Academic Journal of Chemistry
ISSN(e): 2519-7045, ISSN(p): 2521-0211
Vol. 5, Issue. 6, pp: 58-68, 2020
URL: https://arpgweb.com/journal/journal/20
DOI: https://doi.org/10.32861/ajc.56.58.68

Academic Research Publishing Group

Original Research **Open Access**

Continuity Relations, Probability Acceleration, Current Sources and Internal Communications in Interacting Fragments

Roman F. Nalewajski
Department of Theoretical Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Cracow, Poland
Email: nalewajs@chemia.uj.edu.pl

Article History
Received: May 9, 2020
Revised: June 16, 2020
Accepted: June 18, 2020
Published: June 25, 2020

Abstract

Classical issues of local continuities and density partition in molecular quantum mechanics are reexamined. An effective velocity of the probability current is identified as the current-per-particle and its properties are explored. The local probability acceleration and the associated force concept are introduced. They are shown to identically vanish in the stationary electronic states. This acceleration measure also determines the associated productions of physical currents, e.g., the local source of the resultant content of electronic gradient information. The probability partitioning between reactants is revisited and illustrated using the stockholder division rule of Hirshfeld. A simple orbital model is used to describe the polarized (disentangled) and equilibrium (entangled) molecular fragments containing the distinguishable and indistinguishable groups of electrons, respectively, and their mixed quantum character is emphasized. The fragment density matrix is shown to determine the subsystem internal electron communications.

Keywords: Continuity relations; Current productions; Density partition; Fragment entanglement; Probability acceleration; Stockholder division.

1. Introduction

Several intuitive concepts of chemistry still require more rigorous definitions within the molecular quantum mechanics (QM). Indeed, the exact semantics of chemical bonds, the entangled quantum subsystems, atoms-in-molecules (AIM), reactants and molecular fragments in general still escapes an exact description, e.g., [1-4]. The interacting molecular pieces, fragments of both the polarized and equilibrium stages in reactive complexes, are described by the *mixed* quantum states, which require an ensemble description invoking the density operators and density matrices of embedded quantum subsystems [5-9]. The chemical concepts and principles escaping exact definitions in QM, e.g., AIM, and general reactivity rules can be alternatively approached using modern Density Functional Theory (DFT) [10-15] and Information Theory (IT) [16-23], e.g., [1-4, 24-33]. The former constitutes an alternative exact theory for determining the reaction energetics, while the latter can be regarded as a supplementary interpretative framework facilitating the chemical understanding of molecular structures and processes.

For example, IT provides a solid theoretical basis [1-4, 24-28] for the intuitive stockholder AIM of Hirshfeld [34]. The Orbital Communication Theory (OCT) of the chemical bond [1-4, 35-45] has facilitated an alternative IT interpretation of the bonding pattern in molecules and its covalent (communication noise) and ionic (information flow) composition. This approach has also identified the bridge chemical interactions between AIM [46-51], realized via the cascade propagations in molecular information systems, through the orbital intermediates. The nonadditive gradient information of Fisher [16, 17, 33] has been linked [52] to the Electron Localization Function [53-55] of DFT, and resulted in the contragradience (CG) probe for identifying and localizing chemical bonds [1-4, 56].

It is the main purpose of the present analysis to reexamine the continuity relations in QM, resulting from the fundamental Schrödinger equation (SE) for the dynamics of quantum electronic states. The corresponding equations for the modulus and phase components of molecular wavefunctions will be derived and interpreted as the associated continuity relations. The effective velocity of probability "fluid", measured by the probability-current per particle, will be used to define fluxes of physical properties. In such an approach the system electrons are thus acting as carriers of the property densities. The probability acceleration and force concepts will be related to the quantum phase production, which identically vanishes in the stationary quantum states. It will be shown that it also determines the quantum sources of the property currents, e.g., of the resultant gradient information related to the kinetic energy of electrons, which combines the classical (Fisher) and nonclassical (phase/current) contributions. The probability partitioning between reactants will be illustrated using the stockholder division rule of Hirshfeld. As an illustration the simple orbital model will be used to explore the probability densities in the polarized (disentangled) and equilibrium (entangled) molecular fragments containing the distinguishable and indistinguishable groups of electrons, respectively, and their mixed character in the pure quantum state of the whole reactive system will be emphasized.

2. Probability Velocity Descriptor

Due to Heisenberg's Uncertainty Principle the sharply specified particle *location* of the position-representation precludes the precise specification of electronic *momentum*. Therefore, only an *effective* measure of the latter, consistent with the probability-flux definition, is available in QM. In continuity considerations the quantum current-per-particle measure, which itself combines the incompatible position and momentum variables, appears as a natural choice for such an effective local "velocity" descriptor of the probability "fluid" [9, 57-63] (see also Appendix A). In this section we briefly reexamine the quantum justification of this concept and its applicability in local continuity considerations.

For reasons of simplicity let us examine the quantum state at time t, $|\psi(t)\rangle$, of a single electron: $N = 1$. It defines the complex wavefunction in the position representation,

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

where the real functions $R(\boldsymbol{r}, t)$ and $\phi(\boldsymbol{r}, t)$ denote its modulus and phase components, respectively. The square of the former determines particle probability distribution, the state expectation of the position projection $\mathrm{P}_{\boldsymbol{r}} = |\boldsymbol{r}\rangle\langle\boldsymbol{r}| \equiv \mathrm{p}(\boldsymbol{r})$, the quantum operator for the particle position probability density,

$$p(\boldsymbol{r}, t) = \langle\psi(t)|\boldsymbol{r}\rangle\langle\boldsymbol{r}|\psi(t)\rangle \equiv \langle\psi(t)|\mathrm{p}(\boldsymbol{r})|\psi(t)\rangle = \psi(\boldsymbol{r}, t)^{*}\psi(\boldsymbol{r}, t) = R(\boldsymbol{r}, t)^{2} = \langle\boldsymbol{r}|\psi(t)\rangle\langle\psi(t)|\boldsymbol{r}\rangle \equiv \langle\boldsymbol{r}|\mathrm{P}_{\psi}|\boldsymbol{r}\rangle, \tag{2}$$

while the gradient of the latter defines an effective "velocity" of the probability "fluid":

$$\boldsymbol{V}(\boldsymbol{r}, t) = \boldsymbol{j}(\boldsymbol{r}, t)/p(\boldsymbol{r}, t) = (\hbar/m)\, \nabla\{(2\mathrm{i})^{-1}\ln[\psi(\boldsymbol{r}, t)/\psi^{*}(\boldsymbol{r}, t)]\} = (\hbar/m)\, \nabla\phi(\boldsymbol{r}, t) \equiv d\boldsymbol{r}(t)/dt. \tag{3}$$

This probability velocity thus measures the density-per-electron of the density flux $\boldsymbol{j}(\boldsymbol{r}, t)$ (see also Appendix A). The latter reflects the state quantum expectation of the (Hermitian) current operator involving the symmetrized product of (noncommuting) operators of the particle probability density, $\mathrm{p}(\boldsymbol{r}) \equiv \mathrm{P}_{\boldsymbol{r}}$, and the local velocity operator in position representation, reflecting the particle momentum per unit mass, $\mathbf{V} = \mathbf{p}/m$,

$$\mathbf{j}(\boldsymbol{r}) = (2m)^{-1}[\mathrm{P}_{\boldsymbol{r}}\, \mathbf{p} + \mathbf{p}\, \mathrm{P}_{\boldsymbol{r}}] = 2^{-1}[\mathrm{p}(\boldsymbol{r})\, \mathbf{V} + \mathbf{V}\, \mathrm{p}(\boldsymbol{r})]. \tag{4}$$

The position representation of the velocity operator thus reads:

$$m^{-1}\langle\boldsymbol{r}|\mathbf{p}|\boldsymbol{r}'\rangle \equiv m^{-1}\mathbf{p}(\boldsymbol{r}, \boldsymbol{r}') = \langle\boldsymbol{r}|\mathbf{V}|\boldsymbol{r}'\rangle \equiv \mathbf{V}(\boldsymbol{r}, \boldsymbol{r}') = -\mathrm{i}\hbar\, m^{-1}\, \delta(\boldsymbol{r}' - \boldsymbol{r})\, \nabla_{\boldsymbol{r}} \equiv \delta(\boldsymbol{r}' - \boldsymbol{r})\, [\mathbf{p}(\boldsymbol{r})/m] \equiv \delta(\boldsymbol{r}' - \boldsymbol{r})\, \mathbf{V}(\boldsymbol{r}). \tag{5}$$

It gives the associated representations of actions of the momentum and velocity operators on state vectors:

$$\langle\boldsymbol{r}|\mathbf{p}|\psi(t)\rangle = -\mathrm{i}\hbar \int d\boldsymbol{r}'\langle\boldsymbol{r}|\mathbf{p}|\boldsymbol{r}'\rangle\langle\boldsymbol{r}'|\psi(t)\rangle = -\mathrm{i}\hbar \int d\boldsymbol{r}\, \delta(\boldsymbol{r}' - \boldsymbol{r})\, \nabla_{\boldsymbol{r}'}\, \psi(\boldsymbol{r}', t) = -\mathrm{i}\hbar\, \nabla_{\boldsymbol{r}}\, \psi(\boldsymbol{r}, t) \equiv \mathbf{p}(\boldsymbol{r})\, \psi(\boldsymbol{r}, t), \quad \text{and} \tag{6a}$$

$$\langle\boldsymbol{r}|\mathbf{V}|\psi(t)\rangle = -\mathrm{i}\hbar\, m^{-1}\int d\boldsymbol{r}'\langle\boldsymbol{r}|\mathbf{p}|\boldsymbol{r}'\rangle\langle\boldsymbol{r}'|\psi(t)\rangle = -\mathrm{i}\hbar\, m^{-1}\int d\boldsymbol{r}\, \boldsymbol{V}(\boldsymbol{r}, \boldsymbol{r}')\, \psi(\boldsymbol{r}', t) = -\mathrm{i}\hbar\, m^{-1}\, \nabla_{\boldsymbol{r}}\psi(\boldsymbol{r}, t) \equiv \mathbf{V}(\boldsymbol{r})\, \psi(\boldsymbol{r}, t). \tag{6b}$$

Therefore, $\mathbf{p}(\boldsymbol{r}) = -\mathrm{i}\hbar\nabla_{\boldsymbol{r}}$ and $\mathbf{V}(\boldsymbol{r}) = -(\mathrm{i}\hbar/m)\, \nabla_{\boldsymbol{r}}$ stand for the local momentum and velocity operators acting on the wavefunction $\psi(\boldsymbol{r}, t)$.

