}) \equiv \mathrm{R}$,

$$\mathrm{M} = [\mathrm{R}_\mathrm{A}^{\,*}(_\mathrm{R}) \mathrel{\text{¦}} \mathrm{A}^*(\mu_\mathrm{R}) | \mathrm{B}^*(\mu_\mathrm{R}) \mathrel{\text{¦}} \mathrm{R}_\mathrm{B}^{\,*}(\mu_\mathrm{R})] \equiv [\mathrm{M}_\mathrm{A}^{\,*}(\mu_\mathrm{R}) | \mathrm{M}_\mathrm{B}^{\,*}(\mu_\mathrm{R})]$$

$$= [\mathrm{R}^*(\mu_\mathrm{R}) \mathrel{\text{¦}} \mathrm{A}^*(\mu_\mathrm{R}) \mathrel{\text{¦}} \mathrm{B}^*(\mu_\mathrm{R})] \equiv [\mathrm{R}(\mu_\mathrm{R}) \mathrel{\text{¦}} \mathrm{R}(\mu_\mathrm{R})], \tag{14}$$

and hence combines the formally bonded reactant subsystems. Indeed, the substrate chemical potentials equalized at the molecular level in both subsystems, when $\{\mathrm{R}_\alpha^{\,+}(\mu_\mathrm{R}) \equiv \mathrm{R}_\alpha^{\,*} = \mathrm{R}\}$, in fact describe a "molecular" reservoir coupled to the whole reactive system R: $[\mathrm{R} \mathrel{\text{¦}} \mathrm{A}^* \mathrel{\text{¦}} \mathrm{B}^*] = (\mathrm{R} \mathrel{\text{¦}} \mathrm{R})$. The open character of each subsystem also implies that each subsystem effectively exhausts the whole electron probability density $p = \rho/N$ in $\mathrm{R} = \mathrm{R}(\mu_\mathrm{R})$ [Eq. (7)], so that the equilibrium electron densities of the mutually-open subsystems,

$$\rho_\alpha^{\,*}(r) = N_\alpha^{\,*} p(r) = (N_\alpha^{\,*}/N)\, \rho(r) = P_\alpha^{\,*} \rho(r),\ \alpha = \mathrm{A, B}, \tag{15}$$

where $P_\alpha^{\,*} = N_\alpha^{\,*}/N$ denotes the global probability of α^* in R, reconstruct the equilibrium electron density in the whole system:

$$\textstyle\sum_\alpha \rho_\alpha^{\,*}(r) = \rho(r)\, (\sum_\alpha P_\alpha^{\,*}) = \rho(r). \tag{16}$$

Similar external reservoirs are invoked, when one examines independent population displacements of the mutually-closed reactants, e.g., in defining the fragment chemical potentials and the hardness matrix of R^+. In this chain of hypothetical reaction stages the polarized system 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 lifted.

The vector of fragment chemical potentials, $\mu_\mathrm{R}^{\,+} = \{\mu_\alpha^{\,+}\}$, and elements of the associated hardness matrix in reactant resolution, $\eta_\mathrm{R}^{\,+} = \{\eta_{\alpha,\beta}\}$, represent the first and second populational derivatives of the system average electronic energy in the grand-ensemble representation of M [59-61]:

$$\langle E(\mathrm{A,B}) \rangle_{ens.} = \mathrm{E}[\mathrm{A}(\mu_\mathrm{A}^{\,+}), \mathrm{B}(_\mathrm{B}^{\,+})] \equiv \mathrm{E}[\{N_\mathrm{A}(\mu_\mathrm{A}^{\,+}), N_\mathrm{B}(\mu_\mathrm{B}^{\,+})\}, v] = \mathrm{E}[\{N_\gamma\}, v]. \tag{17}$$

The polarized system R^+ thus contains the externally-open substrates $\{\alpha^+(\mu^+)\}$ coupled to their *separate* external reservoirs of electrons, in the mutually-closed composite subsystems,

$$\{\mathrm{M}_\alpha^{\,+} = \mathrm{M}_\alpha^{\,+}(\mu^+) = [\alpha^+ \mathrel{\text{¦}} \mathrm{R}_\alpha^{\,+}(\mu_\alpha^{\,+})]\} \tag{18}$$

of the composite reactive system

$$\mathrm{M}^+ = [\mathrm{R}_\mathrm{A}(\mu_\mathrm{A}^{\,+}) \mathrel{\text{¦}} \mathrm{A}^+ | \mathrm{B}^+ \mathrel{\text{¦}} \mathrm{R}_\mathrm{B}(\mu_\mathrm{B}^{\,+})] \equiv [\mathrm{M}_\mathrm{A}^{\,+}(\mu_\mathrm{A}^{\,+}) | \mathrm{M}_\mathrm{B}^{\,+}(\mu_\mathrm{B}^{\,+})]. \tag{17}$$

The populational derivatives are calculated for the fixed external potential of the whole system, $v = v_\mathrm{A} + v_\mathrm{B}$, reflecting the "frozen" molecular geometry in R:

$$\mu_\alpha^{\,+} \equiv \partial \mathrm{E}[\{N_\gamma\}, v]/\partial N_\alpha|^+,$$

$$\eta_{\alpha,\beta}^{\,+} = \partial^2 E[\{N_\gamma\}, v]/\partial N_\alpha \partial N_\beta|^+ = \partial \mu_\alpha^{\,+}/\partial N_\beta. \tag{18}$$

The associated global descriptors of $\mathrm{R} = (\mathrm{A}^* \mathrel{\text{¦}} \mathrm{B}^*)$ are similarly defined by derivatives of the ensemble average electronic energy

$$\langle E(\mathrm{R}) \rangle_{ens.} = \mathrm{E}[N(\mu), v] \tag{19}$$

of the molecular fragment R in the combined system

$$\mathrm{M} = (\mathrm{R} \mathrel{\text{¦}} \mathrm{R}) = (\mathrm{A}^* \mathrel{\text{¦}} \mathrm{B}^* \mathrel{\text{¦}} \mathrm{R}) = (\mathrm{R} \mathrel{\text{¦}} \mathrm{A}^* \mathrm{B}^* \mathrel{\text{¦}} \mathrm{R}) = (\mathrm{M}_\mathrm{A}^{\,*} \mathrel{\text{¦}} \mathrm{M}_\mathrm{B}^{\,*})$$

with respect to its average electron number N:

$$\mu = \partial \mathrm{E}[N, v]/\partial N|^*,\ \eta = \partial^2 \mathrm{E}[N, v]/\partial N^2|^* = \partial \mu/\partial N. \tag{20}$$

This framework also determines the global and fragment *response* properties, e.g., the mixed second-derivative descriptors of FF

$$f(r) = \partial^2 E[N, v]/\partial v(r)\, \partial N = \partial \rho(r)/\partial N = \partial \mu/\partial v(r), \tag{21}$$

$$F_\alpha(r) = \partial^2 E[\{N_\gamma\}, v]/\partial N_\alpha \partial v(r)|^+ = \partial \rho^+(r)/\partial N_\alpha = \partial \mu_\alpha/\partial v(r). \tag{22}$$

The optimum amount of the (fractional) equilibrium CT,

$$N_\mathrm{CT} = N_\mathrm{A}^{\,*} - N_\mathrm{A}^{\,0} \equiv dN_\mathrm{A} = N_\mathrm{B}^{\,0} - N_\mathrm{B}^{\,*} \equiv -dN_\mathrm{B} > 0, \tag{23}$$

defines the global (in situ) FF derivatives of both substrates in this process:

$$F_\mathrm{A}^{\,\mathrm{CT}} = dN_\mathrm{A}/dN_\mathrm{CT} = 1 \text{ and } F_\mathrm{B}^{\,\mathrm{CT}} = dN_\mathrm{B}/dN_\mathrm{CT} = -1. \tag{24}$$

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The magnitude of equilibrium charge flow is determined by the difference in chemical potentials of the polarized reactants in R$^+$, the CT “gradient”

$$\mu_{CT} = \partial E(N_{CT})/\partial N_{CT} = \sum_\alpha F_\alpha^{CT} \mu_\alpha^{\ +} = \mu_A^{\ +} - \mu_B^{\ +} < 0, \qquad (25)$$

and by effective (*in situ*) hardness (η_{CT}) or softness (S_{CT}) for this process,

$$\eta_{CT} = \partial^2 E(N_{CT})/\partial N_{CT}^{\ 2} = \partial\mu_{CT}/\partial N_{CT} = \sum_\alpha \sum_\beta F_\alpha^{CT} \eta_{\alpha,\beta}^{\ +} F_\beta^{CT}$$

$$= (\eta_{A,A} - \eta_{A,B}) + (\eta_{B,B} - \eta_{B,A}) = \eta_A^{CT} + \eta_B^{CT} \equiv S_{CT}^{\ -1}, \qquad (26)$$

Representing effective CT “Hessian” and its inverse, respectively. The amount of CT,

$$N_{CT} = -\mu_{CT}/_{CT} = -\mu_{CT}\, S_{CT}, \qquad (27)$$

generates the associated (2nd-order) stabilization energy due to this spontaneous transfer of electrons:

$$E_{CT} = \mu_{CT}\, N_{CT}/2 = -\,\mu_{CT}^{\ 2}/(2\eta_{CT}) = -\,\mu_{CT}^{\ 2}\, S_{CT}/2 < 0. \qquad (28)$$

Probability and phase/current distributions in reactive systems

The hypothetical stages of the preceding section involve either the mutually-*closed* [nonbonded (n), disentangled] or *open* [bonded (b), entangled] reactants, e.g., the electron *acceptor* (acidic, A) and *donor* (basic, B) substrates in the bimolecular reactive system of Figure 3: R = A + B. The *initial* stage of the bond rearrangement process marks the *promolecular* reference R$^o \equiv$ (A^o|B^o), consisting of the “frozen” free reactants $\{\alpha^o\}$ of the Separated Reactants Limit (SRL), A^o + B^o, containing the integer numbers of electrons $\{N_\alpha^{\ o}\}$ and brought to their relative positions in the actual “molecular” complex R^o. At this stage, before the bond-breaking–bond-forming process of the chemical reaction, both fragments are electronically and geometrically rigid, exhibiting the equilibrium electron densities $\{\rho_\alpha^{\ o} = \rho_\alpha^{\ o}[N_\alpha^{\ o}, v_\alpha]\}$ of the isolated species, which represent non-equilibrium distributions in presence of reaction partners: $\{\rho_\alpha^{\ o} \neq \rho_\alpha^{\ o}[\{N_\beta^{\ o}\}, v] \equiv \rho_\alpha^{\ +}\}$. Here, $v = v_A + v_B$ stands for “molecular” external potential in Born-Oppenheimer (BO) approximation, due to the rigid nuclear frame of the whole reactive complex at the current relative separation and orientation of both substrates.

Each (isolated) subsystem of the promolecule or SRL can be described by its *pure* quantum state, i.e., a single wavefunction $\psi_\alpha^{\ o}[N_\alpha^{\ o}, v_\alpha]$ of $N_\alpha^{\ o}$ (integer) electrons moving in the fragment external potential v_α due to its own nuclei in their fixed positions. This (complex) wavefunction is defined by its modulus ($R_\alpha^{\ o}$) and phase ($\varphi_\alpha^{\ o}$) components (Figure 3), which generate the fragment electron density $\rho_\alpha(r) = N_\alpha^{\ o} p_\alpha^{\ o}(r)$ and distribution of the effective velocity of the probability distribution $p_\alpha^{\ o}(r)$ in its current $j_\alpha^{\ o}(r)$: $V_\alpha^{\ o}(r) = j_\alpha^{\ o}(r)/p_\alpha^{\ o}(r)$. The former is related to the squared wavefunction modulus, while the latter is determined by the gradient of its phase. The whole promolecular system R^o, of the two separated (noninteracting) substrates, is then described by the product function

$$\Psi^o(N) = \psi_A^{\ o}[N_A^{\ o}, v_A]\, \psi_B^{\ o}[N_B^{\ o}, v_B]$$

$$= \{R_A^{\ o}[N_A^{\ o}, v_A]\, R_B^{\ o}[N_B^{\ o}, v_B]\} \exp\{i(\varphi_A^{\ o}[N_A^{\ o}, v_A] + \varphi_B^{\ o}[N_B^{\ o}, v_B])\}$$

$$\equiv R^o[N, v] \exp\{i\Phi^o[N, v]\}. \qquad (29)$$

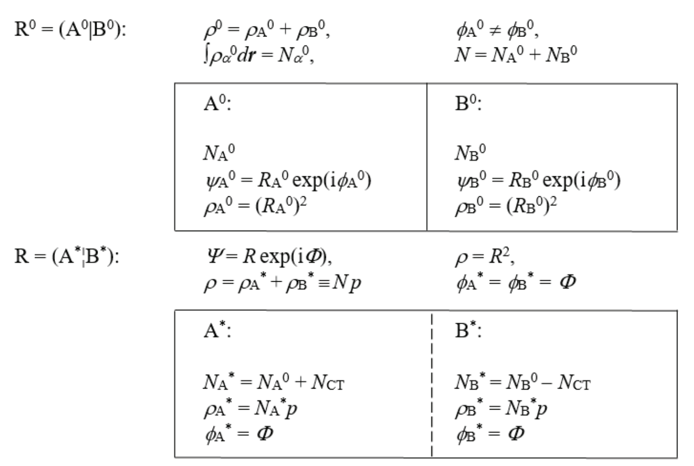

Figure 3: The phase distinction of the mutually-*closed* subsystems in the promolecular donor-acceptor system R^0 = (A^0|B^0) composed of the acidic (A) and basic (B) subsystems, and the phase equalization in the mutually-*open* fragments of the equilibrium molecular system R = (A*¦B*), after the B→A transfer of $N_{CT} > 0$ electrons.