The expectation value of the current operator of Eq. (4) finally reads:

$$\boldsymbol{j}(\boldsymbol{r}, t) = \langle\psi(t)|\mathbf{j}(\boldsymbol{r})|\psi(t)\rangle = [\hbar/(2m\mathrm{i})]\, [\psi(\boldsymbol{r}, t)^{*}\, \nabla\psi(\boldsymbol{r}, t) - \psi(\boldsymbol{r}, t)\, \nabla\psi(\boldsymbol{r}, t)^{*}] = (\hbar/m)\, p(\boldsymbol{r}, t)\, \nabla\phi(\boldsymbol{r}, t) = p(\boldsymbol{r}, t)\, \boldsymbol{V}(\boldsymbol{r}, t). \tag{7}$$

For the sharply specified location of an electron at $\boldsymbol{r}' = \boldsymbol{r}$ (the certain event), when $\psi(\boldsymbol{r}', t) = \langle\boldsymbol{r}'|\boldsymbol{r}\rangle = \delta(\boldsymbol{r}' - \boldsymbol{r})$, and hence also $p(\boldsymbol{r}', t) = \delta(\boldsymbol{r}' - \boldsymbol{r})$, the associated current distribution indeed reflects the particle local velocity:

$$\boldsymbol{j}(\boldsymbol{r}', t) = \delta(\boldsymbol{r}' - \boldsymbol{r})\, \boldsymbol{V}(\boldsymbol{r}, t) = (\hbar/m)\, \delta(\boldsymbol{r}' - \boldsymbol{r})\, \nabla\phi(\boldsymbol{r}, t) \equiv \boldsymbol{V}(\boldsymbol{r}, \boldsymbol{r}'; t).$$

For the continuity laws of the next section it is of crucial importance to distinguish between a reference frame moving with the fluid particles (Lagrangian frame) and a reference frame fixed to a prescribed coordinate system (Eulerian frame). The total derivative d/dt is the time change appearing to an observer who moves with the fluid particle; the partial derivative $\partial/\partial t$ is the local time rate of change observed from a fixed point in the Eulerian reference frame. These derivatives are related to each other,

$$d/dt = \partial/\partial t + \boldsymbol{V}\cdot\nabla,$$

where $\boldsymbol{V}\cdot\nabla$ represents the "convection" term.

In the Schrödinger dynamical "picture" the state vector $|\psi(t)\rangle$ introduces an *explicit* time-dependence of the system wavefunction, while the dynamics of the representation basis vector $|\boldsymbol{r}(t)\rangle$ is the source of an additional, *implicit* time-dependence due to the moving reference/monitoring point. This separation applies to wavefunctions, their components and expectation values:

$$\psi(\boldsymbol{r}, t) = \langle\boldsymbol{r}(t)|\psi(t)\rangle = \psi[\boldsymbol{r}(t), t], \qquad R(\boldsymbol{r}, t) = R[\boldsymbol{r}(t), t], \qquad \phi(\boldsymbol{r}, t) = \phi[\boldsymbol{r}(t), t],$$

$$p(\boldsymbol{r}, t) = p[\boldsymbol{r}(t), t], \qquad \boldsymbol{j}(\boldsymbol{r}, t) = \langle\psi(t)|\mathbf{j}[\boldsymbol{r}(t)]|\psi(t)\rangle = \boldsymbol{j}[\boldsymbol{r}(t), t], \qquad \boldsymbol{V}(\boldsymbol{r}, t) = \boldsymbol{V}[\boldsymbol{r}(t), t].$$

3. Continuity Relations

The Schrödinger dynamics of state vectors or the associated wavefunctions also determines time dependencies of their components (see Appendix B) and the associated average physical descriptors, quantum expectations of corresponding observables. All these time evolutions follow directly from the molecular Schrödinger equation (SE),

$$\mathrm{i}\hbar\, \partial|\psi(t)\rangle/\partial t = \mathrm{H}\, |\psi(t)\rangle, \tag{8a}$$

or the associated dynamics of wavefunctions in the position representation,

$$\mathrm{i}\hbar\, \partial\psi(\boldsymbol{r}, t)/\partial t = \mathrm{H}(\boldsymbol{r})\, \psi(\boldsymbol{r}, t), \tag{8b}$$

and its complex conjugate. Here the energy operator

$$\mathrm{H}(\boldsymbol{r}) = -[\hbar^{2}/(2m)]\, \Delta + v(\boldsymbol{r}) \equiv \mathrm{T}(\boldsymbol{r}) + v(\boldsymbol{r}) \tag{9}$$

stands for the Coulombic Hamiltonian of an electron moving in the external potential $v(\boldsymbol{r})$ due to the system fixed nuclei, and $\mathrm{T}(\boldsymbol{r}) = \mathbf{p}(\boldsymbol{r})^{2}/(2m)$, denotes its kinetic part.

The corresponding time evolutions of the scalar fields

$$f(\boldsymbol{r}, t) \in \{\psi(\boldsymbol{r}, t), R(\boldsymbol{r}, t), \phi(\boldsymbol{r}, t), p(\boldsymbol{r}, t)\}, \tag{10a}$$

with the associated current definitions

$$\boldsymbol{j}_f(\boldsymbol{r}, t) = f(\boldsymbol{r}, t)\, \boldsymbol{V}(\boldsymbol{r}, t), \tag{10b}$$

can be ultimately cast in forms of equations expressing the local continuity of the distribution in question:

$$\partial f(\boldsymbol{r}, t)/\partial t = -\nabla\cdot \boldsymbol{j}_f(\boldsymbol{r}, t) + \sigma_f(\boldsymbol{r}, t). \tag{11}$$

It involves the negative divergence $\nabla\cdot\boldsymbol{j}_f(\boldsymbol{r}, t)$ of the current density and its source contribution $\sigma_f(\boldsymbol{r}, t) = df[\boldsymbol{r}(t), t]/dt$, the total time derivative of the density $f(\boldsymbol{r}, t) = f[\boldsymbol{r}(t), t]$, respectively reflecting the property local *outflow* and *production* terms. Expressing the local source of the classical density $f(\boldsymbol{r}, t)$ in terms of the explicit and implicit time contributions then gives:

$$\sigma_f(\boldsymbol{r}, t) = df[\boldsymbol{r}(t), t]/dt = \partial f(\boldsymbol{r}, t)/\partial t + [d\boldsymbol{r}(t)/dt] \cdot [\partial f(\boldsymbol{r}, t)/\partial \boldsymbol{r}] = \partial f(\boldsymbol{r}, t)/\partial t + \boldsymbol{V}(\boldsymbol{r}, t) \cdot\nabla f(\boldsymbol{r}, t). \tag{12}$$

In accordance with the Ehrenfest principle of QM the above classical expression for the total time-derivative of the property density $f(\boldsymbol{r}, t)$ should be also satisfied by the corresponding quantum expectations, e.g., the probability distribution $p(\boldsymbol{r}, t)$ of Eq. (2), the current density $\boldsymbol{j}(\boldsymbol{r}, t)$ of Eq. (7) and effective velocity measure of Eqs. (3) and (7):

$$\sigma_p(\boldsymbol{r}, t) = dp[\boldsymbol{r}(t), t]/dt = \partial p(\boldsymbol{r}, t)/\partial t + \boldsymbol{V}(\boldsymbol{r}, t) \cdot \nabla p(\boldsymbol{r}, t). \tag{13}$$

Here, the total derivative $dp[\boldsymbol{r}(t), t]/dt$ reflects variations in time of the probability density at the position $\boldsymbol{r}(t)$ "moving" with the flux velocity $\boldsymbol{V}(\boldsymbol{r}, t)$, while $\partial p(\boldsymbol{r}, t)/\partial t$ corresponds to the fixed point in space.

It directly follows from SE of QM that the probability density $p(\boldsymbol{r}, t)$ obeys the following continuity relation (see Appendix B):

$$\sigma_p(\boldsymbol{r}, t) = dp(\boldsymbol{r}, t)/dt = \partial p(\boldsymbol{r}, t)/\partial t + \nabla\cdot \boldsymbol{j}(\boldsymbol{r}, t) = 0 \qquad \text{or} \tag{14}$$

$$\partial p(\boldsymbol{r}, t)/\partial t = -\nabla\cdot \boldsymbol{j}(\boldsymbol{r}, t). \tag{15}$$

It confirms the sourceless character of this distribution:

$$\sigma_p(\boldsymbol{r}, t) \equiv dp(\boldsymbol{r}, t)/dt = 0. \tag{16}$$

Therefore, the balance equation for electron density $\rho(\boldsymbol{r}, t) = Np(\boldsymbol{r}, t)$, for $N > 1$, and the associated definition of electronic-current

$$\boldsymbol{J}(\boldsymbol{r}, t) = N\boldsymbol{j}(\boldsymbol{r}, t) = \rho(\boldsymbol{r}, t)\, \boldsymbol{V}(\boldsymbol{r}, t) \tag{17}$$

reads:

$$N\partial p(\boldsymbol{r}, t)/\partial t = \partial \rho(\boldsymbol{r}, t)/\partial t = -\nabla\cdot \boldsymbol{J}(\boldsymbol{r}, t). \tag{18}$$

In the right-hand-side of the preceding equation, the current divergence term denotes the local outflow part and $\sigma_\rho(\boldsymbol{r},t) = N\sigma_p(\boldsymbol{r},t) = 0$ reflects the vanishing local production of electron density. Indeed, the overall electron number N must be conserved, since the particles are neither "created" nor "destroyed":

$$\sigma_N = \int \sigma_\rho(\boldsymbol{r}, t)\, d\boldsymbol{r} = N\int \sigma_p(\boldsymbol{r}, t)\, d\boldsymbol{r} = 0 \qquad \Rightarrow \qquad \sigma_p(\boldsymbol{r}, t) = 0. \tag{19}$$

A direct consequence of this quantum probability continuity is the vanishing divergence of the velocity field [57-63], related to the phase-Laplacian:

$$\nabla\cdot\boldsymbol{V}(\boldsymbol{r}, t) = (\hbar/m)\, \Delta\phi(\boldsymbol{r}, t) = 0. \tag{20}$$

This can be directly demonstrated by separating in the probability density the explicit time-dependence, due to the state-vector itself, from that due to the particle changing position in the reference vector of the scalar product defining the state wavefunction: $p(\boldsymbol{r}, t) = p[\boldsymbol{r}(t), t]$. The relevant differentiation rule then gives:

$$\begin{aligned} dp(\boldsymbol{r}, t)/dt &= \partial p[\boldsymbol{r}(t), t]/\partial t + [d\boldsymbol{r}(t)/dt] \cdot \partial p[\boldsymbol{r}(t), t]/\partial \boldsymbol{r} = -\nabla\cdot \boldsymbol{j}(\boldsymbol{r}, t) + \boldsymbol{V}(\boldsymbol{r}, t) \cdot\nabla p(\boldsymbol{r}, t) \\ &= -[\boldsymbol{V}(\boldsymbol{r}, t) \cdot\nabla p(\boldsymbol{r}, t) + p(\boldsymbol{r}, t)\, \nabla\cdot\boldsymbol{V}(\boldsymbol{r}, t)] + \boldsymbol{V}(\boldsymbol{r}, t) \cdot\nabla p(\boldsymbol{r}, t) = -p(\boldsymbol{r}, t)\, \nabla\cdot\boldsymbol{V}(\boldsymbol{r}, t) = 0. \end{aligned} \tag{21}$$

The preceding equation thus indeed implies Eq. (20) or $\Delta\phi(\boldsymbol{r}, t) = 0$.

Consider next the (nonclassical) production $\sigma_\phi(\boldsymbol{r}, t)$ of the state phase in the continuity equation for this component,

$$\partial\phi(\boldsymbol{r}, t)/\partial t = -\nabla\cdot \boldsymbol{j}_\phi(\boldsymbol{r}, t) + \sigma_\phi(\boldsymbol{r}, t), \tag{22}$$

where:

$$\boldsymbol{j}_\phi(\boldsymbol{r}, t) = \phi(\boldsymbol{r}, t)\, \boldsymbol{V}(\boldsymbol{r}, t) \qquad \text{and} \tag{23}$$

$$\nabla\cdot \boldsymbol{j}_\phi(\boldsymbol{r}, t) = \nabla\phi(\boldsymbol{r}, t) \cdot \boldsymbol{V}(\boldsymbol{r}, t) = (\hbar/m)\, [\nabla\phi(\boldsymbol{r}, t)]^2. \tag{24}$$

The phase-dynamics equation (see Appendix B),

$$\partial\phi(\boldsymbol{r}, t)/\partial t = [\hbar/(2m)]\{R(\boldsymbol{r}, t)^{-1}\Delta R(\boldsymbol{r}, t) - [\nabla\phi(\boldsymbol{r}, t)]^2\} - v(\boldsymbol{r})/\hbar, \tag{25}$$

follows directly from SE and its complex conjugate. It eventually determines the following density of the (nonvanishing) phase production in Eq. (22),

$$\begin{aligned} \sigma_\phi(\boldsymbol{r}, t) &= d\phi[\boldsymbol{r}(t), t]/dt = \partial\phi(\boldsymbol{r}, t)/\partial t + \boldsymbol{V}(\boldsymbol{r}, t) \cdot\nabla\phi(\boldsymbol{r}, t) = \partial\phi(\boldsymbol{r}, t)/\partial t + (\hbar/m)\, [\nabla\phi(\boldsymbol{r}, t)]^2 \\ &= [\hbar/(2m)]\{R(\boldsymbol{r}, t)^{-1}\Delta R(\boldsymbol{r}, t) + [\nabla\phi(\boldsymbol{r}, t)]^2\} - v(\boldsymbol{r})/\hbar. \end{aligned} \tag{26}$$

4. Probability Acceleration and Current Sources

In the local velocity-source the moving-reference correction of the partial time derivative identically vanishes:

$$\sigma_V(\boldsymbol{r}, t) \equiv d\boldsymbol{V}[\boldsymbol{r}(t), t]/dt = \partial\boldsymbol{V}(\boldsymbol{r}, t)/\partial t + \boldsymbol{V}(\boldsymbol{r}, t)\, \nabla\cdot\boldsymbol{V}(\boldsymbol{r}, t) = \partial\boldsymbol{V}(\boldsymbol{r}, t)/\partial t. \tag{27}$$

These velocity derivatives provide a natural measure of the local "acceleration" of probability fluid,

$$\begin{aligned} \boldsymbol{a}(\boldsymbol{r}, t) &\equiv d^2\boldsymbol{r}(t)/dt^2 = \sigma_V(\boldsymbol{r}, t) = d\boldsymbol{V}(\boldsymbol{r}, t)/dt = (\hbar/m)\, d/dt\, [\nabla\phi(\boldsymbol{r}, t)] = (\hbar/m)\, \nabla\sigma_\phi(\boldsymbol{r}, t) \\ &= \partial\boldsymbol{V}(\boldsymbol{r}, t)/\partial t = (\hbar/m)\, \partial/\partial t\, [\nabla\phi(\boldsymbol{r}, t)] = (\hbar/m)\, \nabla[\partial\phi(\boldsymbol{r}, t)/\partial t], \end{aligned} \tag{28}$$

where we have recognized that differentiations with respect to different variables "$\boldsymbol{r}$" and "t" commute. This *probability acceleration* descriptor thus reflects the gradient of the phase-source $\sigma_\phi(\boldsymbol{r}, t)$, equal to that of the partial derivative of the local phase-dynamics. It also generates the associated local "force",

$$\boldsymbol{F}(\boldsymbol{r}, t) = m\,\boldsymbol{a}(\boldsymbol{r}, t) \equiv -\nabla W(\boldsymbol{r}, t), \tag{29}$$

the negative gradient of the underlying *probability potential* $W(\boldsymbol{r}, t)$. The phase source of Eq. (26) eventually generates the following *probability acceleration* density of Eq. (28):

$$\begin{aligned}\boldsymbol{a}(\boldsymbol{r}, t) &= (\hbar/m)\,\nabla\{[\hbar/(2m)]\,R(\boldsymbol{r}, t)^{-1}\Delta R(\boldsymbol{r}, t) - v(\boldsymbol{r})/\hbar\}\\ &= [\hbar^2/(2m^2)]\,R(\boldsymbol{r}, t)^{-1}\,\{\nabla^3 R(\boldsymbol{r}, t) - [\nabla \ln R(\boldsymbol{r}, t)]\,\Delta R(\boldsymbol{r}, t)\} - \nabla v(\boldsymbol{r})/m,\end{aligned} \tag{30}$$

A reference to Eq. (29) finally gives the following probability potential:

$$W(\boldsymbol{r}, t) = v(\boldsymbol{r}) - [\hbar^2/(2m)]\;R(\boldsymbol{r}, t)^{-1}\Delta R(\boldsymbol{r}, t). \tag{31}$$

As an illustration let us consider the stationary state of an electron,

$$\psi^s(\boldsymbol{r}, t) = R^s(\boldsymbol{r})\,\exp(-\mathrm{i}E^s t/\hbar) \equiv R^s(\boldsymbol{r})\,\exp(-\mathrm{i}\omega^s t), \tag{32}$$

corresponding to the sharply specified energy E^s and exhibiting the time-independent probability distribution $p^s(\boldsymbol{r}) = R^s(\boldsymbol{r})^2$. It satisfies the stationary SE, the eigenvalue problem of the Hamiltonian:

$$\mathrm{H}(\boldsymbol{r})\,R^s(\boldsymbol{r}) = \{-[\hbar^2/(2m)]\,\Delta + v(\boldsymbol{r})\}\,R^s(\boldsymbol{r}) = E^s\,R^s(\boldsymbol{r}) \qquad \text{or} \tag{33}$$

$$-[\hbar^2/(2m)]\;R^s(\boldsymbol{r}, t)^{-1}\Delta R^s(\boldsymbol{r}, t) = E^s - v(\boldsymbol{r}). \tag{34}$$

This stationary state thus gives rise to a constant probability-potential reflecting the system local energy,

$$W^s(\boldsymbol{r}, t) = R^s(\boldsymbol{r})^{-1}\mathrm{H}(\boldsymbol{r})\,R^s(\boldsymbol{r}) = E^s, \tag{35}$$

and hence the vanishing probability acceleration and force:

$$\boldsymbol{F}^s(\boldsymbol{r}, t) = \boldsymbol{a}^s(\boldsymbol{r}, t) = \boldsymbol{0}. \tag{36}$$

This confirms the equilibrium character of $p^s(\boldsymbol{r})$, since the vanishing forces do not create any perturbations for a change in this stationary distribution.

Due to a common velocity component in property currents $\{\boldsymbol{j}_f(\boldsymbol{r}, t) = f(\boldsymbol{r}, t)\boldsymbol{V}(\boldsymbol{r}, t)\}$, the probability acceleration also enters into expressions for their local sources:

$$\sigma_{\boldsymbol{j}}^{f}(\boldsymbol{r}, t) \equiv d\boldsymbol{j}_f(\boldsymbol{r}, t)/dt = \sigma_f(\boldsymbol{r}, t)\;\boldsymbol{V}(\boldsymbol{r}, t) + f(\boldsymbol{r}, t)\;\boldsymbol{a}(\boldsymbol{r}, t). \tag{37}$$

For example, the effective probability "acceleration" of Eqs. (28) and (30) subsequently determines the corresponding local sources of the probability- and phase-currents:

$$\sigma_{\boldsymbol{j}}(\boldsymbol{r}, t) = d\boldsymbol{j}(\boldsymbol{r}, t)/dt = p(\boldsymbol{r}, t)\,\boldsymbol{a}(\boldsymbol{r}, t), \tag{38}$$

$$\sigma_{\boldsymbol{j}}^{\phi}(\boldsymbol{r}, t) = d\boldsymbol{j}_\phi(\boldsymbol{r}, t)/dt = \sigma_\phi(\boldsymbol{r}, t)\boldsymbol{V}(\boldsymbol{r}, t) + \phi(\boldsymbol{r}, t)\,\boldsymbol{a}(\boldsymbol{r}, t), \tag{39}$$

where we have recognized the zero probability-production of Eq. (14) and a nonvanishing phase-source of Eq. (26).

Elsewhere [8], we have demonstrated that $\boldsymbol{a}(\boldsymbol{r}, t)$ also generates the local source of the state resultant gradient-information combining the classical (modulus/probability) and nonclassical (phase/current) contributions:

$$I[\psi(t)] = -4\,\langle\psi(t)|\Delta|\psi(t)\rangle \equiv \int p(\boldsymbol{r}, t)\;I(\boldsymbol{r}, t)\,d\boldsymbol{r} = (8m/\hbar^2)\,\langle\psi(t)|\mathrm{T}|\psi(t)\rangle \equiv \sigma\,T[\psi(t)]. \tag{40}$$

As indicated above, this IT measure also reflects the state average (dimensionless) kinetic energy of electrons,

$$T[\psi(t)] = [\hbar^2/(2m)]\int\{[\nabla R(\boldsymbol{r}, t)]^2 + p(\boldsymbol{r}, t)\,[\nabla\phi(\boldsymbol{r}, t)]^2\}\,d\boldsymbol{r}, \tag{41}$$

and exhibits the density-per-electron

$$I(\boldsymbol{r}, t) = [\nabla \ln \mathrm{p}(\boldsymbol{r}, t)]^2 + 4[\nabla\phi(\boldsymbol{r}, t)]^2 = 4\{[\nabla \ln R(\boldsymbol{r}, t)]^2 - [\mathrm{i}\nabla\phi(\boldsymbol{r}, t)]^2\} \tag{42}$$

combining contributions due to the real and imaginary components of the wavefunction logarithm:

$$\ln\psi(\boldsymbol{r}, t) = \ln R(\boldsymbol{r}, t) + \mathrm{i}\phi(\boldsymbol{r}, t). \tag{43}$$

The net production of this generalized Fisher-type density of the state overall information content has a purely nonclassical origin,

$$\sigma_I(\boldsymbol{r}, t) = dI(\boldsymbol{r}, t)/dt = \partial I(\boldsymbol{r}, t)/\partial t + \nabla\cdot\boldsymbol{j}_I(\boldsymbol{r}, t) = 8\nabla\phi(\boldsymbol{r}, t)\cdot\nabla\sigma_\phi(\boldsymbol{r}, t) = (8m/\hbar)\,\nabla\phi(\boldsymbol{r}, t)\cdot\boldsymbol{a}(\boldsymbol{r}, t), \tag{44}$$

where the density of the resultant information current

$$\boldsymbol{j}_I(\boldsymbol{r}, t) = I(\boldsymbol{r}, t)\,\boldsymbol{V}(\boldsymbol{r}, t) \tag{45}$$

determines its divergence

$$\nabla\cdot\boldsymbol{j}_I(\boldsymbol{r}, t) = (\hbar/m)\,\nabla I(\boldsymbol{r}, t)\cdot\nabla\phi(\boldsymbol{r}, t). \tag{46}$$

To summarize, the classical physical descriptor of the particle probability density exhibits the vanishing source, while the nonclassical distributions of the state phase or current density give rise to finite source contributions in their continuity equations. In resultant descriptors of the state overall information/entropy content they ultimately generate finite production terms due to their phase contributions.