In the *final* (equilibrium) state the “molecular” reactive complex R ≡ (A*¦B*) is composed of the mutually-*open* reactants $\{\alpha^*\}$, symbolically separated by the broken vertical line. They contain fractional numbers $\{N_\alpha^{\ *}\}$ of electrons, modified by the optimum BA CT. This isolated molecular system can be also characterized by the pure quantum state of the whole complex, i.e., a single wavefunction $\Psi[N, v] = R[N, v] \exp\{i\Phi[N, v]\}$. It should be emphasized that the equilibrium reconstructions in electron distributions, already including the CT displacement and the associated CT-induced polarization, also influence the state phase descriptors, since electronic probability flows also carry the densities of other molecular properties. Therefore, the electronic fluxes, governed by energetic variational principle, also determine the associated changes in the information phase/current descriptors of R.

In other words the electronic currents triggered by the mutual opening (entangling) of the two substrates, after equalization of local electronegativity (chemical potential) in the whole reactive complex, is also responsible for the associated changes in the phase description of the chemical process in question. Indeed, the two disentangled promolecular (non-interacting) fragments are initially described by the separate wavefunctions $\psi_A^{\ o}[N_A^{\ o}, v_A]$ and $\psi_B^{\ o}[N_B^{\ o}, v_B]$, corresponding to different probability (modulus) and current (or phase) descriptors of their internal equilibrium states in SRL, while entangled subsystems are related to the same “molecular” wavefunction

$$\Psi(1, 2, ..., N) \equiv \Psi(N) = R[N, v] \exp\{i\Phi[N, v]\}, \qquad (30)$$

and hence the common modulus$_/$phase components of the mutually-open subsystems. This transition of *many*-electron phases $\Phi^o[N, v] \rightarrow \Phi[N, v]$, i.e.,

$$\varphi_A^{\ o}[N_A^{\ o}, v_A] \rightarrow \Phi[N, v] \text{ and } \varphi_B^{\ o}[N_B^{\ o}, v_B] \rightarrow \Phi[N, v], \qquad (31)$$

can be thus regarded as a supplementary process of the *phase*-equalization in the equilibrium state of the whole reactive system.

It should be observed that for N-fermion state the Pauli antisymmetry principle for electronic wavefunctions,

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$$\Psi(1, 2, \ldots, i, \ldots, j, \ldots N) = -\,\Psi(1, 2, \ldots, j, \ldots, i, \ldots N), \qquad (32)$$

calls for the antisymmetric modulus and symmetric phase components:

$$R(1, 2, \ldots, i, \ldots, j, \ldots N) = -\,R(1, 2, \ldots, j, \ldots, i, \ldots N) \text{ and}$$

$$\Phi(1, 2, \ldots, i, \ldots, j, \ldots N) = \Phi(1, 2, \ldots, j, \ldots, i, \ldots N). \qquad (33)$$

As an illustrative example consider the molecular orbital (MO) representation, in terms of Slater determinants (configurations) defined by the given selection

$$\psi(r) = \{\psi_s(r) = R_s(r)\exp[\mathrm{i}\varphi_s(r)]\} \qquad (34)$$

of N *singly*-occupied (orthonormal) molecular spin-orbitals,

$$\Psi(N) = |\psi_1\psi_2\ldots\psi_N| = \det\psi \equiv \mathrm{A}[\psi_1(1)\,\psi_2(2)\ldots\psi_N(N)]$$

$$= (N!)^{-1/2}\textstyle\sum_{\mathrm{P}}(-1)^{n(\mathrm{P})}\,\psi_1(l_1)\,\psi_2(l_2)\ldots\psi_N(l_N) \equiv \sum_{\mathrm{P}}\Psi_{\mathrm{P}}(N), \qquad (35)$$

where A stands for the antisymmetrization operator, P = $(l_1, l_2, \ldots, l_N)$ is the current permutation of positions of N electrons, and n(P) denotes its multiplicity. One recalls that in this Slater determinant configuration all electrons are effectively described by all occupied MO. Each permutation component of Slater determinant $\Psi(N)$,

$$\Psi_{\mathrm{P}}(N) = (N!)^{-1/2}\{(-1)^{n(\mathrm{P})}[R_1(l_1)\,R_2(l_2)\ldots R_N(l_N)]\}\exp\{\mathrm{i}[\varphi_1(l_1) + \varphi_2(l_2) + \ldots + \varphi_N(l_N)]\}$$

$$= R_{\mathrm{P}}[N, v]\exp\{\mathrm{i}\Phi_{\mathrm{P}}[N, v]\}, \qquad (36)$$

indeed exhibits the antisymmetric modulus component $R_{\mathrm{P}}[N, v]$, of the permutation product of MO moduli, and the symmetric phase part $\Phi_{\mathrm{P}}[N, v]$, given by the sum of MO phases.

One further recalls the Harriman-Zumbach-Maschke (HZM) construction in DFT [72,73], of electronic wave functions yielding the specified electron density $\rho(r) = Np(r)$, based upon earlier ideas by Macke [74] and Gilbert [75]. It uses the EO representation, of N occupied MO characterized by equal (molecular) moduli

$$\psi_k(r) = p(r)^{1/2}\exp[\mathrm{i}k{\cdot}f(r)], \qquad (37)$$

and the density dependent vector function $f(r) = f[p; r]$ common to all orbitals, which are orthogonal $\langle\psi_k|\psi_{k'}\rangle = \delta(k - k')$ for different (constant) MO wave vectors in the determinant [72-77]:

$$k_1 \neq k_2 \neq \ldots \neq k_N. \qquad (38)$$

In this EO approximation the overall current due to N-electrons is the sum of orbital contributions:

$$j_N(r) = \textstyle\sum_s\langle\psi_s|\mathrm{j}(r)|\psi_s\rangle \equiv \sum_s j_s(r),$$

$$j_s(r) = (\hbar/m)\,p(r)\,\nabla\varphi_s(r) = (\hbar/m)\,p(r)\,k_s\,\nabla{\cdot}f(r) \equiv p(r)\,V_s(r), \qquad (39)$$

where $V_s(r)$ denotes local probability velocity in ψ_s. Therefore, the resultant current in EO representation is characterized by the configuration *average* wave vector $K_\psi = (\sum_s k_s)/N$:

$$j_N(r) = (\hbar/m)\,\rho(r)\,K_\psi\,\nabla{\cdot}f(r) \equiv \rho(r)\,V_\psi(r), \qquad (40)$$

with $V_\psi(r)$ standing for the configuration average descriptor of the local probability velocity.

Since molecular wavefunctions and their components are in general *many*-electron in character, for the visualization/interpretation purposes one introduces the effective *one*-electron distributions. For example, the electron density $\rho(r) = Np(r)$ or its shape factor (probability) distribution $p(r)$ both refer to the combined event of finding *any* of the system N electrons at position r, for all allowed spin orientations and admissible positions of remaining electrons. Taking into account the electron indistinguishability in QM, with all electrons generating equal contributions to the overall descriptor and each MO being characterized by the same occupation-probability in configuration's Slater determinant, $P_s = 1/N$, gives the following expression for $p(r)$:

$$p(r) = \rho(r)/N \equiv [\textstyle\sum_s p_s(r)]/N = \sum_s P_s p_s(r)$$

$$= \int R[N, v]^2\,\delta(r_1 - r)\,d\tau^N \equiv \int P[N, v]\,\delta(r_1 - r)\,d\tau^N \equiv \varphi(r)^2, \qquad (41)$$

where $P[N, v]$ is the N-electron probability density, $\int d\tau^N$ stands for integrations over the position-coordinates and summation over spin-orientations of all N electrons, and $\varphi(r)$ denotes the effective *one*-electron probability amplitude.

Similar reduction can be envisaged for the phase descriptors. The average local phase $\varphi(r)$ of the molecular configuration in EO representation can be defined as follows:

$$\varphi(r) = \textstyle\sum_s P_s\,\varphi_s(r) = N^{-1}(\sum_s k_s){\cdot}f(r) = K_\psi{\cdot}f(r). \qquad (42)$$

Therefore, the overall current in the N electronic system [Eq. (40)] can be also interpreted in terms of the effective *one*-electron densities:

$$j_N(r) = (\hbar/m)\,\rho(r)\,K_\psi\,\nabla{\cdot}f(r) = (\hbar/m)\,\rho(r)\,\nabla\varphi(r) \equiv \rho(r)\,V_\psi(r). \qquad (43)$$

These representative *one*-electron distributions of the probability and phase/current in N-electron systems describe the complementary facets of the electronic organization: the classical (probability) "structure of being" and the nonclassical (phase/current) "structure of becoming" [78].

Phase equalization

Therefore, the opening of both substrates brings about simultaneous equalizations of their chemical potential (electronegativity) and phase descriptors in the equilibrium (bonded) state of the donor-acceptor reaction complex [10]:

$$\mu_{\mathrm{A}}{}^* = \mu_{\mathrm{B}}{}^* = \mu \quad \text{and} \quad \Phi_{\mathrm{A}}{}^*(\boldsymbol{r}) = \Phi_{\mathrm{B}}{}^*(\boldsymbol{r}) = \Phi(\boldsymbol{r}). \qquad (44)$$

The phase-adjustment thus accompanies the charge reconstruction in the whole reactive system. This equilibrium amount of CT between mutually-open reactants and the accompanying density reconstruction in both substrates thus bring about the equalization of the subsystem phases in the reactive system at the molecular distribution. The *probability*-velocity descriptor $V_\psi(r)$ also determines the currents of other physical properties, e.g., the *phase*-current $j_\varphi(r) = \varphi(r)\,V_\psi(r)$, since

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their densities are also carried by electrons. Therefore, the molecular" FF descriptors of Section 2, which reflect the equilibrium density/population responses of the mutually-open fragments to the global population displacements, can be also applied in the phase-equalization considerations.

Consider the EO description of this process (Figure 4). In the polarized system R$^+$ (Panel *a* of the figure) both reactants preserve their promolecular (integer) numbers of electrons $\{N_\alpha^+ = N_\alpha^o\}$. The EO description of their electron distributions $\{\rho_\alpha^+\}$ can be effected in terms of Slater determinants describing polarized reactants, $\{\Psi_\alpha[N_\alpha^+, v] = \det \psi_\alpha^+\}$, where the fragment EO

$$\psi_\alpha^+ = \{\psi_{i,\alpha}(r) = [p_\alpha^+(r)]^{1/2} \exp\{ik_{i,\alpha} \cdot f[p_\alpha; r]\}, k_{1,\alpha} \neq k_{2,\alpha} \neq \ldots \neq k_{i,\alpha} \neq \ldots, \tag{45a}$$

reconstruct its polarized electron density $\rho_\alpha^+(r) = N_\alpha^+ p_\alpha^+(r)$. Such internal equilibria in the mutually-closed subsystems correspond to the fragment *average* wave-vectors $\{K_\alpha = [\sum_{s(\alpha)} k_s(\alpha)]/N_\alpha^+\}$ and the associated phases $_\alpha(r) = K_\alpha \cdot f_\alpha(r)$, where $f_\alpha(r) = f[p_\alpha; r]$. The global equilibrium (of Panel *b* in Figure 4) similarly describes the whole "molecular" system R with its own set of EO

$$\psi = \{\psi_s(r) = [p(r)]^{1/2} \exp\{ik_s \cdot f[p; r]\}, k_1 \neq k_2 \neq \ldots \neq k_s \neq \ldots, \tag{45b}$$

reconstructing $\rho(r) = Np(r)$. This global equilibrium in the whole reactive system corresponds to molecular wave-vector K_ψ [Eq. (40)] and phase $\varphi(r)$ [Eq. (42)].