We have also demonstrated that the ground state $\psi_0^s \equiv \psi_0$ of an electron implies its stationary probability distribution $p_0^s(\boldsymbol{r}, t) \equiv p_0(\boldsymbol{r})$ corresponding to a constant probability potential, $W_0^s(\boldsymbol{r}, t) = E_0$, and hence also the vanishing probability acceleration and force:

$$\boldsymbol{a}_0^s \equiv \boldsymbol{a}_0 = \boldsymbol{F}_0^s \equiv \boldsymbol{F}_0 = \boldsymbol{0}. \tag{47}$$

Moreover, by invoking the Hohenberg-Kohn theorem of DFT [10], this electronic density uniquely identifies the electronic Hamiltonian, $\mathrm{H} = \mathrm{H}[p_0]$, and the electronic energy: $E_0 = E_v[p_0]$. It also follows from Eqs. (35) and (36) that the state "stationary" character can be effected by the requirement of the vanishing probability acceleration, i.e., the constant phase-source in Eq. (26) and hence also the vanishing local production of the resultant gradient information.

5. Partition/Combination Rules

Consider the partition of electron density $\rho(\boldsymbol{r}) = Np(\boldsymbol{r})$ in a molecule containing $\int\rho(\boldsymbol{r})d\boldsymbol{r} = N$ (integer) electrons into pieces $\{\rho_\alpha(\boldsymbol{r}) = N_\alpha p_\alpha(\boldsymbol{r})\}$ containing $\{\int\rho_\alpha(\boldsymbol{r})\,d\boldsymbol{r} = N_\alpha$ (fractional)$\}$ electrons in constituent fragments,

$$\rho(\boldsymbol{r}) = \textstyle\sum_\alpha \rho_\alpha(\boldsymbol{r}) = \sum_\alpha N_\alpha\,p_\alpha(\boldsymbol{r}), \qquad \int p_\alpha(\boldsymbol{r})\,d\boldsymbol{r} = 1, \tag{48}$$

e.g., the substrate/product subsystems in reactive system. This additive density *partition* scheme can be reversely interpreted as the associated *combination* rule for reconstructing the "molecular" electron distribution from its fragment densities. For definiteness, in what follows we refer to the acidic (A) and basic (B) reactants $X \in (A, B)$ in the acceptor-donor reactive complex R = A----B:

$$\rho_R(\boldsymbol{r}) = N_R\, p_R(\boldsymbol{r}) = \rho_A(\boldsymbol{r}) + \rho_B(\boldsymbol{r}), \qquad \rho_X(\boldsymbol{r}) = N_X\, p_X(\boldsymbol{r}), \qquad \sum_X N_X = N_R. \tag{49}$$

Any division of the "molecular" electron density $\rho_R(\boldsymbol{r})$ implies the associated partition of its (normalized) probability factor $p_R(\boldsymbol{r})$, $\int p_R(\boldsymbol{r})\, d\boldsymbol{r} = 1$, the shape-factor of electron density, into the internally normalized subsystem distributions $\{p_X(\boldsymbol{r}),\ \int p_X(\boldsymbol{r})\, d\boldsymbol{r} = 1\}$,

$$p_R(\boldsymbol{r}) = P_A\, p_A(\boldsymbol{r}) + P_B\, p_B(\boldsymbol{r}), \tag{50}$$

where the condensed fragment probabilities $\{P_X = N_X/N\}$. The overall probability normalization then indeed reflects the combined normalizations of the global $\{P_X\}$ and local $\{p_X(\boldsymbol{r})\}$ probability factors of subsystems:

$$\int p(\boldsymbol{r})\, d\boldsymbol{r} = \sum_X P_X \left[\int p_X(\boldsymbol{r})\, d\boldsymbol{r}\right] = \sum_X P_X = 1. \tag{51}$$

The (mutual) opening of both fragments in the equilibrium reactive system $R^* = (A^* \,¦\, B^*)$, where the vertical *broken* line symbolizes the freedom for electron flows between subsystems, generally establishes the fractional numbers of electrons in subsystems, $\{N_X^* = \int \rho_X^*(\boldsymbol{r}) d\boldsymbol{r}\}$, corresponding to equilibrium subsystem distributions $\{\rho_X^*(\boldsymbol{r}) = N_X^* p_X^*(\boldsymbol{r})\}$. The openness of both fragments implies that their electrons explore the whole "molecular" probability distribution $p_R(\boldsymbol{r})$, so that all such particles become indistinguishable. The probability distributions of such equilibrium fragments thus equalize at global probability distribution for the complex as a whole:

$$\{p_X^*(\boldsymbol{r}) = p_R(\boldsymbol{r})\} \qquad \text{or} \qquad \{\rho_X^*(\boldsymbol{r}) = N_X^*\, p_R(\boldsymbol{r})\}. \tag{52}$$

The combination rule then indeed reconstructs the "molecular" probability density:

$$P_A\, p_A^*(\boldsymbol{r}) + P_B\, p_B^*(\boldsymbol{r}) = (P_A + P_B)\, p_R(\boldsymbol{r}) = p_R(\boldsymbol{r}). \tag{53}$$

As an illustrative example consider the "stockholder" partitioning,

$$\begin{aligned}\rho_X^H(\boldsymbol{r}) &= \rho_X^0(\boldsymbol{r})\, [\rho_R(\boldsymbol{r})/\rho_R^0(\boldsymbol{r})] \equiv \rho_X^0(\boldsymbol{r})\, w_R(\boldsymbol{r}) = [\rho_X^0(\boldsymbol{r})/\rho_R^0(\boldsymbol{r})]\, \rho_R(\boldsymbol{r}) \equiv s_X^0(\boldsymbol{r})\, \rho_R(\boldsymbol{r}),\\ &\rho_A^H(\boldsymbol{r}) + \rho_B^H(\boldsymbol{r}) = \rho_R(\boldsymbol{r}),\end{aligned} \tag{54}$$

where $w_R(\boldsymbol{r})$ and $s_X^0(\boldsymbol{r})$ denote the molecular "*enhacement*" and the fragment "*share*" factors, respectively. In this Hirshfeld (H) [34] scheme, which was shown to have a strong IT justification [1-4, 24, 26-28], all isolated reactant densities $\{\rho_X^0(\boldsymbol{r})\}$ are locally enhanced "molecularly", and each fragment participates in the local "profit" $\rho_R(\boldsymbol{r})$ proportionally to its "share" $s_X^0(\boldsymbol{r})$ in the "promolecular" reference consisting of the "frozen" densities of isolated-subsystems $\{X^0\}$ shifted to their positions in the "molecular" reactive complex R. This isoelectronic reference distribution

$$\rho_R^0(\boldsymbol{r}) = \rho_A^0(\boldsymbol{r}) + \rho_B^0(\boldsymbol{r}) \equiv N p_R^0(\boldsymbol{r}), \qquad \int \rho_R^0(\boldsymbol{r})\, d\boldsymbol{r} = \int \rho_R(\boldsymbol{r})\, d\boldsymbol{r} = N, \tag{55}$$

represents the system "promolecule" $R^0 = (A^0 \mid B^0)$ consisting of the isolated-reactant densities shifted to their molecular locations at the current stage of the reactant approach. This reference also defines the associated condensed probabilities $\{P_X^0 = N_X^0/N\}$ and subsystem distributions:

$$\{p_X^0(\boldsymbol{r}) = \rho_X^0(\boldsymbol{r})/N_X^0\}, \qquad N_X^0 = \int \rho_X^0(\boldsymbol{r})\, d\boldsymbol{r}\ \text{(integer)}. \tag{56}$$

The internally-normalized probability distributions of the Hirshfeld reactants $\{X^H\}$ then read:

$$\begin{aligned}p_X^H(\boldsymbol{r}) &= \rho_X^H(\boldsymbol{r})/N_X^H = [\rho_X^0(\boldsymbol{r})/N_X^H]\, w_R(\boldsymbol{r}) = s_X^0(\boldsymbol{r})\, [\rho_R(\boldsymbol{r})/N_X^H],\\ &N_X^H = \int \rho_X^H(\boldsymbol{r})\, d\boldsymbol{r}, \qquad \int p_X^H(\boldsymbol{r})\, d\boldsymbol{r} = 1, \qquad X = A, B.\end{aligned} \tag{57}$$

Their molecularly-normalized analogs,

$$p_X(\boldsymbol{r}) \equiv \rho_X^H(\boldsymbol{r})/N = P_X^H\, [\rho_X^H(\boldsymbol{r})/N_X^H] = P_X^H\, p_X^H(\boldsymbol{r}) = P_X^0\, [\rho_X^H(\boldsymbol{r})/N_X^0] = [P_X^0\, p_X^0(\boldsymbol{r})]\, w_R(\boldsymbol{r}), \tag{58}$$

are thus normalized to subsystem condensed probabilities in the whole reactive system:

$$\int p_X(\boldsymbol{r})\, d\boldsymbol{r} = N_X^H/N = P_X^H. \tag{59}$$

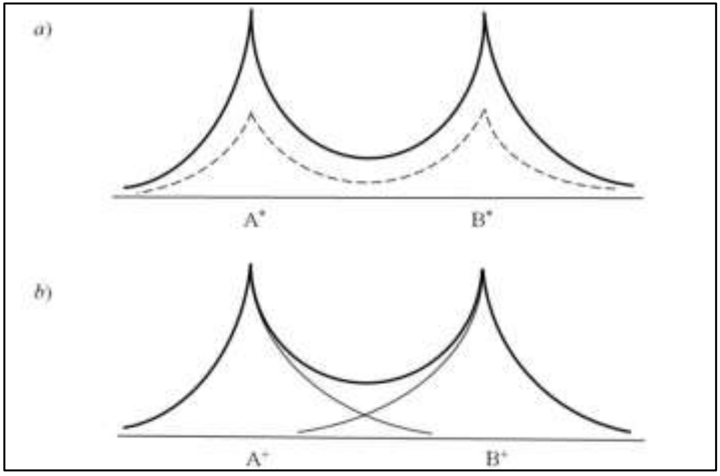
They fulfil the probability-combination rule of Eq. (50):

$$\sum_X p_X(\boldsymbol{r}) = \sum_X P_X^H\, p_X^H(\boldsymbol{r}) = \left[\sum_X \rho_X^H(\boldsymbol{r})\right]/N = \rho_R(\boldsymbol{r})/N = p_R(\boldsymbol{r}). \tag{60}$$

6. Polarized and Equilibrium Subsystems

As an illustration consider the familiar orbital description of the simplest model of the density-reconstruction in the donor-acceptor system, at polarization $R^+ = (A^+ \mid B^+)$ and equilibrium $R^* = (A^* \,¦\, B^*)$ reaction stages, respectively, schematically illustrated in Fig. 1. These complexes respectively consist of the mutually *closed* and *open* basic (B) and acidic (A) reactants. For simplicity reasons, let us assume the isolated reactants containing a single electron each: $N_A^0 = N_B^0 = 1$. The interacting fragments can be either *entangled* (*e*) (bonded), when they represent pieces of the quantum system described by the pure "molecular" state of the whole complex, or disentangled (*d*) (nonbonded), when each subsystem is in its own quantum state, pure or mixed. The two electrons in $R^*(1, 2)$ are indistinguishable, while those in $R^+(1, 2)$ represent the distinguishable electrons: $R^+(1, 2) = [A^+(1) \mid B^+(2)]$. For example, in a diatomic A----B system the wavefunction of the entangled atoms-in-molecules (AIM) is constructed using Slater determinants built from the occupied delocalized molecular orbitals (MO) (Fig. 1a), while the disentangled species are described by the Hartree products of the occupied localized atomic orbitals (AO) (Fig. 1b).