To summarize, in EO representation the electron distributions of distinguishable (interacting) fragments $\{\alpha^+\}$ of R$^+$ are characterized by the set of (polarized) *subsystem* densities $\{\rho_\alpha^+\}$ and the associated (localized) orbitals $\{\psi_\alpha^+\}$, while the equilibrium substrates $\{\alpha^*\}$ in R are described by the *molecular* density ρ and (delocalized) orbitals ψ. Therefore, the corresponding phase descriptors of such internal and global equilibria are unique functionals of the "argument" distributions and the associated populations:

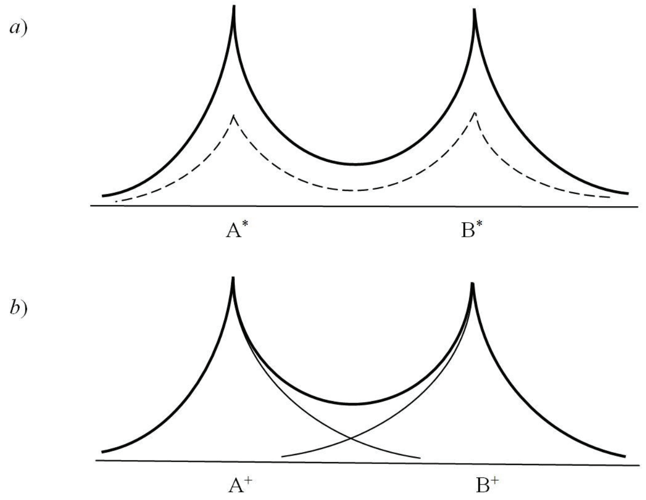

Figure 4: Schematic profiles of two "delocalized" (molecular) EO $\{\psi_k(\alpha^*)\}$, in the whole reactive system (Panel *a*), and "localized" (reactant) MO $\{\psi_k(\alpha^+)\}$, in the polarized reactive system (Panel *b*), for the entangled R$^* = (\mathrm{A}^*{\mid}\mathrm{B}^*)$ and disentangled R$^+ = (\mathrm{A}^+|\mathrm{B}^+)$ fragments of the donor-acceptor system, respectively. The subsystem EO $\{_k(\alpha^+)\}$ reconstruct the electron density ρ_α^+ in the polarized fragment, while the "molecular" functions yield the electron distribution ρ in R as a whole.

$$\{\varphi_\alpha^+(r) = \varphi_\alpha^+[\{\rho_\beta^+\}; r]\} = \varphi_\alpha^+[\{\rho_\beta^+[N_\beta^o, v]\}; r]\} = \varphi_\alpha^+[\{N_\beta^o\}, v; r] \text{ and} \tag{46}$$

$$\varphi_\alpha^*(r) = \varphi_\alpha^*[\{\rho_\beta^*[\rho]\}; r] = \varphi_\alpha^*[\rho; r] = \varphi(r) = \varphi[\rho[N, v]; r] = \varphi[N, v; r]. \tag{47}$$

Moreover, since B→A CT is ultimately responsible for establishing the molecular density $\rho(r)$ and its equilibrium pieces $\{_\beta^*[\rho]\}$, all these distributions and the associated equilibrium populations $\{N_\beta^* = \int \rho_\beta^* dr\}$ are functions of the current amount N_{CT} of this electronic flow descriptor:

$$\{\rho_\beta^*(r) = \rho_\beta^*(N_{\mathrm{CT}}; r) \Rightarrow N_\beta^* = N_\beta^*(N_{\mathrm{CT}})\} \text{ and } \rho(r) = \rho(N_{\mathrm{CT}}; r). \tag{48}$$

A reference to Eq. (44) indicates that the effective phases-per-electron in the mutually-open subsystems equalize at the global equilibrium, after the optimum amount of CT [Eq. (27)], so that their local difference identically vanishes:

$$\varphi_{\mathrm{CT}}(r) \equiv \varphi_{\mathrm{A}}^*(r) - \varphi_{\mathrm{B}}^*(r) = 0. \tag{49}$$

This (*in situ*) phase "gradient" can indeed be regarded as populational CT-derivative of the effective phase density of *N* electrons, in the reactive complex as a whole [see Eq. (24)],

$$\Phi(r) = N\varphi(r) = (N_{\mathrm{A}}^* + N_{\mathrm{B}}^*)\,\varphi(r) = N_{\mathrm{A}}^*\varphi_{\mathrm{A}}^*(r) + N_{\mathrm{B}}^*\varphi_{\mathrm{B}}^*(r) \equiv \Phi_{\mathrm{A}}^*(r) + \Phi_{\mathrm{B}}^*(r), \tag{50}$$

$$d\Phi(r)/dN_{\mathrm{CT}} = [dN_{\mathrm{A}}^*/dN_{\mathrm{CT}}][\partial\Phi_{\mathrm{A}}^*(r)/\partial N_{\mathrm{A}}^*] + [dN_{\mathrm{B}}^*/dN_{\mathrm{CT}}][\Phi_{\mathrm{B}}^*(r)/\partial N_{\mathrm{B}}^*]$$

$$= F_{\mathrm{A}}^{\mathrm{CT}}\varphi_{\mathrm{A}}^*(r) + F_{\mathrm{B}}^{\mathrm{CT}}\varphi_{\mathrm{B}}^*(r) = \varphi_{\mathrm{A}}^*(r) - \varphi_{\mathrm{B}}^*(r). \tag{51}$$

In R$^+$ the nonequalized phases of both reactants generate the (*in situ*) phase "force"

$$\varphi_{\mathrm{CT}}^+(r) \equiv \varphi_{\mathrm{A}}^+(r) - \varphi_{\mathrm{B}}^+(r) \neq 0, \tag{52}$$

which also vanishes after the optimum CT of Eq. (27):

$$\varphi_{\mathrm{CT}}^+(r) + N_{\mathrm{CT}}\,[d\varphi_{\mathrm{CT}}(r)/dN_{\mathrm{CT}}] \equiv \varphi_{\mathrm{CT}}^+(r) + N_{\mathrm{CT}}\,\xi_{\mathrm{CT}}(r) = 0. \tag{53}$$

The above descriptor of the (*in situ*) phase "hardness" represents the CT Hessian

$$\xi_{\mathrm{CT}}(r) = d\varphi_{\mathrm{CT}}(r)/dN_{\mathrm{CT}} = d^2\Phi(r)/dN_{\mathrm{CT}}^{\,2}, \tag{54}$$

which also determines the equilibrium amount of CT [compare Eq. (27)]:

$$N_{\mathrm{CT}} = -\varphi_{\mathrm{CT}}^+(r)/\xi_{\mathrm{CT}}(r). \tag{55}$$

Local energy concept

Consider, for simplicity reasons, the quantum state $|\psi(t)\rangle$ of a single electron at time *t*, and the associated (complex) wavefunction in the position representation,

$$\psi(r, t) = \langle r|\psi(t)\rangle = R(r, t)\exp[i\varphi(r, t)], \tag{56}$$

defined by its modulus $R(r,t)$ and phase $\varphi(r,t) \geq 0$ parts. The state logarithm then additively separates these two independent components:

$$2\ln\psi(r,t) = 2\ln R(r,t) + 2\mathrm{i}\varphi(r,t) = \ln p(r,t) + 2\mathrm{i}\varphi(r,t), \qquad (57)$$

where $p(r,t) = R(r,t)^2$ denotes the spatial probability density. The real part of the wavefunction is thus seen to determine the logarithm of the state classical (probability) component, while the imaginary part accounts for the nonclassical (phase) distribution:

$$\mathrm{Re}[2\ln\psi(r,t)] = 2\ln R(r,t) = \ln p(r,t) \text{ and } \mathrm{Im}[\ln\psi(r,t)] = \varphi(r,t). \quad (58)$$

In molecular scenario an electron is moving in the external potential $v(r)$ due to the fixed positions of the system constituent nuclei. In this BO approximation the (Hermitian) electronic Hamiltonian

$$\mathrm{H}(r) = -[\hbar^2/(2m)]\Delta + v(r) \equiv \mathrm{T}(r) + v(r) \qquad (59)$$

determines the quantum dynamics of molecular electronic state, in accordance with the time-dependent SE:

$$\mathrm{i}\hbar[\partial\psi(r,t)/\partial t] = \mathrm{H}(r)\psi(r,t). \qquad (60)$$

This fundamental equation and its complex conjugate ultimately imply the associated dynamic equations for the wavefunction components or temporal evolutions of the associated physical distributions of the spatial probability and current densities (see also Section 9).

Consider the stationary state corresponding to the sharply specified energy $E_{st.}$,

$$\psi_{st.}(r,t) = R_{st.}(r)\exp[-\mathrm{i}(E_{st.}/\hbar)t] = R_{st.}(r)\exp(-\mathrm{i}\omega_{st.}t), \qquad (61)$$

when $\varphi_{st.}(r,t) = \varphi_{st.}(t) = -_{st.}t$. In such “equilibrium”, *zero*-current state

$$j_{st.}(r,t) = (\hbar/m)\,p_{st.}(r)\,\nabla\varphi_{st.}(t) = 0, \qquad (62)$$

the probability distribution is *time*-independent:

$$p_{st.}(r,t) = |\psi_{st.}(r,t)|^2 = R_{st.}(r)^2 \equiv p_{st.}(r). \qquad (63)$$

These eigenstates of electronic Hamiltonian,

$$\mathrm{H}(r)\psi_{st.}(r,t) = E_{st.}\psi_{st.}(r,t) \text{ or } \mathrm{H}(r)R_{st.}(r) = E_{st.}R_{st.}(r), \qquad (64)$$

thus correspond to the spatially equalized local energy

$$E(r,t) \equiv \psi(r,t)^{-1}\mathrm{H}(r)\psi(r,t), \qquad (65)$$

$$E_{st.}(r) \equiv R_{st.}(r)^{-1}\mathrm{H}(r)R_{st.}(r) = E_{st.}. \qquad (66)$$

This principle of the local-energy equalization can be also interpreted as the related equalization rule or the spatial phase. Indeed, the local wave-number/phase concepts,

$$\omega(r,t) \equiv E(r,t)/\hbar \text{ and } \varphi(r,t) = -\omega(r,t)\,t, \qquad (67)$$

directly imply their spatial equalization in the stationary electronic state:

$$\omega_{st.}(r,t) = E_{st.}/\hbar = \omega_{st.} = const. \text{ and } \Phi_{st.}(r,t) = -(E_{st.}/\hbar)\,t = -\omega_{st.}t = \Phi_{st.}(t). \qquad (68)$$

The quantum *stationary*-equilibrium is thus marked by the local phase equalization throughout the whole physical space. It should be realized that due to complex nature of wavefunctions the local energy of Eq. (65) is also complex in character: $E(r,t) \neq E(r,t)^*$. This further implies the complex concepts of local phase/wave-number, e.g.,

$$\omega(r,t) = c(r,t) + \mathrm{i}\,b(r,t),$$

$$c(r,t) = \mathrm{Re}[\omega(r,t)] = [\omega(r,t) + \omega(r,t)^*]/2,$$

$$b(r,t) = \mathrm{Im}[\omega(r,t)] = [\omega(r,t) - \omega(r,t)^*]/(2\mathrm{i}), \qquad (69)$$

which determine dynamic equations for the additive components of the state wavefunction [Eq. (57)]. Rewriting local SE in terms of complex wave-number components gives:

$$\psi(r,t)^{-1}[\partial\psi(r,t)/\partial t] = \partial\ln\psi(r,t)/\partial t = \partial\ln R(r,t)/\partial t + \mathrm{i}\,\partial\varphi(r,t)/\partial t$$

$$= -\mathrm{i}\omega(r,t) = -\mathrm{i}c(r,t) + b(r,t). \qquad (70)$$

The real terms in this complex equation determine the *modulus*-dynamics,

$$\partial\ln R(r,t)/\partial t = b(r,t), \qquad (71)$$

while its imaginary terms determine time-evolution of the wavefunction phase:

$$\partial\varphi(r,t)/\partial t = -c(r,t). \qquad (72)$$

To summarize, the (complex) local energy generates a transparent description of the non-equilibrium time evolution of wave-function components: its real contribution shapes the *phase*-dynamics, while the *modulus*-dynamics is governed by the imaginary components of $E(r,t)$ and $\omega(r,t)$. The spatial equalization of these complex wave-number or local-phase concepts marks the stationary equilibrium in QM.

Independent origins of information content in electronic states

The independent (real) parts of the electronic wavefunction in Eq. (56) ultimately define the state physical descriptors of the spatial probability density $p(r,t) = R(r,t)^2$ and its current

$$j(r,t) \equiv \langle\psi|\mathrm{j}(r)|\psi\rangle = [\hbar/(2m\mathrm{i})]\,[\psi(r,t)^*\nabla\psi(r,t) - \psi(r,t)\nabla\psi(r,t)^*]$$

$$= (\hbar/m)\,p(r,t)\nabla\varphi(r,t) \equiv p(r,t)\,V(r,t). \qquad (73)$$

The effective probability velocity introduced in the preceding equation,

$$V(r,t) \equiv P(r,t)/m = (\hbar/m)\,\nabla\varphi(r,t) \equiv j(r,t)/p(r,t), \qquad (74)$$

thus measures a density of the current-per-particle. It reflects the local momentum density $P(r,t) \equiv \hbar k(r,t)$, with $k(r,t) = \nabla\varphi(r,t)$ standing for its wave-vector factor.

To summarize, the real and imaginary components of electronic wavefunction determine the independent probability and velocity densities, respectively. They account for the “static” and “dynamic” (convection) aspects of the state probability distribution, which we call

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the stuctures of “being” and “becoming” [78], and determine the overall (resultant) descriptors of the state uncertainty (entropy) content $S[\psi]$ or the overall gradient information $I[\psi]$ [4,79-83]:

$$S[\psi] = S[p] + S[\varphi] = S[p, \varphi] \text{ and } I[\psi] = I[p] + I[\varphi] = I[p, \varphi]. \qquad (75)$$

Their probability terms $S[p]$ and $I[p]$, due to the logarithm of the state probability density, constitute the classical information-theoretic (IT) concepts of Shannon’s global entropy [19],

$$S[p] = -\int p(r,t) \ln p(r,t)\, dr, \qquad (76)$$

and Fisher’s information functional for locality events [17]:

$$I[p] = \int p(r,t)\, [\nabla \ln p(r,t)]^2\, dr = \int p(r,t)^{-1}\, [\nabla p(r,t)]^2\, dr. \qquad (77)$$

These generalized IT measures have been used to describe the equilibria in the substrate subsystems and to monitor electronic reconstructions in chemical reactions [8-10,84-87].

In resultant measures these classical functionals are supplemented by the corresponding nonclassical complements $S[\varphi]$ and $I[\varphi] = I[j]$, due to wavefunction phase or the associated electronic current. For example, in the overall (“scalar”) entropy [4,79] the (positive) classical descriptor is combined with the (negative) average phase contribution,

$$S[\psi] = S[p] - 2\int p(r,t)\, \varphi(r,t)\, dr \equiv S[p] + S[\varphi]$$

$$= -\int p(r,t)[\ln p(r,t) + 2\varphi(r,t)]\, dr \equiv \int p(r,t)\, S(r,t)\, dr, \qquad (78)$$

while the complex (“vector”) uncertainty measure [4,81] represents the expectation value of the (non-Hermitian) entropy operator $\mathrm{S} = -2\ln\psi$:

$$S[\psi] \equiv \langle\psi|2\ln\psi|\psi\rangle = S[p] - 2\mathrm{i}\int p(r,t)\, \varphi(r,t)\, dr \equiv S[p] + \mathrm{i}\, S[\varphi] = S[p, \varphi]$$

$$= -\int p(r,t)[\ln p(r,t) + 2\mathrm{i}\varphi(r,t)]\, dr \equiv \int p(r,t)\, S(r,t)\, dr. \qquad (79)$$

The negative nonclassical entropy effectively lowers the state classical uncertainty measure $S[p]$. Indeed, any presence of finite currents implies more state spatial “order” (less “uncertainty”).

The resultant measure of the state average gradient information [4,79-83].

$$I[\psi] \equiv -4\, \langle\psi|\Delta|\psi\rangle = 4\langle\nabla\psi|\nabla\psi\rangle = (8m/\hbar^2)\, \langle\psi|\mathrm{T}|\psi\rangle \equiv \kappa\, T[\psi]$$

$$= I[p] + 4\int p(r,t)\, [\nabla\varphi(r,t)]^2\, dr \equiv I[p] + I[\varphi]$$

$$= I[p] + (2m/\hbar)^2 \int p(r,t)^{-1} j(r,t)^2\, dr \equiv I[p] + I[j]$$

$$= p(r,t)\{[\nabla \ln p(r,t)]^2 + 4[\nabla\varphi(r,t)]^2\}\, dr \equiv \int p(r,t)\, I(r,t)\, dr, \qquad (80)$$

reflects the (dimensionless) kinetic energy of electrons: $T[\psi] = \langle\psi|\mathrm{T}|\psi\rangle = \kappa^{-1}\, I[\psi]$. One also introduces the resultant measure of the gradient entropy, again with the negative nonclassical contribution [4],

$$M[\psi] = M[p] + M[\varphi] \equiv I[p] - I[\varphi], \qquad (81)$$

which recognizes the fact that a nonvanishing current pattern introduces extra “order”, less “uncertainty”, compared to the classical descriptor $M[p] = I[p]$.

Information reactivity criteria

The (externally) open microscopic systems require the *mixed*-state description, in terms of the *ensemble*-average physical quantities accounting for the imposed thermodynamic conditions. In reactivity problems the specified temperature T of the “heat bath”, and of electronic chemical potential μ (or electronegativity $\chi = -$) of a macroscopic “electron reservoir”, call for the grand-ensemble approach [14,62,63]. The system equilibrium (*mixed*) quantum state is then represented by the statistical mixture of the system *pure* states, defined by their (externally-imposed) equilibrium probabilities. Indeed, only the *ensemble*-average value of the overall number of electrons $N \equiv \langle N\rangle_{ens.}$ in the externally-open molecule $\mathrm{M}(v)$, identified by its external potential $v(r)$, exhibits a continuous (fractional) spectrum of values in the ensemble composed system $\mathrm{M} = [\mathrm{M}(v)\text{¦}\mathrm{R}]$ consisting of the molecular fragment $\mathrm{M}(v)$ open with respect to an external (macroscopic) electron reservoir R. This justifies the very concept of populational derivatives of the system ensemble-average energy.

Such N-derivatives of electronic energy are involved in definitions of several reactivity criteria, e.g., the chemical potential or electronegativity [14,62-66] and the hardness (softness) [14,67] and FF [14,68] descriptors of molecular and reactive systems. In IT treatments one introduces analogous concepts of the populational derivatives of the ensemble average (resultant) gradient information [9,85-88]. Since reactivity phenomena involve electron flows between the *mutually*-open substrates, only in such generalized, ensemble framework can one precisely define the relevant reactivity criteria, determine the hypothetical states of the promoted subsystems and eventually measure effects of their chemical coordination. In this ensemble approach the energetic and information principles are exactly equivalent, giving rise to identical predictions of thermodynamic equilibria, charge rearrangements and average descriptors of molecular systems and their fragments.

The populational derivatives of the average energy and resultant information in reactive systems thus invoke the grand-ensemble composite representation $\langle \mathrm{M}(v)\rangle_{ens.}$ of a given molecular system $\mathrm{M}(v)$. Thermodynamic conditions in the (microscopic) molecular system in question are then imposed by the hypothetical (macroscopic) heat bath $\mathrm{B}(T)$ and external electron reservoir $\mathrm{R}(\mu)$. The effective mixed-state then corresponds to the equilibrium probabilities $\mathrm{P}(\mu, T; v) \equiv \{P_j^i(\mu, T; v)\}$ of the molecular (pure) stationary states $\{|\Psi_j^i\rangle \equiv |\Psi_j(N_i)\rangle\}$, where $|\Psi_j^i\rangle$ denotes j-th state of N_i (integer) electrons, which define the equilibrium density operator:

$$\mathrm{D}(\mu, T; v) = \textstyle\sum_i\sum_j |_j^i\rangle\, P_j^i(\mu, T; v)\, \langle\Psi_j^i|,\ \sum_i\sum_j P_j^i(\mu, T; v) \equiv \sum_i P^i(\mu, T; v) = 1. \qquad (82)$$

This statistical mixture of molecular stationary states gives rise to the corresponding ensemble-average values of the system electronic energy and its resultant gradient information. The former is defined by quantum expectations of electronic Hamiltonians $\{\mathrm{H}_i = \mathrm{H}(N_i, v)\}$,

$$\langle E\rangle_{ens.} = \textstyle\sum_i\sum_j P_j^i(\mu, T; v)\, \langle\Psi_j^i|\ \mathrm{H}_i|_j^i\rangle = \sum_i\sum_j P_j^i(\mu, T; v)\, E_j^i \equiv \mathcal{E}(\mu, T; v) \equiv \mathcal{E}(\mathrm{D}), \qquad (83)$$

while the latter corresponds to expectations of the (Hermitian)

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operators $\{\mathrm{I}_i = \mathrm{I}(N_i)\}$ for the resultant gradient information of N_i electrons, related to the system kinetic-energy operators $\{\mathrm{T}(N_i)\}$,

$$\mathrm{I}_i = (8m/\hbar^2)\,\mathrm{T}(N_i) \equiv \kappa\,\mathrm{T}_i, \tag{84}$$

$$\langle I\rangle_{ens.} = \sum_i\sum_j P_j^i(\mu, T; v)\,\langle {}_j^i|\mathrm{I}_i|{}_j^i\rangle \equiv \sum_i\sum_j P_j^i(\mu, T; v)\,I_j^i \equiv I(\mu, T; v) \equiv I(\mathrm{D}), \tag{85}$$

Thus the average gradient information $I(\mathrm{D})$ reflects the (dimensionless) average kinetic energy $\langle T\rangle_{ens.} \equiv T(\mu, T; v) \equiv T(\mathrm{D})$,

$$T(\mathrm{D}) = \sum_i\sum_j P_j^i(\mu, T; v)\,\langle {}_j^i|\mathrm{T}_i|\Psi_j^i\rangle \equiv \sum_i\sum_j P_j^i(\mu, T; v)\,T_j^i = \kappa^{-1} I(\mathrm{D}),$$

$$T_j^i = \langle \Psi_j^i|\mathrm{T}_i|{}_j^i\rangle = \kappa^{-1} I_j^i. \tag{86}$$

The equilibrium probabilities $\mathrm{P}(\mu, T; v)$ result from the minimum principle of the grand-potential

$$\Omega(\mathrm{D}) = E(\mathrm{D}) - \mu N(\mathrm{D}) - TS(\mathrm{D}), \tag{87}$$

$$\delta\Omega(\mathrm{D})|_{\mathrm{P}(\mu, T;\, v)} = 0. \tag{88}$$

Here, the average number of electrons

$$\langle N\rangle_{ens.} = N(\mathrm{D}) = \sum_i N_i\,[\sum_j P_j^i(\mu, T; v)] \equiv \sum_i N_i\,P^i(\mu, T; v) \tag{89}$$

and the average entropy

$$\langle S\rangle_{ens.} = \mathrm{tr}(\mathrm{DS}) = S(\mathrm{D}) \equiv -k_{\mathrm{B}\,i}\sum_j P_j^i(\mu, T; v)\,\ln P_j^i(\mu, T; v) \tag{90}$$

with k_{B} denoting the Boltzmann constant.

The entropy constrained energy principle of Eq. (88) can be also interpreted as equivalent potential-energy constrained information rule, for the minimum of resultant gradient-information:

$$\delta[I(\mathrm{D}) - \lambda W(\mathrm{D}) - \zeta N(\mathrm{D}) - \tau S(\mathrm{D})]_{\mathrm{P}(\mu, T;\, v)} = 0. \tag{91}$$

It contains an additional constraint of the fixed overall potential energy, $\langle W\rangle_{ens.} = W(\mathrm{D})$, multiplied by the Lagrange multiplier $\lambda = -\kappa$, and includes "scaled" intensities associated with the remaining constraints: the information potential $\zeta = \kappa\,\mu$ enforcing the prescribed electron number, $N(\mathrm{D}) = N$, and the information temperature $\tau \equiv \kappa\,T$ for the subsidiary entropy condition: $S(\mathrm{D}) = S$. The complementary principles of Eqs. (88) and (91) determine the same set of the equilibrium state probabilities.

Several N-derivatives of the ensemble averages of electronic energy or resultant gradient-information define useful reactivity criteria. The physical equivalence of the energy and information principles indicates that such reactivity concepts are mutually related, being both capable of describing CT phenomena in donor-acceptor systems. The ensemble interpretation applies to both the "diagonal" and "mixed" second derivatives of the average electronic energy, which involve the differentiation with respect to electron-population variable. For example, in energy representation the global chemical hardness [67] reflects the N-derivative of the chemical potential,

$$\eta = \partial^2 E/\partial N^2 = \partial\mu/\partial N > 0, \tag{92}$$

while the information hardness measures the N-derivative of the information potential:

$$\omega = \partial^2 I/\partial N^2 = \partial\zeta/\partial N = \kappa\,\eta > 0. \tag{93}$$

The positive signs of these "diagonal" (hardness) derivatives assure the external stability of $\langle \mathrm{M}(v)\rangle_{ens.}$, with respect to charge flows between the molecular system and its electron reservoir, in accordance with the Le Châtelier and Le Châtelier-Braun principles of thermodynamics [89].

The global FF [68] is defined by the "mixed" second derivative of the average energy:

$$f(r) = \partial/\partial N\,[\delta E/\delta v(r)] = \partial\rho(r)/\partial N = \delta/\delta v(r)\,(\partial E/\partial N\,) = \delta\mu/\delta v(r), \tag{94}$$

where we have applied the Maxwell cross-differentiation identity. It can be thus interpreted as either the density response per unit populational displacement, or as the response in global chemical potential to unit displacement in the local external potential. The analogous derivative of the average gradient information similarly reads:

$$\varphi(r) = \partial/\partial N\,[\delta I/\delta v(r)] = \delta/\delta v(r)\,(\partial I/\partial N) = \kappa f(r) = \delta\zeta/\delta v(r). \tag{95}$$

The *in situ* CT-derivatives of the average resultant gradient-information in the reactive system R = A----B follow the corresponding energy criteria of Eqs. (25)-(28). They include the *in situ* information potential related to μ_{CT},

$$\zeta_{\mathrm{CT}} = \partial I(N_{\mathrm{CT}})/\partial N_{\mathrm{CT}} = \kappa\,\mu_{\mathrm{CT}}, \tag{96}$$

and the CT information hardness related to $\eta_{\mathrm{CT}} = S_{\mathrm{CT}}^{-1}$,

$$\omega_{\mathrm{CT}} = \partial^2 I(N_{\mathrm{CT}})/\partial N_{\mathrm{CT}}^{\;2} = \partial\zeta(N_{\mathrm{CT}})/\partial N_{\mathrm{CT}} = \kappa\,\eta_{\mathrm{CT}} \equiv \theta_{\mathrm{CT}}^{\;-1}, \tag{97}$$

inverse of the CT *information*-softness $\theta_{\mathrm{CT}} = \partial N_{\mathrm{CT}}/\partial\zeta$. In terms of these *in situ* descriptors the optimum amount of the B→A CT in the acid-base reactive system thus reads:

$$N_{\mathrm{CT}} = -\,\mu_{\mathrm{CT}}/\eta_{\mathrm{CT}} = -\mu_{\mathrm{CT}}S_{\mathrm{CT}} = -\,\zeta_{\mathrm{CT}}/\omega_{\mathrm{CT}} = -\zeta_{\mathrm{CT}}\,\theta_{\mathrm{CT}}. \tag{98}$$

Therefore, the *in situ* derivatives $\{\zeta_{\mathrm{CT}},\ \omega_{\mathrm{CT}} = \theta_{\mathrm{CT}}^{\;-1}\}$ of the average measure of the resultant gradient-information content provide alternative reactivity descriptors, analogous to the energetic criteria of the chemical potential and hardness or softness indices $\{\mu_{\mathrm{CT}}, \eta_{\mathrm{CT}} = S_{\mathrm{CT}}^{\;-1}\}$ of a classical, energy-centered theory of chemical reactivity. This again demonstrates the physical equivalence of the energy and information principles in describing the CT phenomena in molecular systems. One thus concludes that the resultant gradient information, the quantum generalization of the classical Fisher measure, constitutes a reliable basis for an "entropic" description of reactivity phenomena.

Gaining information by eliminating uncertainties

In both the classical probability theory and in position representation of QM the admissible locations $\{r\}$ of an electron exhaust the whole physical space and constitute the complete set of elementary (exclusive) position events. The classical *probability scheme* $\{r \to p(r)\}$ of Figure 5, infinite and continuous, describes a state of the position *indeterminacy* (uncertainty). It is best reflected by Shannon's entropy $S[p]$, since we know only probabilities $p(r) = |\psi(r)|^2$ of possible definite outcomes in

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the underlying particle-localization experiment. This average entropy descriptor measures a "spread" (width) of the probability distribution. Another suitable classical IT probe of the average information content in $p(r)$ is provided by Fisher's probability functional $I[p]$. This gradient measure of the position *determinacy* (localization) reflects a "compactness" (hight) of the probability distribution, thus complementing the Shannon descriptor.