Figure-1. Schematic profiles of the delocalized MO (Panel *a*) and localized AO (Panel *b*) electron distributions in the diatomic entangled $R^* = (A^* ¦ B^*)$ and disentangled $R^+ = (A^+|B^+)$ donor-acceptor systems combining the base (B) and acid (A) reactants



In adopted (ground-state) orbital model the entangled (indistinquishable) electrons of $R^*(1, 2) = (A^* ¦ B^*)$ are thus described by the antisymmetrized product of the two *molecular* spin-orbitals, while the (interacting) disentangled fragments of two (distinguishable) electrons in $R^+(1, 2) = [A^+(1) \,|\, B^+(2)]$ correspond to product of the substrate *atomic* orbitals (AO) dependent on their internal coordinates. The wavefunction of the bonded (entangled) substrates can be thus approximated by the Slater determinant of two spin-paired (delocalized) states derived from a single (doubly-occupied) MO (see Fig. 1*a*),

$$\psi^+(\boldsymbol{q}) = \psi(\boldsymbol{r})\,\alpha(\sigma) \quad \text{and} \quad \psi^-(\boldsymbol{q}) = \psi(\boldsymbol{r})\,\beta(\sigma)\}, \qquad \psi(\boldsymbol{r}) = R(\boldsymbol{r})\,\exp[\mathrm{i}\phi(\boldsymbol{r})], \tag{61}$$

where $\alpha(\sigma)$ and $\beta(\sigma)$ stand for two admissible spin states of an electron, corresponding to spin orientations $\sigma = +\tfrac{1}{2}\hbar$ and $\sigma = -\tfrac{1}{2}\hbar$, respectively. In such a *two*-particle (singlet) state,

$$\Psi_R{}^e(2) = |\psi^+\,\psi^-| = \psi(\boldsymbol{r}_1)\,\psi(\boldsymbol{r}_2)\,\{2^{-1/2}[\alpha(\sigma_1)\,\beta(\sigma_2) - \alpha(\sigma_2)\,\beta(\sigma_1)]\} \equiv R(\boldsymbol{r}_1)\,R(\boldsymbol{r}_2)\exp\{\mathrm{i}[\phi(1) + \phi(\boldsymbol{r}_2)]\}\,U(\sigma_1, \sigma_2), \tag{62}$$

each electron corresponds to the “molecular” modulus and phase components, generating the common probability $p(\boldsymbol{r}) = R(\boldsymbol{r})^2$ and current $\boldsymbol{j}(\boldsymbol{r}) = (\hbar/m)\,p(\boldsymbol{r})\,\nabla\phi(\boldsymbol{r})$ descriptors of the whole reactive system. Each entangled subsystem is thus characterized by the “molecular” probability and phase distributions of R^* as a whole:

$$p_A(\boldsymbol{r}) = p_B(\boldsymbol{r}) = p(\boldsymbol{r}) = R(\boldsymbol{r})^2 \equiv p_R(\boldsymbol{r}) \quad \text{or} \quad \rho_A{}^*(\boldsymbol{r}) = N_A{}^* p_R(\boldsymbol{r}),\ \ \rho_B{}^*(\boldsymbol{r}) = N_B{}^* p_R(\boldsymbol{r}),$$
$$N_A{}^* = N_A{}^0 + N_{CT}, \qquad N_B{}^* = N_B{}^0 - N_{CT}, \qquad \phi_A(\boldsymbol{r}) = \phi_B(\boldsymbol{r}) = \phi(\boldsymbol{r}) \equiv \phi_R(\boldsymbol{r}). \tag{63}$$

This entangled state thus predicts the following rule for combining electronic currents of subsystems exhibiting the equilibrium condensed probabilities $\{P_X{}^* = N_X{}^*/N\}$:

$$\begin{aligned}\boldsymbol{j}_R{}^e(\boldsymbol{r}) &\equiv P_A{}^*\,\boldsymbol{j}_A{}^e(\boldsymbol{r}) + P_B{}^*\,\boldsymbol{j}_B{}^e(\boldsymbol{r}) = (\hbar/m)\,[P_A{}^*\,p_A(\boldsymbol{r})\,\nabla\phi_A(\boldsymbol{r}) + P_B{}^*\,p_B(\boldsymbol{r})\,\nabla\phi_B(\boldsymbol{r})]\\ &= (\hbar/m)\,p_R(\boldsymbol{r})\,(P_A{}^* + P_B{}^*)\nabla\phi_R(\boldsymbol{r}) = \boldsymbol{j}_R(\boldsymbol{r}).\end{aligned} \tag{64}$$

The disentangled subsystems of $R^+(1, 2) = [A^+(1) \,|\, B^+(2)]$ similarly correspond to the product of the fragment spin-paired (localized) AO states (Fig. 1*b*),

$$\varphi_X(\boldsymbol{r}) = R_X(\boldsymbol{r})\exp[\mathrm{i}f_X(\boldsymbol{r})], \qquad X = A, B,$$
$$\Psi_R{}^d(2) = \varphi_A{}^+(\boldsymbol{r}_1)\,\varphi_B{}^-(\boldsymbol{r}_2) = R_A(\boldsymbol{r}_1)\,R_B(\boldsymbol{r}_2)\exp\{\mathrm{i}[f_A(\boldsymbol{r}_1) + f_B(\boldsymbol{r}_2)]\} \equiv \alpha(\sigma_1)\,\beta(\sigma_2). \tag{65}$$

Each fragment/electron in this nonbonded state thus exhibits separate modulus and phase components of its AO wavefunctions, thus generating different probability and current distributions in each polarized subsystem:

$$p_A(\boldsymbol{r}) = R_A(\boldsymbol{r})^2 \neq p_B(\boldsymbol{r}) = R_B(\boldsymbol{r})^2 \quad \text{and} \quad f_A(\boldsymbol{r}) \neq f_B(\boldsymbol{r}). \tag{66}$$

The average resultant probability current in $R^+(1, 2)$,

$$\boldsymbol{j}_R{}^d(\boldsymbol{r}) = P_A{}^+\,\boldsymbol{j}_A{}^d(\boldsymbol{r}) + P_B{}^+\,\boldsymbol{j}_B{}^d(\boldsymbol{r}) = (\hbar/m)\,[P_A{}^0\,p_A(\boldsymbol{r})\,\nabla f_A(\boldsymbol{r}) + P_B{}^0\,p_B(\boldsymbol{r})\,\nabla f_B(\boldsymbol{r})], \qquad \{P_X{}^+ = P_X{}^0 = N_X{}^0/N\}, \tag{67}$$

thus cannot be related to any “molecular” probability or phase distributions, describing the whole system.

7. Communications in Interacting Subsystems

In describing the interacting subsystems it is useful to apply the density matrix formalism of QM [5, 6]. Consider again the acid and base reactants in the polarized complex $R^+ = [A^+(x) \,|\, B^+(\xi)]$ of the equilibrium mutually-closed acceptor (acidic A) and donor (basic B) reactants, where x and ξ denote their corresponding internal coordinates. For example, in the topological, *physical*-space partitioning of the molecular electron density, into pieces belonging to separate basins of the physical space [64], these coordinates describe the disjoint sets of the position variables in these exclusive regions of space, while in the functional-space division schemes, e.g., the stockholder partition of Hirshfeld [34], each of these coordinates explores the whole physical space of particle positions in the separate groups of electrons attributed to reactants.

The physical properties of such subsystems are represented by the quantum operators acting on the fragment internal degrees-of-freedom. For example, the interacting-fragment Hamiltonians $\{\mathrm{H}_X(N_X)\}$ act on the position variables of N_X electrons belonging to X. The stationary subsystem states in A, the eigenstates of $\mathrm{H}_A(N_A) \equiv \mathrm{H}_A(x)$,

$$\mathrm{H}_A(x)\,\varphi_s(x) = E_s(A^+)\,\varphi_s(x), \tag{68}$$

form the complete set

$$\boldsymbol{\varphi}(\mathrm{A}) = \{\varphi_s(\mathrm{A}) = R_s(\mathrm{A})\exp[\mathrm{i}\phi_s(\mathrm{A})] \equiv \langle x|s(\mathrm{A})\rangle\}$$

capable of expanding the pure quantum state $\psi(x, \xi)$ of the reactive system as a whole:

$$\psi(x, \xi) = \textstyle\sum_s \varphi_s(x)\, \Phi_s(\xi), \qquad \Phi_s(\xi) = \int \varphi_s^*(x)\, \psi(x, \xi)\, dx \equiv \langle s(\mathrm{A})|\psi\rangle_{\mathrm{A}}. \tag{69}$$

The quantum operator of the physical property $L(\mathrm{A})$ of subsystem A^+ acts only on variables x: $\mathrm{L}(\mathrm{A}) = \mathrm{L}_x$. Its expectation value in "molecular" state $\psi(x, \xi)$ then reads:

$$\begin{aligned}\langle L\rangle_\psi &= \iint \psi^*(x, \xi)\, \mathrm{L}_x\, \psi(x, \xi)\, dx\, d\xi = \textstyle\sum_s\sum_{s'} [\int \Phi_{s'}^*(\xi)\, \Phi_s(\xi)\, d\xi]\, [\int \varphi_{s'}^*(x)\, \mathrm{L}_x\, \varphi_s(x)\, dx] \\ &\equiv \textstyle\sum_s\sum_{s'} \rho_{s,s'}(\mathrm{A})\, L_{s',s}(\mathrm{A}) \equiv \mathrm{tr}_{\mathrm{A}}[\boldsymbol{\rho}(\mathrm{A})\, \mathbf{L}(\mathrm{A})].\end{aligned} \tag{70}$$

Here $\boldsymbol{\rho}(\mathrm{A}) = \{\rho_{s',s}(\mathrm{A})\}$ stands for the density matrix of subsystem $\mathrm{A}^+(x)$, already integrated over coordinates of electrons in the complementary subsystem $\mathrm{B}^+(\xi)$. In the position representation this effective description of quantum state of molecular fragment can be itself interpreted as the trace over the product of "molecular" and subsystem kernels:

$$\begin{aligned}\rho_{s',s}(\mathrm{A}) &= \int \Phi_s(\xi)\, \Phi_{s'}^*(\xi)\, d\xi = \int\{\int[\int \psi(x, \xi)\, \psi^*(x', \xi)\, d\xi]\, [\varphi_{s'}(x')\, \varphi_s^*(x)]\, dx'\}\, dx \\ &\equiv \int\{[\int \varrho_\psi(x, x')\, \Omega_{s',s}(x', x)\, dx']\, dx \equiv \mathrm{tr}[\boldsymbol{\varrho}_\psi\, \boldsymbol{\Omega}_{\mathrm{A}}].\end{aligned} \tag{71}$$

This partial trace concept enables one to calculate the ensemble average of the subsystem property $L(\mathrm{A})$ as if this part of R^+ were isolated, being in the effective *mixed* state defined by the subsystem density matrix $\boldsymbol{\rho}(\mathrm{A})$ in the (discrete) representation $\{\varphi_s(\mathrm{A})\}$ [7].