The information given us by carrying out the given experiment consists in removing the uncertainty existing before the experiment [90]. If we carry out the particle-localization trial we obtain some information, since its outcome means that we then know exactly, which particle position has actually been detected. This implies that after repeated probes performed for the specified quantum state the initial uncertainty contained in the position *probability scheme* has been completely eliminated. The average information gained by the repeated localization tests thus amounts to the removed position uncertainty. The larger the uncertainty in $\rho(r)$, the larger the amount of information obtained when we find out which electron position has actually been detected after the experiment. In other words, the amount of information given us by the realization of the classical, probability scheme alone equals to the global entropy in the classical scheme of Figure 5.

In QM, however, one deals with the *wavefunction scheme* $\{r \rightarrow \psi(r)\}$ of Figure 5, in which the classical map $\{r \rightarrow p(r)\}$ constitutes only a part of the overall (complex) mapping. In fact, the wavefunction mapping implies a simultaneous ascribing to an electron position the local modulus and phase arguments of the state wavefunction, or the related local probability and current/velocity quantities. This *two-level* scheme in QM ultimately calls for the *resultant* measures of the entropy/information content in quantum states, combining the classical (probability) and nonclassical (phase/current) contributions. The difference between the resultant and classical information contents can be best compared to that between the (phase-dependent) hologram and (phase-independent) ordinary photograph.

It is interesting to note that in QM the localization experiments cannot remove all the uncertainty contained in general electronic states, exhibiting nonvanishing local phase component, $\varphi(r, t) > 0$, and hence also a finite current density $j(r, t) \neq 0$, which identically vanishes only in the stationary state of Eq. (61): $j_{st.}(r, t) = V_{st.}(r, t) = 0$. For such equilibrium wavefunctions an experimental determination of electronic position completely removes all the uncertainty contained in the spatial wavefunction $R_{st.}(r)$. Indeed, the quantum scheme of Figure 5 then reduces to classical mapping.

Since the current operator includes the momentum operator of an electron,

$$\mathbf{j}(r) = (2m)^{-1}[\mathbf{P}\,\mathrm{p}(r) + \mathrm{p}(r)\,\mathbf{P}],$$

$$\mathbf{P}(r) = -\mathrm{i}\hbar\nabla,\ \mathrm{p}(r) = |r\rangle\langle r,\ \{\mathrm{r}\,|r'\rangle = r'\,|r'\rangle\}, \qquad (99)$$

which does not commute with the position operator r = r, [r, P] = i$\hbar$, the incompatible observables r and j(r) do not have common eigenstates. In other words, in QM these quantities cannot be sharply defined *simultaneously*, in accordance with the familiar Heisenberg's uncertainty principle. Therefore, the position dispersion σ_r cannot be simultaneously eliminated with the current dispersion $\sigma_{j(r)}$ in a single type of experiment, e.g., of the particle-localization, since a removal of $_{j(r)}$ calls for the momentum experimental setup, which is incompatible with that required for determining the electron position. Therefore, only the *independent* (separate) localization and momentum experiments can fully eliminate the position and current uncertainties contained in a general electronic state.

It follows from Heisenberg's uncertainty principle of QM that the limiting, lowest value of the product of squared dispersions $\sigma_{j(r)}$ and σ_r,

$$\sigma_X = \langle\psi|(\mathrm{X} - \langle X\rangle_\psi)^2|\psi\rangle^{1/2} \text{ and } \langle X\rangle_\psi = \langle\psi|\mathrm{X}|\psi\rangle,\ X \in \{r, j(r)\}, \qquad (100)$$

is determined by the state squared expectation of the commutator of the two operators involved:

$$[\sigma_{j(r)}(t)]^2\ [\sigma_r(t)]^2 > -\langle\psi(t)|[\mathrm{j}(r),\ \mathrm{r}]|\psi\ \ (t)\rangle^2/4 = \{\mathrm{i}\ \langle\psi(t)|[\mathrm{j}(r),\ \mathrm{r}]|\psi(t)\rangle/2\}^2, \qquad (101)$$

where

$$[\mathrm{j}(r), \mathrm{r}] = (2m)^{-1}\{[\mathrm{P}, \mathrm{r}]\,\mathrm{p}(r) + \mathrm{p}(r)\,[\mathrm{P}, \mathrm{r}]\} = \hbar p(r)/(m\mathrm{i}). \qquad (102)$$

Hence, the lowest value of the product of the simultaneous dispersions satisfies the inequality:

$$\sigma_{j(r)}(t)\,\sigma_r(t) > \langle\psi(t)|\mathrm{p}(r)|\psi(t)\rangle\,\hbar/(2m) = [\hbar/(2m)]\,p(r, t). \qquad (103)$$

This lower-bound is thus proportional to local probability density $p(r, t) > 0$.

Consequently, in the quantum (wavefunction) mapping to the state probability and current distributions, $\psi(r, t) \rightarrow [p(r, t), j(r, t)]$, the overall quantum uncertainty cannot be completely eliminated by a *single* type of experiment, due to the known determinacy limitations imposed by the Heisenberg principle. However, these two sources of the information (removed uncertainty) are in principle accessible experimentally by performing *separate* position and momentum probes of the specified quantum state $\psi(r, t)$.

Therefore, accounting for the position and current indeterminacies requires carrying out the incompatible experiments for determining the particle position and its momentum. Although a simultaneous elimination of these uncertainties is impossible, the independent position and current (momentum) experiments can provide measures of the entropy or information contained in such incompatible distributions. Eliminating the (static) uncertainty in the spatial probability distribution, by performing the *position* probe, still leaves the (dynamic) *current* uncertainty, which can be accounted for in the overall (resultant) descriptor only by carrying out an additional *momentum* experiment.

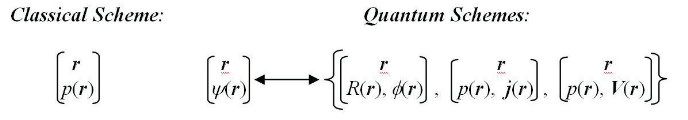

Figure 5: Classical (probability) and quantum (wavefunction) information schemes in molecular quantum mechanics. The quantum mapping $\{r \rightarrow \psi(r)\}$ implies both the classical $\{r \rightarrow p(r)\}$ and nonclassical attributions $\{r \rightarrow [\varphi(r), j(r) \text{ or } V(r)]\}$.

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Thus, a single-type experiment, e.g., that for determining particle's location, which underlies the position representation of the state wavefunction $\psi(r, t)$, accounts for the position entropy $S[p]$ or information $I[p]$, leaving the phase uncertainty $S[\varphi]$ and information $I[\varphi]$ unaccounted for. The nonclassical entropy contribution, inaccessible in the position-only experiments, marks the difference between the resultant and classical information functionals. It is reflected by the (negative) nonclassical contribution $S[\varphi] < 0$ in the state overall scalar entropy [Eq. (78)] and the corresponding (imaginary) component of the vector measure [Eq. (79)].

In the position-representation of QM the nonclassical *uncertainty* thus effectively lowers the *information* received from the localization-only experiment. The removable uncertainty in $\psi(r)$ is then less than its classical content $S[\rho]$ or $M[\rho] = I[\rho]$. In other words, the nonvanishing current pattern introduces an extra *determinacy* in the overall electronic structure, which diminishes its resultant uncertainty (*indeterminacy*) descriptors. These differences can be thus considered as the associated amounts of information contained in the phase/current/velocity distributions, which require the momentum (dynamical) experimental setup.

Continuity relations

It is of crucial importance in continuity laws of QM to distinguish between the reference frame moving with the particle (Lagrangian frame) and the reference frame fixed to the prescribed coordinate system (Eulerian frame). The total derivative d/dt is the time change appearing to an observer who moves with the probability flux, while the partial derivative ∂/t is the local time rate of change observed from a fixed point in the Eulerian reference frame. These derivatives are related to each other by the chain-rule transformation,

$$d/dt = \partial/\partial t + V(r, t)\cdot\nabla, \tag{104}$$

where the velocity-dependent part $V(r, t)\cdot\nabla$ generates the "convection" term.

In Schrödinger's dynamical picture the state vector $|\psi(t)\rangle$ introduces an *explicit* time-dependence of the system wavefunction, while the dynamics of the basis vector $|r(t)\rangle$ of the position representation is the source of an additional, *implicit* time-dependence of electronic wavefunction $\psi(r, t) = \psi[r(t), t]$, due to the moving reference (monitoring) point. This separation applies to wavefunctions, their components, and expectation values of physical observables. In Table 1 we have summarized the dynamic equations for the wavefunction modulus and phase components together with the continuity relations for the state probability, current and information densities, which directly follow from the wavefunction dynamics of SE.

It directly follows from SE that the probability field is sourceless:

$$\partial p(r, t)/\partial t = 2R(r, t)\,[\partial R(r, t)/\partial t] = -\nabla\cdot j(r, t) = -V(r, t)\cdot\nabla p(r, t) \text{ or}$$

$$\sigma_p(r, t) \equiv dp(r, t)/dt = \partial p(r, t)/\partial t + \nabla\cdot j(r, t) = \partial\rho(r, t)/\partial t + \nabla p(r, t)\cdot V(r, t) = 0. \tag{105}$$

Indeed, separating the explicit time dependence of $p(r, t)$ from the implicit dependence originating from $r(t)$, $p(r, t) = p[r(t), t]$, gives:

$$\sigma_p(r, t) = \partial p[r(t), t]/\partial t + (dr/dt)\cdot\partial p(r, t)/\partial r$$

$$= \partial p(r, t)/\partial t + V(r, t)\cdot\nabla p(r, t)$$

$$= \partial p(r, t)/\partial t + \nabla\cdot j(r, t). \tag{106}$$

Above, the total *time*-derivative $dp(r, t)/dt$ determines the vanishing local probability "source": $\sigma_p(r, t) = 0$. It measures the time rate of change in an infinitesimal volume element of probability fluid *moving* with velocity $V(r, t) = dr(t)/dt$, while the partial derivative $\partial p[r(t), t]/\partial t$ refers to volume element around the *fixed* point in space. The divergence of probability flux in the preceding equation,

$$\nabla\cdot j(r, t) = \nabla p(r, t)\cdot V(r, t) + p(r, t)\nabla\cdot V(r, t) = \nabla p(r, t)\cdot V(r, t), \tag{107}$$

thus implies the vanishing divergence of the velocity field $V(r, t)$, related to the phase Laplacian $\nabla^2\varphi(r, t) = \Delta\varphi(r, t)$,

$$\nabla\cdot V(r, t) = (\hbar/m)\,\Delta\varphi(r, t) = 0 \text{ or } \Delta\varphi(r, t) = 0. \tag{108}$$

As in fluid dynamics, in these transport equations the operators $(V\cdot)$ and $\nabla^2 = \Delta$ represent the "convection" and "diffusion", respectively. Thus, the local evolution of the particle probability is governed by the density "convection" [Eq. (105)], while the preceding equation implies the vanishing "diffusion" of the phase distribution. It also follows from the expression for a local information source in the table, that it is determined by the "convection" term of the phase source.

When expressed in terms of the modulus and phase components of the state wavefunction SE reads:

$$\mathrm{i}\hbar\,[\partial\psi(r, t)/\partial t] = \mathrm{i}\hbar\,\{[\partial R(r, t)/\partial t] + \mathrm{i}R(r, t)\,[\partial\varphi(r, t)/\partial t]\}\exp[\mathrm{i}\varphi(r, t)] = \mathrm{H}(r)\psi(r, t)$$

$$= [-\hbar^2(2m)^{-1}\{\Delta R(r, t) + 2\mathrm{i}R(r, t)\,\nabla\varphi\,(r, t)\;\; R(r, t)\,[\varphi(r, t)]^2\}$$

$$+ v(r)\,R(r, t)]\exp[\mathrm{i}\varphi(r, t)], \tag{109}$$

where we have used Eq. (108). Dividing both sides of this equation by $\hbar R(r, t)$ and multiplying by $\exp[-\mathrm{i}\varphi(r, t)]$ gives the following complex relation:

$$\mathrm{i}\,[\partial \ln R(r, t)/\partial t] - \partial\varphi(r, t)/\partial t = -[\hbar/(2m)]\{R(r, t)^{-1}\Delta R(r, t) + 2\mathrm{i}[\nabla \ln R(r, t)]\cdot\nabla\varphi(r, t) - [\varphi(r, t)]^2\} + v(r)/\hbar. \tag{110}$$

Comparing the *imaginary* parts of the preceding equation generates the dynamic equation for the time evolution of the modulus part of electronic state,

$$\partial \ln R(r, t)/\partial t = -\,[(\hbar/m)\,\nabla\varphi(r, t)]\cdot\nabla \ln R(r, t) = -\,V(r, t)\,\nabla \ln R(r, t), \tag{111}$$

which can be directly transformed into the probability-continuity relation

$$\partial p(r, t)/\partial t = -\nabla\cdot j(r, t) \text{ or } \sigma_p(r, t) = dp(r, t)/dt = 0. \tag{112}$$

Equating the *real* parts of Eq. (110) similarly determines the phase-dynamics

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$$\partial\varphi(r,t)/\partial t = [\hbar/(2m)]\,[R(r,t)^{-1}\Delta R(r,t) - [\varphi(r,t)]^2] - v(r)/\hbar. \qquad (113)$$

The preceding equation ultimately determines the production term $\sigma_\varphi(r,t) = d\varphi(r,t)/dt$ in the phase continuity relation

$$\partial\varphi(r,t)/\partial t = -\cdot J(r,t) + \sigma_\varphi(r,t), \qquad (114)$$

since the effective velocity $V(r,t)$ of the *probability*-current $j(r,t) = p(r,t)\,V(r,t)$ also determines the *phase*-flux and its divergence:

$J(r,t) = \varphi(r,t)\,V(r,t)$ and

$$\nabla\cdot J(r,t) = V(r,t)\cdot\nabla\varphi(r,t) = (\hbar/m)\,[\nabla\varphi(r,t)]^2. \qquad (115)$$

The latter represents the convection term in the phase-continuity equation. This complementary flow descriptor ultimately generates a finite *phase*-source:

$$\sigma_\varphi(r,t) \equiv d\varphi(r,t)/dt = \partial\varphi(r,t)/\partial t + V(r,t)\cdot\nabla\varphi(r,t) \neq 0. \qquad (116)$$

Hence, using Eq. (113) finally gives:

$$\sigma_\varphi(r,t) = [\hbar/(2m)]\{R(r,t)^{-1}\Delta R(r,t) + [\nabla\varphi(r,t)]^2\} - v(r)/\hbar. \qquad (117)$$

This phase production is seen to group the probability-diffusion and phase-convection terms supplemented by the external potential contribution.