In accordance with the Superposition Principle (SP) of QM [66], the expansion coefficient $\Phi_s(\xi) = \langle s(\mathrm{A})|\psi\rangle_{\mathrm{A}}$ generates the amplitude of conditional probability of observing the fragment state $|s(\mathrm{A})\rangle$ in the molecular state $|\psi\rangle$. It determines the amplitude of the diagonal communication between the input and output state $|s(\mathrm{A})\rangle$ of the fragment internal communication system,

$$\begin{aligned}A[s(\mathrm{A})\rightarrow s(\mathrm{A})|\psi] &= \int \Phi_s(\xi)\, \Phi_s^*(\xi)\, d\xi = \rho_{s',s}(\mathrm{A}) \\ &= \int \langle s(\mathrm{A})|\psi\rangle_{\mathrm{A}} \langle\psi|s(\mathrm{A})\rangle_{\mathrm{A}}\, d\xi \equiv \langle s(\mathrm{A})|\psi\rangle\langle\psi|s(\mathrm{A})\rangle \equiv \langle s(\mathrm{A})|\mathrm{P}_\psi|s(\mathrm{A})\rangle \equiv A_{\mathrm{A}}(s\rightarrow s|\psi),\end{aligned} \tag{72}$$

reflected by the associated conditional probability of this electronic communication:

$$\begin{aligned}P_{\mathrm{A}}(s\rightarrow s|\psi) &= |\rho_{s,s}(\mathrm{A})|^2 = |A_{\mathrm{A}}(s\rightarrow s|\psi)|^2 = \int \langle s(\mathrm{A})|\mathrm{P}_\psi|s(\mathrm{A})\rangle_{\mathrm{A}} \langle s(\mathrm{A})|\mathrm{P}_\psi|s(\mathrm{A})\rangle_{\mathrm{A}}\, d\xi \\ &\equiv \langle s(\mathrm{A})|\mathrm{P}_\psi \mathrm{P}_s(\mathrm{A}) \mathrm{P}_\psi|s(\mathrm{A})\rangle \equiv \langle s(\mathrm{A})|\mathrm{P}_s(\psi)|s(\mathrm{A})\rangle.\end{aligned} \tag{73}$$

The off-diagonal elements of the fragment density matrix $\boldsymbol{\rho}(\mathrm{A})$ have an analogous communication interpretation:

$$\rho_{s',s}(\mathrm{A}) = \int \Phi_s(\xi)\, \Phi_{s'}^*(\xi)\, d\xi = \langle s(\mathrm{A})|\psi\rangle_{\mathrm{A}} \langle\psi|s'(\mathrm{A})\rangle_{\mathrm{A}} \equiv \langle s(\mathrm{A})|\mathrm{P}_\psi|s'(\mathrm{A})\rangle = A_{\mathrm{A}}(s\rightarrow s'|\psi), \tag{74}$$

$$\begin{aligned}P_{\mathrm{A}}(s\rightarrow s'|\psi) &= |\rho_{s,s'}(\mathrm{A})|^2 = |A_{\mathrm{A}}(s\rightarrow s|\psi)|^2 = \langle s(\mathrm{A})|[\mathrm{P}_\psi|s'(\mathrm{A})\rangle\langle s'(\mathrm{A})|\mathrm{P}_\psi]|s(\mathrm{A})\rangle \\ &= \langle s(\mathrm{A})|\mathrm{P}_{s'}(\psi)|s(\mathrm{A})\rangle = \langle s'(\mathrm{A})|\mathrm{P}_s(\psi)|s'(\mathrm{A})\rangle.\end{aligned} \tag{75}$$

This molecular probability link between the "input" (s) and "output" (s') stationary states of subsystem A, thus represents the quantum expectation in the input (output) state of the effective projector onto the fragment output (input) state, respectively. These probabilities exhibit the following "input" and "output" normalizations,

$$\textstyle\sum_s P_{\mathrm{A}}(s\rightarrow s'|\psi) = P[s'(\mathrm{A})|\psi] \quad \text{and} \quad \sum_{s'} P_{\mathrm{A}}(s\rightarrow s'|\psi) = P[s(\mathrm{A})|\psi], \tag{76}$$

since the fragment basis is complete, $\sum_s |s(\mathrm{A})\rangle\langle s(\mathrm{A})| = 1$, and the pure-state projection is idempotent: $\mathrm{P}_\psi^2 = \mathrm{P}_\psi$.

Such internal communications in molecular subsystems eventually generate the IT descriptors of their patterns of chemical bonds [1-4, 35-45]. In this communication theory of the chemical bond the conditional-entropy of the network "output" states $\boldsymbol{\varphi}'(\mathrm{A})$, given the specified "input" states $\boldsymbol{\varphi}(\mathrm{A})$, describes the average "noise" in the internal communications $\boldsymbol{\varphi}(\mathrm{A})\rightarrow\boldsymbol{\varphi}'(\mathrm{A})$ in fragment A, which reflects its IT overall bond "covalency". The complementary mutual-information descriptor of this information scattering, measuring the network average information flow, then reflects the system overall IT bond "iconicity".

Writing Eq. (70) in the subsystem position representation,

$$\langle L\rangle_\psi = \iint \rho_{\mathrm{A}}(x, x')\, \langle x'|\mathrm{L}_x|x\rangle\, dx\, dx', \tag{77}$$

where $\langle x'|\mathrm{L}_x|x\rangle = \mathrm{L}_x\delta(x' - x)$, one obtains the following expression for the subsystem density matrix:

$$\rho_{\mathrm{A}}(x, x') = \int \psi^*(x', \xi)\, \psi(x, \xi)\, d\xi = \textstyle\sum_s\sum_{s'} \rho_{s,s'}(\mathrm{A})\, \varphi_{s'}^*(x')\, \varphi_s(x) \equiv \sum_s\sum_{s'} \rho_{s,s'}(\mathrm{A})\, \Omega_{s',s}(x, x') \equiv \mathrm{tr}_{\mathrm{A}}[\boldsymbol{\rho}(\mathrm{A})\, \boldsymbol{\Omega}_{\mathrm{A}}(x, x')]. \tag{78}$$

Its diagonal elements, for $x = x'$, determine the probabilities of "local" "events" in subsystem A:

$$\rho_{\mathrm{A}}(x, x) = \int \psi^*(x, \xi)\, \psi(x, \xi)\, d\xi = \int P(x, \xi)\, d\xi = p_{\mathrm{A}}(x), \tag{79}$$

where $P(x, \xi) = |\psi(x, \xi)|^2$ stands for the molecular probability of the joint "events" in both subsystems.

To summarize, the (interacting) subsystem in reactive complex R described by the pure quantum state of the whole system cannot be described by a single wavefunction. They have to be instead characterized by the fragment effective density matrices reflecting the associated (incoherent) mixtures of subsystem states. The above expressions for the expectation values of subsystem operators in the fragment effective mixed quantum states are independent of the applied representation. The corresponding dynamics of the reactant density matrices are also uniquely determined by the molecular SE.

It should be also realized that the tensor product of subsystem spaces,

$$\begin{aligned}&\boldsymbol{\psi} = \boldsymbol{\varphi}(\mathrm{A}) \otimes \boldsymbol{\varphi}(\mathrm{B}) = \{\varphi_s(x)\, \varphi_u(\xi) \equiv \psi_w(x, \xi)\}, \\ &\quad \langle\psi_w|\psi_{w'}\rangle = [\int \varphi_s(x)^*\, \varphi_{s'}(x)\, dx]\, [\int \varphi_u(\xi)^*\, \varphi_{u'}(\xi)\, d\xi] = \langle\varphi_s|\varphi_{s'}\rangle_{\mathrm{A}} \langle\varphi_u|\varphi_{u'}\rangle_{\mathrm{B}} = \delta_{s,s'}\, \delta_{u,u'} = \delta_{w,w'}, \\ &\quad \mathrm{P}_{\boldsymbol{\psi}} = |\boldsymbol{\psi}\rangle\langle\boldsymbol{\psi}| = \textstyle\sum_w \mathrm{P}_w = 1,\end{aligned} \tag{80}$$

constitutes an alternative (orthonormal, complete) basis for expanding the given state $\psi(x, \xi)$ of the whole system:

$$\begin{aligned}&\psi(x, \xi) = \textstyle\sum_w \psi_w(x, \xi)\, C_w \equiv \boldsymbol{\psi}\boldsymbol{C}, \qquad \boldsymbol{C} = \langle\boldsymbol{\psi}|\psi\rangle = \{C_w = \langle\psi_w|\psi\rangle\}, \\ &\quad C_w = \int[\int \varphi_s(x)^*\, \psi(x, \xi)\, dx]\, \varphi_u(\xi)^*\, d\xi = \int \varphi_u(\xi)^*\, \Phi_s(\xi)\, d\xi.\end{aligned} \tag{81}$$

The square of the above expansion coefficient then determines the conditional probability of observing in ψ the product state ψ_w:

$$P(w|\psi) = |C_w|^2 = \langle\psi|\mathrm{P}_w|\psi\rangle = \langle\psi_w|\mathrm{P}_\psi|\psi_w\rangle, \qquad \textstyle\sum_w P(w|\psi) = \langle\psi|\sum_w \mathrm{P}_w|\psi\rangle = \langle\psi|\psi\rangle = 1. \tag{82}$$

These probabilities determine the system density operator in this fragment-state representation:

$$\mathrm{D}(\psi) = \sum_w |\psi_w\rangle\, P(w|\psi)\, \langle \psi_w| \equiv \sum_{s(\mathrm{A})} \sum_{u(\mathrm{B})} |\varphi_s(\mathrm{A})\, \varphi_u(\mathrm{B})\rangle\, P(w|\psi)\, \langle\varphi_u(\mathrm{B})\, \varphi_s(\mathrm{A})|. \qquad (83)$$

It should be finally observed that such a mixed character of effective quantum states describing the interacting molecular fragments also implies that one can associate with such subsystems only the ensemble-average state descriptors. Therefore, for the (incoherent) statistical mixture of the product states of Eq. (80) defined by $\mathrm{D}(\psi)$ only the ensemble average state components can be attributed:

$$\langle R(\mathrm{A})\rangle_\psi = \sum_w P(w|\psi)\, R_s(\mathrm{A}) \quad \text{or} \quad \langle R(\mathrm{B})\rangle_\psi = \sum_w P(w|\psi)\, R_u(\mathrm{B}), \quad \text{and}$$
$$\langle \phi(\mathrm{A})\rangle_\psi = \sum_w P(w|\psi)\, \phi_s(\mathrm{A}) \quad \text{or} \quad \langle \phi(\mathrm{B})\rangle_\psi = \sum_w P(w|\psi)\, \phi_u(\mathrm{B}). \qquad (84)$$

However, these embedded-fragment ensembles have been derived from the specified (pure) quantum state $\psi(x, \xi) = R(x, \xi) \exp[\mathrm{i}\phi(x, \xi)]$ of the whole "molecular" system, which represents their common quantum origin. The modulus, $R(x, \xi)$, and phase, $\phi(x, \xi)$, components of this (parameter) reference state thus also describe its embedded subsystems.