Finally, by comparing Eqs. (71) and (72) with Eqs. (111) and (113), respectively, one arrives at the following expressions for the real and imaginary parts of the local wave-number of Eq. (69) in terms of additive components of the wavefunction logarithm [Eq. (57)]:

$$c(r,t) = -\partial\varphi(r,t)/\partial t = -[\hbar/(2m)]\,\{R(r,t)^{-1}\Delta R(r,t) - [\nabla\varphi(r,t)]^2\} + v(r)/\hbar$$

$$= -[\hbar/(2m)]\,\{\Delta\ln R(r,t) + [\nabla\ln R(r,t)]^2 - [\nabla\varphi(r,t)]^2\} + v(r)/\hbar \qquad (118)$$

and

$$b(r,t) = \partial\ln R(r,t)/\partial t = -(\hbar/m)\,\nabla\varphi(r,t)\cdot\nabla\ln R(r,t) = -V(r,t)\cdot\nabla\ln R(r,t). \qquad (119)$$

It also follows from dynamic equations for the wavefunction components that the phase-gradient enters the time evolutions of both the modulus and phase components of the wavefunction. Thus the presence of the local phase [Eq. (67)] in the nonstationary quantum state affects both the electron probability and current evolutions in molecular systems.

To summarize, the effective velocity of the probability-current also determines the phase-flux in molecules. The source (net production) of the classical *probability*-variable of electronic states identically vanishes, while that of their nonclassical, *phase*-part remains finite. In overall descriptors of the state information or entropy contents they ultimately generate finite production terms due to the phase-contributions in resultant IT measures [4,9,83,88,91].

The nonclassical information $I[\varphi]$ generates a nonvanishing (integral) source of the average resultant gradient information $I[\psi]$:

$$\sigma_I = dI[\varphi]/dt \equiv \int p(r,t)\sigma_I(r,t)\,dr = (8m/\hbar)\int j(r,t)\cdot\nabla\sigma_\varphi(r,t)\,dr. \qquad (120)$$

Its density $\sigma_I(r,t)$ is seen to be determined by the product of local probability “flux” $j(r,t)$ and the „affinity“ factor proportional to gradient of phase source of Eq. (117),

$$\sigma_\varphi(r,t) = d\varphi(r,t)/dt = \partial\varphi(r,t)/\partial t + \nabla\cdot J(r,t) = \partial\varphi(r,t)/\partial t + V(r,t)\cdot\nabla\varphi(r,t)$$

$$= [\hbar/(2m)]\,\{R(r,t)^{-1}\Delta R(r,t) + [\nabla\varphi(r,t)]^2\} - v(r)/\hbar \neq 0, \qquad (121)$$

following from SE for wavefunction components (Table 1).

Probability acceleration and current sources

Of interest also is the local production of probability current $j(r,t)$,

$$\sigma_j(r,t) \equiv dj(r,t)/dt = \sigma_p(r,t)\,V(r,t) + p(r,t)\,[dV(r,t)/dt] = p(r,t)\,\sigma_V(r,t)$$

$$= (\hbar/m)\,p(r,t)\,d/dt[\nabla\varphi(r,t)] = (\hbar/m)\,p(r,t)\nabla[d\varphi(r,t)/dt]$$

$$= (\hbar/m)\,p(r,t)\nabla\sigma_\varphi(r,t). \qquad (122)$$

Hence, using Eq. (121) gives:

$$\sigma_j(r,t) = [\hbar^2/(2m^2)]\,[R(r,t)\,\nabla^3 R(r,t) - \Delta R(r,t)\,\nabla R(r,t)] - [\rho(r,t)/m]\,\nabla v(r). \qquad (123)$$

The total time-derivative of $V(r,t)$ provides a natural measure of the local “acceleration” of probability fluid [69]:

$$a(r,t) \equiv dV(r,t)/dt \equiv \sigma_V(r,t) = (\hbar/m)\ d/dt\,[\nabla\varphi(r,t)] = (\hbar/m)\,\nabla\sigma_\varphi(r,t), \qquad (124)$$

since differentiations with respect to different variables “r” and “t” commute. This descriptor thus reflects the gradient of the phase-source [see also Eq. (122)]. It also generates the associated local probability “force”,

$$F(r,t) = m\,a(r,t) \equiv -\nabla W(r,t), \qquad (125)$$

the negative gradient of the underlying probability “potential”

$$W(r,t) = -\hbar\sigma_\varphi(r,t) + C(t). \qquad (126)$$

Therefore, the *phase*-source also reflects the *probability potential*, which generates forces acting on the electron distribution in molecular systems. In Table 1 we have summarized the dynamic equations for the wavefunction modulus and phase components, as well as continuity relations of the state probability, current and information densities, which directly follow from the molecular SE.

The phase source of Eq. (121) generates the following probability “acceleration”:

$$a(r,t) = (\hbar/m)\,\nabla\{[\hbar/(2m)]\,R(r,t)^{-1}\Delta R(r,t) - v(r)/\hbar\}$$

$$= [\hbar^2/(2m^2)]\,R(r,t)^{-1}\{\nabla^3 R(r,t) - [\nabla\ln R(r,t)]\,\Delta R(r,t)\} - \nabla v(r)/m. \qquad (127)$$

A reference to Eq. (126) gives the corresponding probability potential:

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$$W(r,t) = -[\hbar^2/(2m)]\{R(r,t)^{-1}\Delta R(r,t) + [\nabla\varphi(r,t)]^2\} + v(r). \qquad (128)$$

As an illustration let us again consider the stationary state of Eq. (61), corresponding to the sharply specified energy $E_{st.}$ determining the time-dependent phase $\varphi_{st.}(t) = -\omega_{st.}t$, and exhibiting the time-independent probability distribution $p_{st.}(r)$. It satisfies the stationary SE for the time-independent probability amplitude $R_{st.}(r)$,

$$-[\hbar^2/(2m)]\, R_{st.}(r)^{-1}\Delta R_{st.}(r) = E_{st.} - v(r). \qquad (129)$$

thus generating a constant phase source $\sigma_{\varphi}^{st.}(r) = -\omega_{st.}$ and equalized probability potential $W_{st.}(r) = E_{st.}$ reflecting the state local energy:

$$R_{st.}(r)^{-1}\mathrm{H}(r)\,R_{st.}(r) = E_{st.}. \qquad (130)$$

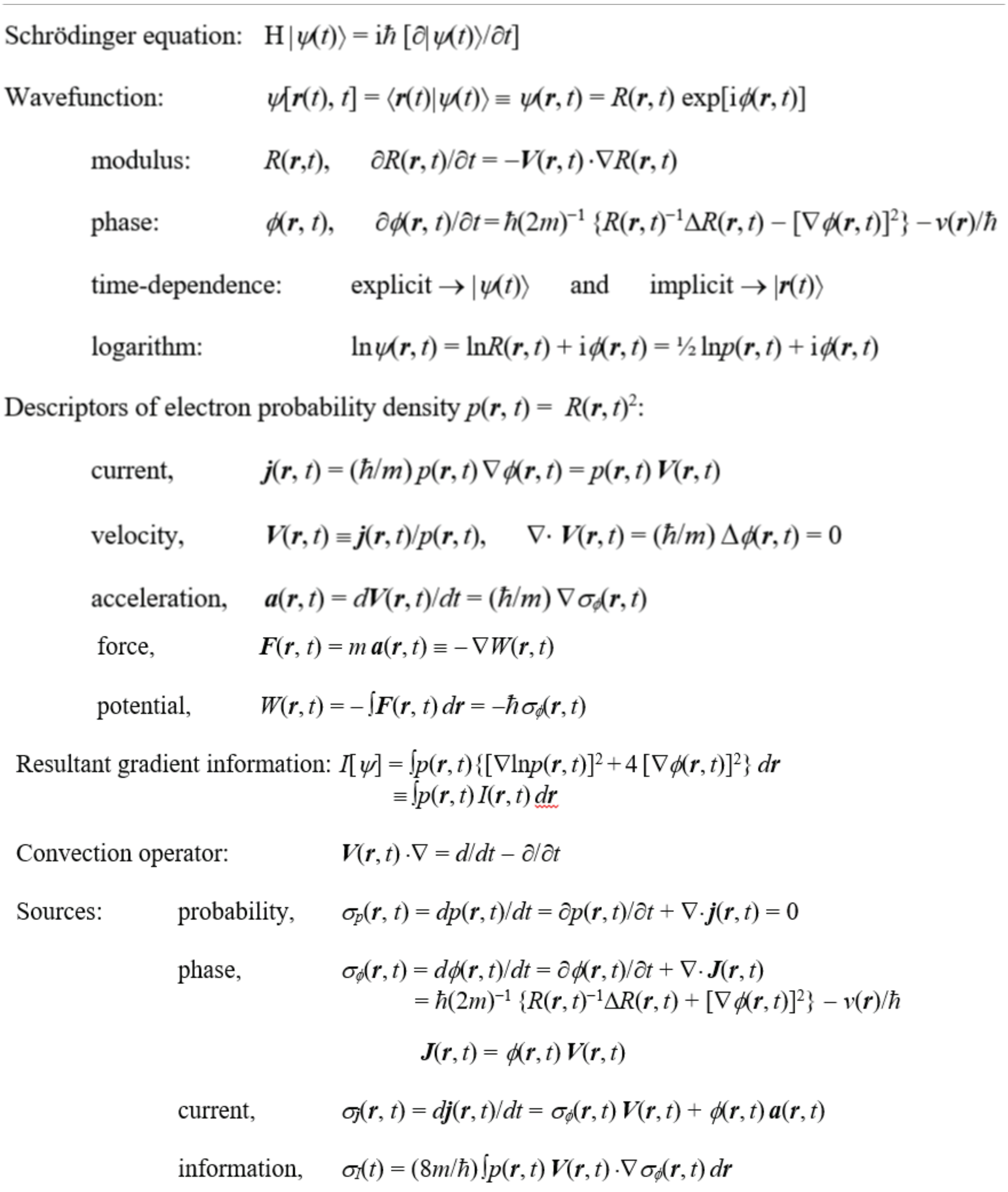
Therefore, the stationary probability distribution is indeed characterized by the vanishing acceleration and force descriptors:

$$F_{st.}(r,t) = a_{st.}(r,t) = 0. \qquad (131)$$

This confirms the equilibrium character of $p_{st.}(r)$, since the vanishing probability force does not create perturbations for a change in this stationary distribution.

Due to a common velocity component in the current density for the

Table 1: Summary of wavefunction components of the quantum state $|\psi(t)\rangle$ of an electron, their dynamics, physical descriptors and local sources.