8. Conclusion

In this analysis we have used SE of QM to derive the continuity relations for the molecular classical (probability) and nonclassical (current) physical distributions, reflecting the modulus and phase components of the state wavefunction, respectively. The probability distribution determines the electronic structure of "being", while the current density establishes the dynamic structure "of becoming" [67]. Both these physical distributions contribute to the resultant measures of the entropy/information content of molecular electronic states [4, 68-71]. A nonvanishing production term in the phase continuity equation then implies finite local sources of the resultant information/entropy descriptors which combine the classical and nonclassical gradient contributions. The complementary classical information and entropy measures of Fisher and Shannon have also been used to monitor the progress of elementary chemical reactions [72-74].

It follows from the continuity relations that an effective "velocity" descriptor of the probability "fluid", identified as the local current-per-particle, exhibits the vanishing divergence reflecting the zero phase-Laplacian. It subsequently determines the associated concepts of the probability "acceleration" and "force", the negative gradient of the probability potential, all related to the gradient of the quantum phase-source. It has been argued that in stationary states the constant probability potential reflects the state local-energy, thus implying the vanishing acceleration and force descriptors of the electron distribution.

The probability partition/combination problem has been briefly reexamined, and illustrated using the stockholder principle of Hirshfeld, which has a solid justification in IT. The distinction has been made between the hypothetical reaction stages consisting of the polarized (nonbonded, mutually-closed) and equilibrium (bonded, mutually-open) substrates in donor-acceptor systems. In the disentangled subsystems of the polarized complex the (mixed) quantum states of their (distinguishable) groups of electrons are linked to the localized subsystem distributions and underlying *fragment* orbitals, while (indistinguishable) electrons in the entangled parts of the reactive complex are described by the pure quantum state of the reactive system as a whole, constructed from the delocalized *molecular* orbitals. This global quantum state also refers to its reactant pieces, both reflecting the molecular probability distribution and characterized by the same molecular phase component. Each bonded subsystem has to be described by the fragment density matrix.

Appendix A: An Effective Measure of Local Velocity

According to the Ehrenfest principle of QM the time dependencies of the expectation values of the position and momentum operators follow the corresponding relations between the associated classical quantities. For example, it follows from the Schrödinger dynamics that the average velocity descriptor,

$$\langle \boldsymbol{V}(t)\rangle = d\langle \boldsymbol{r}(t)\rangle/dt, \qquad (\mathrm{A1})$$

where the average position at time t

$$\langle \mathbf{r}(t)\rangle = \langle \psi(t)|\mathbf{r}|\psi(t)\rangle = \int p(\boldsymbol{r}, t)\, \boldsymbol{r}\, d\boldsymbol{r}, \qquad (\mathrm{A2})$$

reflects the average momentum per unit mass:

$$\langle \boldsymbol{V}(t)\rangle = (\mathrm{i}/\hbar)\, \langle[\mathrm{H}, \mathbf{r}]\rangle = (\mathrm{i}/\hbar)\, \langle[\mathrm{T}, \mathbf{r}]\rangle = \langle \boldsymbol{p}(t)\rangle/m. \qquad (\mathrm{A3})$$

Moreover, the definition of Eq. (A2) and the probability continuity of Eq. (14) give

$$\langle \boldsymbol{V}(t)\rangle = d\langle \boldsymbol{r}(t)\rangle/dt = \int\{[dp(\boldsymbol{r}, t)/dt]\, \boldsymbol{r} + p(\boldsymbol{r}, t)\, [d\boldsymbol{r}(t)/dt]\}\, d\boldsymbol{r} = \int p(\boldsymbol{r}, t)\, [d\boldsymbol{r}(t)/dt]\, d\boldsymbol{r}, \qquad (\mathrm{A4})$$

while Eq. (A3) reads [see also Eq. (3)]:

$$\langle \boldsymbol{p}(t)\rangle/m = (-\mathrm{i}\hbar/m) \int \psi^*(\boldsymbol{r}, t)\, \nabla\, \psi(\boldsymbol{r}, t)\, d\boldsymbol{r} = (\mathrm{i}\hbar/m) \int \psi(\boldsymbol{r}, t)\, \nabla\, \psi^*(\boldsymbol{r}, t)\, d\boldsymbol{r}$$
$$= [\hbar/(2\mathrm{i}m)]\, \{\int[\psi^*(\boldsymbol{r}, t)\, \nabla\, \psi(\boldsymbol{r}, t) - \int \psi(\boldsymbol{r}, t)\, \nabla\, \psi^*(\boldsymbol{r}, t)]\, d\boldsymbol{r} = \int \boldsymbol{j}(\boldsymbol{r}, t)\, d\boldsymbol{r} = \int p(\boldsymbol{r}, t)\, \boldsymbol{V}(\boldsymbol{r}, t)\, d\boldsymbol{r}. \qquad (\mathrm{A5})$$

Therefore, comparing two preceding equations finally gives:

$$d\boldsymbol{r}(t)/dt = \boldsymbol{V}(\boldsymbol{r}, t) = \boldsymbol{j}(\boldsymbol{r}, t)/p(\boldsymbol{r}, t). \qquad (\mathrm{A6})$$

Appendix B: Schrödinger Equations for Wavefunction Components

Let us examine the dynamics/continuity implications of SE for the modulus and phase components of the particle wavefunction. The molecular SE expressed in terms of wavefunction components reads:

$$\mathrm{i}\hbar\, \partial\psi(\boldsymbol{r}, t)/\partial t = \mathrm{i}\hbar\, [\partial R(\boldsymbol{r}, t)/\partial t + \mathrm{i}R(\boldsymbol{r}, t)\, \partial\phi(\boldsymbol{r}, t)/\partial t]\, \exp[\mathrm{i}\phi(\boldsymbol{r}, t)] = \mathrm{H}(\boldsymbol{r})\, \psi(\boldsymbol{r}, t)$$
$$= [-\hbar^2(2m)^{-1}\{\Delta R(\boldsymbol{r}, t) + 2\mathrm{i}\nabla R(\boldsymbol{r}, t) \cdot \nabla\phi\, (\boldsymbol{r}, t) - R(\boldsymbol{r}, t)\, [\nabla\phi(\boldsymbol{r}, t)]^2\} + v(\boldsymbol{r})\, R(\boldsymbol{r}, t)]\, \exp(\mathrm{i}\phi), \qquad (\mathrm{B1})$$

where we have used Eq. (20). Multiplying both sides of the preceding equation by $\exp(-\mathrm{i}\phi)$ and dividing by $\hbar R$ finally gives the following complex relation:

$$\mathrm{i}\,\partial \ln R(\boldsymbol{r},t)/\partial t - \partial \phi(\boldsymbol{r},t)/\partial t = -\hbar\,(2m)^{-1}\{R(\boldsymbol{r},t)^{-1}\Delta R(\boldsymbol{r},t) + 2\mathrm{i}\nabla \ln R(\boldsymbol{r},t)\cdot\nabla\phi(\boldsymbol{r},t) - [\nabla\phi(\boldsymbol{r},t)]^2\} + v(\boldsymbol{r})/\hbar. \tag{B2}$$

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

$$\partial \ln R(\boldsymbol{r},t)/\partial t = -\,(\hbar/m)\,\nabla\phi(\boldsymbol{r},t)\cdot\nabla \ln R(\boldsymbol{r},t) = -\,\boldsymbol{V}(\boldsymbol{r},t)\cdot\nabla \ln R(\boldsymbol{r},t), \tag{B3}$$

which can be directly transformed into probability continuity Eq. (15):

$$\partial p(\boldsymbol{r},t)/\partial t = -\nabla\cdot\boldsymbol{j}(\boldsymbol{r},t) \quad \text{or} \quad \sigma_p(\boldsymbol{r},t) = dp(\boldsymbol{r},t)/dt = 0. \tag{B4}$$

Equating the *real* parts of Eq. (B2) similarly determines the phase-dynamics of Eq. (25):

$$\partial\phi(\boldsymbol{r},t)/\partial t = \hbar(2m)^{-1}\,\{R(\boldsymbol{r},t)^{-1}\Delta R(\boldsymbol{r},t) - [\nabla\phi(\boldsymbol{r},t)]^2\} - v(\boldsymbol{r})/\hbar. \tag{B5}$$

The latter equation also determines the phase-production $\sigma_\phi(\boldsymbol{r},t) = d\phi(\boldsymbol{r},t)/dt \neq 0$ [Eq. (26)] for the flux definition of Eq. (23), in the phase continuity relation

$$\partial\phi(\boldsymbol{r},t)/\partial t = -\nabla\cdot\boldsymbol{j}_\phi(\boldsymbol{r},t) + \sigma_\phi(\boldsymbol{r},t). \tag{B6}$$

References

[1] Nalewajski, R. F., 2006. *Information theory of molecular systems*. Elsevier: Amsterdam.

[2] Nalewajski, R. F., 2010. *Information origins of the chemical bond*. New York: Nova Science Publishers.

[3] Nalewajski, R. F., 2012. *Perspectives in electronic structure theory*. Heidelberg: Springer.

[4] Nalewajski, R. F., 2016. *Quantum information theory of molecular states*. New York: Nova Science Publishers.

[5] Davydov, A. S., 1965. *Quantum mechanics*. Oxford: Pergamon Press.

[6] Cohen-Tannoudji, C., Diu, B., and Laloë, F., 1977. *Quantum mechanics*. New York: Wiley.

[7] Nalewajski, R. F., 2020. "Interacting subsystems and their molecular ensembles." *Acad. J. Chem.*, vol. 5, pp. 25-30.

[8] Nalewajski, R. F., 2020. "Information-theoretic descriptors of molecular states and electronic communications between reactants". *Entropy*, vol. 22, pp. 749-769.

[9] Nalewajski, R. F., 2020. "Phase equalization, charge transfer, information flows and electron communications in donor-acceptor systems." *Appl. Sci.*, vol. 10, pp. 3615-3646.

[10] Hohenberg, P. and Kohn, W., 1964. "Inhomogeneous electron gas." *Phys. Rev.*, vol. 136B, pp. 864-971.

[11] Kohn, W. and Sham, L. J., 1965. "Self-consistent equations including exchange and correlation effects." *Phys. Rev.*, vol. 140A, pp. 133-1138.

[12] 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*, vol. 76, pp. 6062-6065.

[13] Parr, R. G. and Yang, W., 1989. *Density-functional theory of atoms and molecules*. New York: Oxford University Press.

[14] Dreizler, R. M. and Gross, E. K. U., 1990. *Density functional theory: An approach to the quantum many-body problem*. Berlin: Springer.

[15] Nalewajski, R. F., 1996. *Density functional theory I-IV. Topics in Current Chemistry*, vols. 180-183. Berlin: Springer.

[16] Fisher, R. A., 1925. "Theory of statistical estimation." *Proc. Cambridge Phil. Soc.*, vol. 22, pp. 700-725.

[17] Frieden, B. R., 2004. *Physics from the Fisher information - a unification*. Cambridge: Cambridge University Press.

[18] Shannon, C. E., 1948. "The mathematical theory of communication." *Bell. System. Tech. J.*, vol. 7, pp. 379-493, 623-656.

[19] Shannon, C. E. and Weaver, W., 1949. *The mathematical theory of communication*. Urbana: University of Illinois.

[20] Kullback, S. and Leibler, R. A., 1951. "On information and sufficiency." *Ann. Math. Stat.*, vol. 22, pp. 79-86.

[21] Kullback, S., 1959. *Information theory and statistics*. New York: Wiley.

[22] Abramson, N., 1963. *Information theory and coding*. New York: McGraw-Hill.

[23] Pfeifer, P. E., 1978. *Concepts of probability theory*. New York: Dover.

[24] Nalewajski, R. F. and Parr, R. G., 2000. "Information theory, atoms-in-molecules and molecular similarity." *Proc. Natl. Acad. Sci. USA*, vol. 97, pp. 8879-8882.

[25] Nalewajski, R. F. and Broniatowska, E., 2003. "Information distance approach to Hammond Postulate." *Chem. Phys. Lett.*, vol. 376, pp. 33-39.

[26] Nalewajski, R. F. and Parr, R. G., 2001. "Information-theoretic thermodynamics of molecules and their Hirshfeld fragments." *J. Phys. Chem. A.*, vol. 105, pp. 7391-7400.

[27] Nalewajski, R. F., 2002. "Hirshfeld analysis of molecular densities: subsystem probabilities and charge sensitivities." *Phys. Chem. Chem. Phys.*, vol. 4, pp. 1710-1721.

[28] Parr, R. G., Ayers, P. W., and Nalewajski, R. F., 2005. "What is an atom in a molecule? ." *J. Phys. Chem. A.*, vol. 109, pp. 3957-3959.

[29] Nalewajski, R. F. and Broniatowska, E., 2007. "Atoms-in-Molecules from the stockholder partition of molecular two-electron distribution." *Theoret. Chem. Acc.*, vol. 117, pp. 7-27.

[30] Heidar-Zadeh, F., Ayers, P. W., Verstraelen, T., Vinogradov, I., Vöhringer-Martinez, E., and Bultinck, P., 2018. "Information-theoretic approaches to Atoms-in-Molecules: Hirshfeld family of partitioning schemes." *J. Phys. Chem. A.*, vol. 122, pp. 4219-4245.

[31] Nalewajski, R. F., Świtka, E., and Michalak, A., 2002. "Information distance analysis of molecular electron densities." *Int. J. Quantum. Chem.*, vol. 87, pp. 198-213.

[32] Nalewajski, R. F. and Broniatowska, E., 2003. "Entropy displacement analysis of electron distributions in molecules and their Hirshfeld atoms." *J. Phys. Chem. A.*, vol. 107, pp. 6270-6280.

[33] Nalewajski, R. F., 2008. "Use of Fisher information in quantum chemistry." *Int. J. Quantum. Chem.* (Jankowski, K., issue), vol. 108, pp. 2230-2252.

[34] Hirshfeld, F. L., 1977. "Bonded-atom fragments for describing molecular charge densities." *Theoret. Chim. Acta.* (Berlin), vol. 44, pp. 129-138.

[35] Nalewajski, R. F., 2000. "Entropic measures of bond multiplicity from the information theory." *J. Phys. Chem. A.*, vol. 104, pp. 11940-11951.

[36] Nalewajski, R. F., 2004. "Entropy descriptors of the chemical bond in Information Theory: I. Basic concepts and relations". *Mol. Phys.* vol. 102, pp. 531-546. "Entropy descriptors of the chemical bond in Information Theory: II. Application to simple orbital models." *Mol. Phys.*, vol. 102, pp. 547-566.

[37] Nalewajski, R. F., 2004. "Entropic and difference bond multiplicities from the two-electron probabilities in orbital resolution." *Chem. Phys. Lett.*, vol. 386, pp. 265-271.

[38] Nalewajski, R. F., 2005. "Reduced communication channels of molecular fragments and their entropy/information bond indices." *Theoret. Chem. Acc.*, vol. 114, pp. 4-18.

[39] Nalewajski, R. F., 2005. "Partial communication channels of molecular fragments and their entropy/information indices." *Mol. Phys.*, vol. 103, pp. 451-470.

[40] Nalewajski, R. F., 2011. "Entropy/information descriptors of the chemical bond revisited." *J. Math. Chem.*, vol. 49, pp. 2308-2329.

[41] Nalewajski, R. F., 2014. "Quantum information descriptors and communications in molecules." *J. Math. Chem.*, vol. 52, pp. 1292-1323.

[42] Nalewajski, R. F., 2009. "Multiple, localized and delocalized/conjugated bonds in the orbital-communication theory of molecular systems." *Adv. Quant. Chem.*, vol. 56, pp. 217-250.

[43] Nalewajski, R. F., Szczepanik, D., and Mrozek, J., 2011. "Bond differentiation and orbital decoupling in the orbital communication theory of the chemical bond." *Adv. Quant. Chem.*, vol. 61, pp. 1-48.

[44] Nalewajski, R. F., Szczepanik, D., and Mrozek, J., 2012. "Basis set dependence of molecular information channels and their entropic bond descriptors." *J. Math. Chem.*, vol. 50, pp. 1437-1457.

[45] Nalewajski, R. F., 2017. "Electron communications and chemical bonds". In *Frontiers of quantum chemistry*, Wójcik, M., Nakatsuji, H., Kirtman, B., Ozaki, Y. (eds.). Singapore: Springer. pp. 315-351.

[46] Nalewajski, R. F., 2011. "Through-space and through-bridge components of chemical bonds." *J. Math. Chem.*, vol. 49, pp. 371-392.

[47] Nalewajski, R. F., 2011. "Chemical bonds from through-bridge orbital communica-tions in prototype molecular systems." *J. Math. Chem.*, vol. 49, pp. 546-561.

[48] Nalewajski, R. F., 2011. "On interference of orbital communications in molecular systems." *J. Math. Chem.*, vol. 49, pp. 806-815.

[49] Nalewajski, R. F. and Gurdek, P., 2011. "On the implicit bond-dependency origins of bridge interactions." *J. Math. Chem.*, vol. 49, pp. 1226-1237.

[50] Nalewajski, R. F., 2012. "Direct (through-space) and indirect (through-bridge) components of molecular bond multiplicities." *Int. J. Quantum. Chem.*, vol. 112, pp. 2355-2370.

[51] Nalewajski, R. F. and Gurdek, P., 2012. "Bond-order and entropic probes of the chemical bonds." *Struct. Chem.*, vol. 23, pp. 1383-1398.

[52] Nalewajski, R. F., Köster, A. M., and Escalante, S., 2005. "Electron localization function as information measure." *J. Phys. Chem. A.*, vol. 109, pp. 10038-10043.

[53] Becke, A. D. and Edgecombe, K. E., 1990. "A simple measure of electron localization in atomic and molecular systems." *J. Chem. Phys.*, vol. 92, pp. 5397-5403.

[54] Silvi, B. and Savin, A., 1994. "Classification of chemical bonds based on topological analysis of electron localization functions." *Nature*, vol. 371, pp. 683-686.

[55] Savin, A., Nesper, R., Wengert, S., and Fässler, T. F., 1997. "ELF: the electron localization function." *Angew. Chem. Int. Ed. Engl.*, vol. 36, pp. 1808-1832.

[56] Nalewajski, R. F., de Silva, P., and Mrozek, J., 2010. "Use of nonadditive Fisher information in probing the chemical bonds." *J. Mol. Struct. Theochem.*, vol. 954, pp. 57-74.

[57] Nalewajski, R. F., 2020. "Resultant information approach to donor-acceptor systems." In *An introduction to electronic structure theory*. New York: Nova Science Publishers, in press.

[58] Nalewajski, R. F., 2018. "Information equilibria, subsystem entanglement and dynamics of the overall entropic descriptors of molecular electronic structure." *J. Mol. Model.* (Chattaraj, P., issue), vol. 24, pp. 212-227.

[59] Nalewajski, R. F., 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.*, vol. 9, pp. 1262-1292.

[60] Nalewajski, R. F., 2019. "On entropy/information description of reactivity phenomena." In *Advances in mathematics research*, vol. 26, Baswell, A. R. (ed.), pp. 97-157. New York: Nova Science Publishers.

[61] Nalewajski, R. F., 2019. "Role of electronic kinetic energy (resultant gradient information) in chemical reactivity." *J. Mol. Model.* (Latajka, Z., issue), vol. 25, pp. 259-278.

[62] Nalewajski, R. F., 2019. "Resultant information description of electronic states and chemical processes." *J. Phys. Chem. A.*, vol. 123, pp. 45-60.

[63] Nalewajski, R. F., 2020. "On classical and quantum entropy/information descriptors of molecular electronic states." In *Research methodologies and practical applications of chemistry*, Pogliani, L., Haghi, A. K., Islam, N. (eds.). Waretown: Apple Academic Press, in press.

[64] Bader, R. F. W., 1990. *Atoms in Molecules*. New York: Oxford University Press.

[65] Nalewajski, R. F., 2020. "Nonadditive entropic criteria for density partitioning and phase equilibria." In *Research methodologies and practical applications of chemistry*, Pogliani, L., Haghi, A. K., Islam, N. (eds.). Waretown: Apple Academic Press, in press.

[66] Dirac PAM, 1967. *The principles of quantum mechanics*. Oxford: Oxford University Press.

[67] Prigogine, I., 1980. *From being to becoming: time and complexity in the physical sciences*. San Francisco: Freeman, W. H. and Co.

[68] Nalewajski, R. F., 2017. "Quantum information measures and their use in Chemistry." *Current Phys. Chem.*, vol. 7, pp. 94-117.

[69] Nalewajski, R. F., 2013. "Exploring molecular equilibria using quantum information measures." *Ann. Phys.* (Leipzig), vol. 525, pp. 256-268.

[70] Nalewajski, R. F., 2014. "On phase/current components of entropy/information descriptors of molecular states." *Mol. Phys.*, vol. 112, pp. 2587-2601.

[71] Nalewajski, R. F., 2016. "Complex entropy and resultant information measures." *J. Math. Chem.*, vol. 54, pp. 1777-1782.

[72] López-Rosa, S., 2010. *Information theoretic measures of atomic and molecular systems*. PhD Thesis, University of Granada.

[73] López-Rosa, S., Esquivel, R. O., Angulo, J. C., Antolín, J., Dehesa, J. S., and Flores-Gallegos, N., 2010. "Fisher information study in position and momentum spaces for elementary chemical reactions." *J. Chem. Theory. Comput.*, vol. 6, pp. 145-154.

[74] Esquivel, R. O., Liu, S., Angulo, J. C., Dehesa, J. S., Antolín, J., and Molina-Espíritu, M., 2011. "Fisher information and steric effect: study of internal rotation barrier in ethane." *J. Phys. Chem. A.*, vol. 115, pp. 4406-4415.