Schrödinger equation: $\mathrm{H}\,|\psi(t)\rangle = i\hbar\,[\partial|\psi(t)\rangle/\partial t]$

Wavefunction: $\psi[\boldsymbol{r}(t), t] = \langle \boldsymbol{r}(t)|\psi(t)\rangle \equiv \psi(\boldsymbol{r}, t) = R(\boldsymbol{r}, t)\exp[i\phi(\boldsymbol{r}, t)]$

modulus: $R(\boldsymbol{r},t)$, $\quad \partial R(\boldsymbol{r}, t)/\partial t = -\boldsymbol{V}(\boldsymbol{r}, t)\cdot\nabla R(\boldsymbol{r}, t)$

phase: $\phi(\boldsymbol{r}, t)$, $\quad \partial\phi(\boldsymbol{r}, t)/\partial t = \hbar(2m)^{-1}\{R(\boldsymbol{r}, t)^{-1}\Delta R(\boldsymbol{r}, t) - [\nabla\phi(\boldsymbol{r}, t)]^2\} - v(\boldsymbol{r})/\hbar$

time-dependence: explicit $\to |\psi(t)\rangle$ and implicit $\to |\boldsymbol{r}(t)\rangle$

logarithm: $\ln\psi(\boldsymbol{r}, t) = \ln R(\boldsymbol{r}, t) + i\phi(\boldsymbol{r}, t) = \tfrac{1}{2}\ln p(\boldsymbol{r}, t) + i\phi(\boldsymbol{r}, t)$

Descriptors of electron probability density $p(\boldsymbol{r}, t) = R(\boldsymbol{r}, t)^2$:

current, $\quad \boldsymbol{j}(\boldsymbol{r}, t) = (\hbar/m)\,p(\boldsymbol{r}, t)\,\nabla\phi(\boldsymbol{r}, t) = p(\boldsymbol{r}, t)\,\boldsymbol{V}(\boldsymbol{r}, t)$

velocity, $\quad \boldsymbol{V}(\boldsymbol{r}, t) \equiv \boldsymbol{j}(\boldsymbol{r}, t)/p(\boldsymbol{r}, t)$, $\quad \nabla\cdot\boldsymbol{V}(\boldsymbol{r}, t) = (\hbar/m)\,\Delta\phi(\boldsymbol{r}, t) = 0$

acceleration, $\quad \boldsymbol{a}(\boldsymbol{r}, t) = d\boldsymbol{V}(\boldsymbol{r}, t)/dt = (\hbar/m)\,\nabla\sigma_{\phi}(\boldsymbol{r}, t)$

force, $\quad \boldsymbol{F}(\boldsymbol{r}, t) = m\,\boldsymbol{a}(\boldsymbol{r}, t) \equiv -\nabla W(\boldsymbol{r}, t)$

potential, $\quad W(\boldsymbol{r}, t) = -\int \boldsymbol{F}(\boldsymbol{r}, t)\,d\boldsymbol{r} = -\hbar\,\sigma_{\phi}(\boldsymbol{r}, t)$

Resultant gradient information: $I[\psi] = \int p(\boldsymbol{r}, t)\{[\nabla\ln p(\boldsymbol{r}, t)]^2 + 4\,[\nabla\phi(\boldsymbol{r}, t)]^2\}\,d\boldsymbol{r}$
$\equiv \int p(\boldsymbol{r}, t)\,I(\boldsymbol{r}, t)\,d\boldsymbol{r}$

Convection operator: $\boldsymbol{V}(\boldsymbol{r}, t)\cdot\nabla = d/dt - \partial/\partial t$

Sources: probability, $\quad \sigma_p(\boldsymbol{r}, t) = dp(\boldsymbol{r}, t)/dt = \partial p(\boldsymbol{r}, t)/\partial t + \nabla\cdot\boldsymbol{j}(\boldsymbol{r}, t) = 0$

phase, $\quad \sigma_{\phi}(\boldsymbol{r}, t) = d\phi(\boldsymbol{r}, t)/dt = \partial\phi(\boldsymbol{r}, t)/\partial t + \nabla\cdot\boldsymbol{J}(\boldsymbol{r}, t)$
$= \hbar(2m)^{-1}\{R(\boldsymbol{r}, t)^{-1}\Delta R(\boldsymbol{r}, t) + [\nabla\phi(\boldsymbol{r}, t)]^2\} - v(\boldsymbol{r})/\hbar$

$\boldsymbol{J}(\boldsymbol{r}, t) = \phi(\boldsymbol{r}, t)\,\boldsymbol{V}(\boldsymbol{r}, t)$

current, $\quad \sigma_J(\boldsymbol{r}, t) = d\boldsymbol{j}(\boldsymbol{r}, t)/dt = \sigma_{\phi}(\boldsymbol{r}, t)\,\boldsymbol{V}(\boldsymbol{r}, t) + \phi(\boldsymbol{r}, t)\,\boldsymbol{a}(\boldsymbol{r}, t)$

information, $\quad \sigma_I(t) = (8m/\hbar)\int p(\boldsymbol{r}, t)\,\boldsymbol{V}(\boldsymbol{r}, t)\cdot\nabla\sigma_{\phi}(\boldsymbol{r}, t)\,d\boldsymbol{r}$

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distribution $f(r,t)$ of a general (scalar) physical or information property f, $J_f(r, t) = f(r, t)\, V(r, t)$, the probability acceleration also enters into expressions for local sources of such property currents [69]:

$$\sigma_J^{\,f}(r,t) \equiv dJ_f(r,t)/dt = \sigma_f(r,t)\, V(r,t) + f(r,t)\, a(r,t). \qquad (132)$$

For example, this probability acceleration determines local sources of probability- and phase-currents:

$$\sigma_J^{\,p}(r,t) = dj(r,t)/dt = p(r,t)\, a(r,t) = \sigma_j(r,t)\,, \qquad (133)$$

$$\sigma_J^{\,\varphi}(r,t) = dJ(r,t)/dt = \sigma_\varphi(r,t)\, V(r,t) + \varphi(r,t)\, a(r,t), \qquad (134)$$

where we have recognized the vanishing local *probability*-production, $\sigma_p(r,t) = 0$, and a finite *phase*-source: $\sigma_\varphi(r,t) \neq 0$.

The net production of the resultant measure of the state gradient information has been also shown to have a purely nonclassical origin. Its local density per electron also involves the probability acceleration distribution:

$$\sigma_I(r,t) = dI(r,t)/dt = \partial I(r,t)/\partial t + \nabla \cdot J_I(r,t)$$

$$= 8\nabla\Phi(r,t)\cdot\nabla\sigma_\Phi(r,t) = (8m/\hbar)\,\nabla\Phi(r,t)\cdot a(r,t), \qquad (135)$$

where resultant-information current $\boldsymbol{J}_I(r,t) = I(\boldsymbol{r},t)\boldsymbol{V}(\boldsymbol{r},t)$ determines its divergence:

$$\nabla\cdot\boldsymbol{J}_I(\boldsymbol{r},t) = (\hbar/m)\,\nabla I(r,t)\cdot\nabla\Phi(\boldsymbol{r},t). \qquad (136)$$

Conclusion

The classical and nonclassical information contributions can be regarded as reflecting the complementary structures of “being” and “becoming” [78] in molecular electronic states. The electron density alone reflects only the “static”, (“photographic”) structure of “being”, missing the “dynamic” structure of “becoming” contained in the state (“hologramic”) distributions of phase or its gradient generating the probability velocity. Both these manifestations of the electronic “organization” in molecular states ultimately contribute to the overall “hologramic” pattern of the structural entropy/information content of generally complex electronic wavefunctions. In quantum IT treatment the classical terms probe the entropic content of the incoherent (disentangled) local electronic “events”, while their nonclassical supplements provide the information complement due to coherence (entanglement) of such elementary electronic events. The nonclassical, phase/current contribution of the combined IT measure allows one to distinguish the information content of states generating the same electron density but differing in their probability velocity distributions.

Entropic theories of molecular electronic structure thus call for the resultant generalization of classical (probability) measures of the information/entropy content in molecular systems. They combine contributions due to the wavefunction modulus and phase components in a holistic IT treatment of the position representation. This constitutes an alternative approach to classical exploration of the *separate* probability distributions in the complementary position and momentum spaces, e.g., [92-94]. The resultant IT concepts unite the classical (probability) and nonclassical (current) contributions in a *single* representation, thus offering tools for examining the interplay between the molecular structures of “being” and “becoming”. The association of the resultant gradient information with the (dimensionless) electronic kinetic-energy additionally allows one to use the molecular virial theorem [95] in general reactivity considerations, e.g., [9,85,86]. The information distinction between the bonded (entangled) and nonbonded (disentangled) states of molecular subsystems, e.g., substrates in reaction complex, also calls for such a generalized IT description [83,96-98]. The classical terms probe the incoherent (disentangled) local “events”, while their nonclassical supplements explore the information supplement due to their mutual coherence (entanglement) in the “hologramic” electronic structure.

In the present analysis we have summarized the relevant dynamical equations and continuity relations for the basic modulus (probability) and phase (current) degrees-of-freedom of electronic states, and examined their contributions to the resultant entropy/information descriptors. The local-energy interpretation of time-evolutions of the wavefunction modulus and phase components has also been given. We have also argued, using the intuitive relation between the “uncertainty”-removed and the “information”-gained in an experiment, that the classical and nonclassical information contributions are not accessible in the *simultaneous* position and current (momentum) experiments. Nonetheless, they are available from *separate* position and momentum probes, which require the incompatible experimental setups.

(Appendix A,B)

References

1. Nalewajski RF (2006) Information Theory of Molecular Systems. Elsevier, Amsterdam.
2. Nalewajski RF (2010) Information Origins of the Chemical Bond. Nova Science Publishers, New York.
3. Nalewajski RF (2012) Perspectives in Electronic Structure Theory. Springer, Heidelberg. **Link:** http://bit.ly/3b9CRaE
4. Nalewajski RF (2016) Quantum Information Theory of Molecular States. Nova Science Publishers, New York.
5. Davydov AS (1965) Quantum Mechanics. Pergamon Press, Oxford.
6. Cohen-Tannoudji C, Diu B, Laloë F (1977) Quantum Mechanics. Wiley, New York.
7. Nalewajski RF (2020) Interacting subsystems and their molecular ensembles. Acad J Chem 5: 25-30. **Link:** http://bit.ly/3s0mkvs
8. Nalewajski RF (2020) Information-theoretic descriptors of molecular states and electronic communications between reactants, Matta CF (ed.). Entropy 22: 749-769. **Link:** https://bit.ly/3rUAnCO
9. Nalewajski RF (2019) Understanding electronic structure and chemical reactivity: quantum-information perspective. In The Application of Quantum Mechanics to the Reactivity of Molecules, Sousa S (ed). Appl Sci 9: 1262-1292. **Link:** https://bit.ly/358KxGs
10. Nalewajski RF (2020) Phase equalization, charge transfer, information flows and electron communications in donor-acceptor systems. In The Application of Quantum Mechanics to the Reactivity of Molecules, Sousa S (ed). Appl Sci 10: 3615-3646. **Link:** https://bit.ly/3nfounD

Citation: Nalewajski RF (2021) Equalization principles in open subsystems, origins of information descriptors and state-continuity relations. Open Journal of Chemistry 7(1): 004-021. DOI: https://dx.doi.org/10.17352/ojc.000023

11. Hohenberg P, Kohn W (1964) Inhomogeneous electron gas. Phys Rev 136B: 864-971. **Link:** https://bit.ly/38e2Yet

12. Kohn W, Sham LJ (1965) Self-consistent equations including exchange and correlation effects. Phys Rev 140A: 133-1138. **Link:** https://bit.ly/3omRvze

13. Levy M (1979) Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-representability problem. Proc Natl Acad Sci USA 76: 6062-6065. **Link:** https://bit.ly/3b8ycWv

14. Parr RG, Yang W (1989) Density-Functional Theory of Atoms and Molecules. Oxford University Press, New York. **Link:** http://bit.ly/35g4fQt

15. Dreizler RM, Gross EKU (1990) Density Functional Theory: an Approach to the Quantum Many-Body Problem. Springer, Berlin. **Link:** http://bit.ly/3olj5N3

16. Nalewajski RF (ed) (1996) Density Functional Theory I-IV. Topics in Current Chemistry 180-183. **Link:** http://bit.ly/3s0CBk7

17. Fisher RA (1925) Theory of statistical estimation. Proc Cambridge Phil Soc 22: 700-725. **Link:** http://bit.ly/35v4NlR

18. Frieden BR (2004) Physics from the Fisher Information – a Unification. Cambridge University Press, Cambridge.

19. Shannon CE (1948) The mathematical theory of communication. Bell System Tech J 7: 379-493. **Link:** https://bit.ly/2MtUily

20. Shannon CE, Weaver W (1949) The Mathematical Theory of Communication. University of Illinois, Urbana.

21. Kullback S, Leibler RA (1951) On information and sufficiency. Ann Math Stat 22: 79-86. **Link:** https://bit.ly/3pROtmH

22. Kullback S (1959) Information Theory and Statistics. Wiley, New York.

23. Abramson N (1963) Information Theory and Coding. McGraw-Hill, New York. **Link:** http://bit.ly/2L92m13

24. Pfeifer PE (1978) Concepts of Probability Theory. Dover, New York. **Link:** http://bit.ly/3hPlXj0

25. Nalewajski RF, Parr RG (2000) Information theory, atoms-in-molecules and molecular similarity. Proc Natl Acad Sci USA 97: 8879-8882. **Link:** http://bit.ly/35gnM38

26. Nalewajski RF, Broniatowska E (2003) Information distance approach to Hammond Postulate. Chem Phys Lett 376: 33-39. **Link:** http://bit.ly/2LoeZVQ

27. Nalewajski RF, Parr RG (2001) Information-theoretic thermodynamics of molecules and their Hirshfeld fragments. J Phys Chem A 105: 7391-7400. **Link:** https://bit.ly/398Xgda

28. Nalewajski RF (2002) Hirshfeld analysis of molecular densities: subsystem probabilities and charge sensitivities. Phys Chem Chem Phys 4: 1710-1721. **Link:** http://rsc.li/2Lttzvu

29. Nalewajski RF, Broniatowska E (2003) Entropy displacement analysis of electron distributions in molecules and their Hirshfeld atoms. J Phys Chem A 107: 6270-6280. **Link:** https://bit.ly/3pSzQjc

30. Parr RG, Ayers PW, Nalewajski RF (2005) What is an atom in a molecule? J Phys Chem A 109: 3957-3959. **Link:** https://bit.ly/2XdJPDj

31. Nalewajski RF, Broniatowska E (2007) Atoms-in-Molecules from the stockholder partition of molecular two-electron distribution. Theoret Chem Acc 117: 7-27. **Link:** https://bit.ly/3pXKLrT

32. Heidar-Zadeh F, Ayers PW, Verstraelen T, Vinogradov I, Vöhringer-Martinez E, et al. (2018) Information-theoretic approaches to Atoms-in-Molecules: Hirshfeld family of partitioning schemes. J Phys Chem A 122: 4219-4245. **Link:** http://bit.ly/38joC14

33. Nalewajski RF, Świtka E, Michalak A (2002) Information distance analysis of molecular electron densities. Int J Quantum Chem 87: 198-213. **Link:** https://bit.ly/3pTVkME

34. Nalewajski RF (2008) Use of Fisher information in quantum chemistry. Int J Quantum Chem (Jankowski K issue) 108: 2230-2252. **Link:** https://bit.ly/3oiYyJd

35. Hirshfeld FL (1977) Bonded-atom fragments for describing molecular charge densities. Theoret Chim Acta (Berl) 44: 129-138. **Link:** https://bit.ly/38fJyGk

36. Nalewajski RF (2000) Entropic measures of bond multiplicity from the information theory. J Phys Chem A 104: 11940-11951. **Link:** https://bit.ly/38fyiK6

37. Nalewajski RF (2004) Entropy descriptors of the chemical bond in Information Theory: I. Basic concepts and relations. Mol Phys 102:531-546; II. Application to simple orbital models. Mol Phys 102: 547-566.

38. Nalewajski RF (2004) Entropic and difference bond multiplicities from the two-electron probabilities in orbital resolution. Chem Phys Lett 386: 265-271. **Link:** http://bit.ly/2L4vg2s

39. Nalewajski RF (2005) Reduced communication channels of molecular fragments and their entropy/information bond indices. Theoret Chem Acc 114: 4-18. **Link:** https://bit.ly/3rX30PV

40. Nalewajski RF (2005) Partial communication channels of molecular fragments and their entropy/information indices. Mol Phys 103: 451-470. **Link:** http://bit.ly/3hKtWh4

41. Nalewajski RF (2011) Entropy/information descriptors of the chemical bond revisited. J Math Chem 49: 2308-2329. **Link:** https://bit.ly/3bbVFGd

42. Nalewajski RF (2014) Quantum information descriptors and communications in molecules. J Math Chem 52: 1292-1323. **Link:** http://bit.ly/2JTI1wk

43. Nalewajski RF (2009) Multiple, localized and delocalized/conjugated bonds in the orbital-communication theory of molecular systems. Adv Quant Chem 56: 217-250. **Link:** http://bit.ly/3oezpiC

44. Nalewajski RF, Szczepanik D, Mrozek J (2011) Bond differentiation and orbital decoupling in the orbital communication theory of the chemical bond. Adv Quant Chem 61: 1-48. **Link:** http://bit.ly/2MxiCt3

45. Nalewajski RF, Szczepanik D, Mrozek J (2012) Basis set dependence of molecular information channels and their entropic bond descriptors. J Math Chem 50: 1437-1457. Link: https://bit.ly/3nm3sDI

46. Nalewajski RF (2017) Electron communications and chemical bonds. In Frontiers of Quantum Chemistry, Wójcik M, Nakatsuji H, Kirtman B, Ozaki Y (eds). Springer, Singapore 315-351. **Link:** http://bit.ly/3bagwcT

47. Nalewajski RF (2020) Information-theoretic concepts in theory of electronic structure and chemical reactivity. In Chemical Reactivity Theories: Principles and Approaches, Kaya S, Szentpály (Taylor and Francis, London).

48. Nalewajski RF (2011) Through-space and through-bridge components of chemical bonds. J Math Chem 49: 371-392. **Link:** https://bit.ly/396ekjX

49. Nalewajski RF (2011) Chemical bonds from through-bridge orbital communications in prototype molecular systems. J Math Chem 49: 546-561. **Link:** https://bit.ly/2MDv9eI

50. Nalewajski RF (2011) On interference of orbital communications in molecular systems. J Math Chem 49: 806-815. **Link:** https://bit.ly/3biUPaV

51. Nalewajski RF, Gurdek P (2011) On the implicit bond-dependency origins of bridge interactions. J Math Chem 49: 1226-1237. **Link:** https://bit.ly/2KXo1cN

52. Nalewajski RF (2012) Direct (through-space) and indirect (through-bridge) components of molecular bond multiplicities. Int J Quantum Chem 112: 2355-2370. **Link:** https://bit.ly/2XhOzrm

Citation: Nalewajski RF (2021) Equalization principles in open subsystems, origins of information descriptors and state-continuity relations. Open Journal of Chemistry 7(1): 004-021. DOI: https://dx.doi.org/10.17352/ojc.000023

53. Nalewajski RF, Gurdek P (2012) Bond-order and entropic probes of the chemical bonds. Struct Chem 23: 1383-1398. **Link:** https://bit.ly/3pL9sYq

54. Nalewajski RF, Köster AM, Escalante S (2005) Electron localization function as information measure. J Phys Chem A 109: 10038-10043. **Link:** https://bit.ly/38hZecc

55. Becke AD, Edgecombe KE (1990) A simple measure of electron localization in atomic and molecular systems. J Chem Phys 92: 5397-5403. **Link:** https://bit.ly/3neg2EZ

56. Silvi B, Savin A (1994) Classification of chemical bonds based on topological analysis of electron localization functions. Nature 371: 683-686. **Link:** https://go.nature.com/35haZ0C

57. Savin A, Nesper R, Wengert S, Fässler TF (1997) ELF: the electron localization function. Angew Chem Int Ed Engl 36: 1808-1832. **Link:** https://bit.ly/39473RZ

58. Nalewajski RF, de Silva P, Mrozek J (2010) Use of nonadditive Fisher information in probing the chemical bonds. J Mol Struct: THEOCHEM 954: 57-74. **Link:** https://bit.ly/3ovvWw4

59. Nalewajski RF, Korchowiec J, Michalak A (1996) Reactivity criteria in charge sensitivity analysis. In Density Functional Theory IV, Nalewajski RF (Ed). Topics in Current Chemistry 183: 25-141.

60. Nalewajski RF, Korchowiec J (1997) Charge Sensitivity Approach to Electronic Structure and Chemical Reactivity. World Scientific, Singapore 312. **Link:** https://bit.ly/3pTBwsu

61. Nalewajski RF (1994) Sensitivity analysis of charge transfer systems: in situ quantities, intersecting-state model and its implications. Int J Quantum Chem 49: 675-703. **Link:** https://bit.ly/3nkiqtS

62. Gyftopoulos EP, Hatsopoulos GN (1968) Quantum-thermodynamic definition of electronegativity. Proc Natl Acad Sci USA 60: 786-793. **Link:** https://bit.ly/2L5gKHM

63. Perdew JP, Parr RG, Levy M, Balduz JL (1982) Density functional theory for fractional particle number: derivative discontinuities of the energy. Phys Rev Lett 49: 1691-1694. **Link:** http://bit.ly/3hNwzyK

64. Mulliken RS (1934) A new electronegativity scale: together with data on valence states and on ionization potentials and electron affinities. J Chem Phys 2: 782-793. **Link:** http://bit.ly/398BmqD

65. Iczkowski RP, Margrave JL (1961) Electronegativity. J Am Chem Soc 83: 3547-3551. **Link:** https://bit.ly/3be8Mqq

66. Parr RG, Donnelly RA, Levy M, Palke WE (1978) Electronegativity: the density functional viewpoint. J Chem Phys 69: 4431-4439. **Link:** http://bit.ly/2L5h1ui

67. Parr RG, Pearson RG (1983) Absolute hardness: companion parameter to absolute electronegativity. J Am Chem Soc 105: 7512-7516. **Link:** https://bit.ly/2LkB47M

68. Parr RG, Yang W (1984) Density functional approach to the frontier-electron theory of chemical reactivity. J Am Chem Soc 106: 4049-4050. **Link:** https://bit.ly/2XfWqWw

69. Nalewajski RF (2020) Continuity relations, probability acceleration, current sources and internal communications in interacting fragments. Acad J Chem 5: 58-58. **Link:** https://bit.ly/3b7aWrU

70. Nalewajski RF (2020) Information-theoretic concepts in theory of electronic structure and chemical reactivity. In Chemical Reactivity Theories: Principles and Approaches, Kaya S, von Szentpály P. (eds.). Taylor & Francis, London, in press.

71. Nalewajski RF (2020) Phase modeling in donor-acceptor systems, continuity relations and resultant entropy/information descriptors. In Chemical Reactivity Theories: Principles and Approaches, Kaya S, von Szentpály P. (eds.). Taylor & Francis, London, in press.

72. Harriman JE (1980) Orthonormal orbitals for the representation of an arbitrary density. Phys Rev A 24: 680-682. **Link:** http://bit.ly/38fW9sU

73. Zumbach G, Maschke K (1983) New approach to the calculation of density functionals. Phys Rev A 28:544-554. **Link:** http://bit.ly/2Xd5D23

74. Macke W (1955) Zur wellermechanis chen behand lung von vielkoeper problemen. Ann Phys 17: 1-9.

75. Gilbert TL (1975) Hohenberg-Kohn theorem for nonlocal external potentials. Phys Rev B 12: 2111-2120. **Link:** http://bit.ly/2XhjdRM

76. Nalewajski RF (2019) Equidensity orbitals in resultant-information description of electronic states. In Chemical Concepts from Theory and Computation, Liu S (ed), Theoret Chem Acc 138: 108-123. **Link:** https://bit.ly/38ggRcc

77. Nalewajski RF (2019) Resultant information description of electronic states and chemical processes. J Phys Chem A (Geerlings P issue) 123: 9737–9752. **Link:** http://bit.ly/3pTTX0c

78. Prigogine I (1980) From Being to Becoming: Time and Complexity in the Physical Sciences. Freeman WH & Co, San Francisco. **Link:** https://bit.ly/35g3F5n

79. Nalewajski RF (2013) Exploring molecular equilibria using quantum information measures. Ann Phys (Leipzig) 525: 256-268. **Link:** https://bit.ly/3bkrnB0

80. Nalewajski RF (2014) On phase/current components of entropy/information descriptors of molecular states. Mol Phys 112: 2587-2601. **Link:** http://bit.ly/3bd9kg8

81. Nalewajski RF (2016) Complex entropy and resultant information measures. J Math Chem 54: 1777-1782. **Link:** https://bit.ly/2LkBVFw

82. Nalewajski RF (2017) Quantum information measures and their use in chemistry. Current Phys Chem 7: 94-117. **Link:** https://bit.ly/3nkTYZv

83. Nalewajski RF (2018) Information equilibria, subsystem entanglement and dynamics of the overall entropic descriptors of molecular electronic structure. J Mol Model (Chattaraj P issue) 24: 212-227. Link: http://bit.ly/3bb5XX0

84. Nalewajski RF (2019) On entropy/information description of reactivity phenomena. In Advances in Mathematics Research vol 26, Baswell AR (ed). Nova Science Publishers, New York 97-157.

85. Nalewajski RF (2019) Role of electronic kinetic energy (resultant gradient information) in chemical reactivity. J Mol Model (Latajka Z issue) 25: 259-278. **Link:** https://bit.ly/2XboyKy

86. Nalewajski RF (2019) Resultant information description of electronic states and chemical processes. J Phys Chem A 123: 45-60. **Link:** http://bit.ly/3pTTX0c

87. Nalewajski RF (2020) On classical and quantum entropy/information descriptors of molecular electronic states. In Research Methodologies and Practical Applications of Chemistry, Pogliani L, Haghi AK, Islam N (eds). Apple Academic Press/CRC Press, Palm Bay, in press.

88. Nalewajski RF (2020) Quantum Information Perspective on Chemical Reactivity. In Mathematics Applied to Engineering in Action: Advanced Theories, Methods, and Models, Islam N, Bir-Singh S, Ranjan P, Haghi AK (eds). Apple Academic Press, Palm Bay 1-40.

89. Callen HB (1962) Thermodynamics: an Introduction to the Physical Theories of Equilibrium Thermostatics and Irreversible Thermodynamics. Wiley, New York.

90. Khinchin AI (1957) Mathematical Foundations of Information Theory. Dover, New York.

91. Nalewajski RF (2020) Information-theoretic descriptors of molecular states and electronic communications between reactants. In Information Theoretic

Citation: Nalewajski RF (2021) Equalization principles in open subsystems, origins of information descriptors and state-continuity relations. Open Journal of Chemistry 7(1): 004-021. DOI: https://dx.doi.org/10.17352/ojc.000023

Approaches to Atoms and Molecules, Matta CF, (ed). Entropy 22: 749-769. **Link:** https://bit.ly/2MuBokQ

92. López-Rosa S (2010) Information Theoretic Measures of Atomic and Molecular Systems. PhD Thesis, University of Granada. **Link:** http://bit.ly/2MCkWiG

93. López-Rosa S, Esquivel RO, Angulo JC, Antolín J, Dehesa JS, et al. (2010) Fisher information study in position and momentum spaces for elementary chemical reactions. J Chem Theory Comput 6: 145-154. **Link:** http://bit.ly/3bd77l2

94. Esquivel RO, Liu S, Angulo JC, Dehesa JS, Antolín J, Molina-Espíritu M (2011) Fisher information and steric effect: study of internal rotation barrier in ethane. J Phys Chem A 115: 4406-4415.

95. Nalewajski RF (1980) Virial theorem implications for the minimum energy reaction paths. Chem Phys 50: 127-136. **Link:** http://bit.ly/3ohXZPO

96. Nalewajski RF (2016) On entangled states of molecular fragments. Trends in Phys Chem 16: 71-85.

97. Nalewajski RF (2019) Entropy continuity, electron diffusion and fragment entanglement in equilibrium states. In Advances in Mathematics Research vol 22, Baswell AR (ed). Nova Science Publishers, New York 1-42.

98. Lugt HJ (1983) Vortex Flow in Nature and Technology. Wiley, New York. **Link:** http://bit.ly/3b9CLzO

Citation: Nalewajski RF (2021) Equalization principles in open subsystems, origins of information descriptors and state-continuity relations. Open Journal of Chemistry 7(1): 004-021. DOI: https://dx.doi.org/10.17352/ojc.000023