Academic Journal of Chemistry
ISSN(e): 2519-7045, ISSN(p): 2521-0211
Vol. 5, Issue. 4, pp: 25-30, 2020
URL: https://arpgweb.com/journal/journal/20
DOI: https://doi.org/10.32861/ajc.54.25.30

Academic Research Publishing Group

Original Research **Open Access**

Interacting Subsystems and Their Molecular Ensembles

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Article History
Received: March 5, 2020
Revised: March 30, 2020
Accepted: April 8, 2020
Published: April 11, 2020

Abstract

The molecular density-partition problem is reexamined and the information-theoretic (IT) justification of the stockholder division rule is summarized. The ensemble representations of the promolecular and molecular mixed states of constituent atoms are identified and the electron probabilities in the isoelectronic stockholder atoms-in-molecules (AIM) are used to define the molecular-orbital ensembles for the bonded Hirshfeld atoms. In the pure quantum state of the whole molecular system its interacting (entangled) fragments are described by the subsystem density operators, with the subsystem physical properties being generated by the partial traces involving the fragment density matrices.

Keywords: Bonded atoms; Density matrices; Orbital ensembles; Stockholder partition.

1. Introduction

The Information Theory (IT) [1-8] has been successfully applied in an entropic interpretation of the molecular electronic structure, e.g., [9-12]. In particular, it has provided the IT basis [13-17] for the intuitive stockholder Atoms-in-Molecules (AIM) of Hirshfeld [18] and patterns of entropic bond multiplicities have been extracted from electronic communications in molecules [9-12, 19-24]. The nonadditive Fisher (gradient) information [2, 3, 9-12, 25, 26] has also been linked to Electron Localization Function (ELF) [27-29] of modern Density Functional Theory (DFT) [30-35]. This analysis has enabled a formulation of the novel Contragradience (CG) probe for localizing chemical bonds [9-12, 36], while the communication theory of the chemical bond has identified the bridge interactions between AIM [11, 37-39], realized via the “cascade” propagations in molecular information systems, through orbital intermediates.

In the present analysis we intend to reexamine the molecular density/probability partitioning problems, e.g., into pieces attributed to interacting AIM or reactants. We shall focus on the IT basis of the stockholder principle of Hirshfeld [18] and argue that such subsystems can be properly described only by the *mixed* states of molecular Quantum Mechanics (QM) corresponding to statistical mixtures of the fragment states. The relevant ensembles representing the isolated and bonded molecular subsystems will be identified and fragment density matrices, for the pure state of the whole system, will be introduced.

2. Density Partition/Combination Problem

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

$$\rho(\mathbf{r}) = \sum_\alpha \rho_\alpha(\mathbf{r}) = \sum_\alpha N_\alpha p_\alpha(\mathbf{r}), \qquad (1)$$

e.g., Atoms-in-Molecules (AIM), substrate/products in reactive system, functional groups, etc. This general density *partition* scheme can be thus reversely interpreted as the associated *combination* rule for reconstructing the molecular electron distribution from its fragment densities.

As also argued in Eq. (1), any division of the molecular electron density implies the associated partition of its (normalized) probability factor $p(\mathbf{r})$, $\int p(\mathbf{r})d\mathbf{r} = 1$, the shape-factor of the density, into the separately normalized subsystem distributions $\{p_\alpha(\mathbf{r})\}$, $\int p_\alpha(\mathbf{r})d\mathbf{r} = 1$, giving rise to the reconstruction formula

$$\sum_\alpha P_\alpha p_\alpha(\mathbf{r}) = p(\mathbf{r}), \qquad (2)$$

where the condensed fragment probability $P_\alpha = N_\alpha/N$. The overall probability normalization then indeed reflects the combined normalizations of the global $\{P_\alpha\}$ and local $\{p_\alpha(\mathbf{r})\}$ probability factors of molecular subsystems:

$$\int p(\mathbf{r})\, d\mathbf{r} = (\sum_\alpha P_\alpha)\, [\int p_\alpha(\mathbf{r})\, d\mathbf{r}] = 1. \qquad (3)$$

As an illustration, consider now the simplest case of the partitioning into two complementary fragments $\alpha \in \{A, B\}$, e.g., AIM in a diatomic molecule M = A—B or the acidic (A) and basic (B) reactants in the reactive (acceptor-donor) complex R = [A----B]. The additive partition principle of Eq. (1),

$$\rho(\mathbf{r}) = \rho_A(\mathbf{r}) + \rho_B(\mathbf{r}), \qquad (4)$$

then translates into the associated probability division/combination rule:

$$p(\boldsymbol{r}) = P_{\mathrm{A}}\, p_{\mathrm{A}}(\boldsymbol{r}) + P_{\mathrm{B}}\, p_{\mathrm{B}}(\boldsymbol{r}). \tag{5}$$

The latter correctly describes the *mutual-opening* of both fragments, e.g., in the equilibrium molecular system $\mathrm{M}^* = (\mathrm{A}^*\vert\mathrm{B}^*)$ or in the reactive complex $\mathrm{R}^* = [\mathrm{A}^*\vert\mathrm{B}^*]$, for the mutually *open* subsystems containing the fractional numbers $\{N_\alpha{}^*\}$ of electrons, when their probability distributions equalize at the global density:

$$\{p_\alpha{}^*(\boldsymbol{r}) = p(\boldsymbol{r})\} \quad \text{and} \quad \{\rho_\alpha{}^*(\boldsymbol{r}) = N_\alpha{}^*\, p(\boldsymbol{r})\}. \tag{6}$$

Indeed, the relevant probability combination rule then reads:

$$p(\boldsymbol{r}) = P_{\mathrm{A}}\, p_{\mathrm{A}}{}^*(\boldsymbol{r}) + P_{\mathrm{B}}\, p_{\mathrm{B}}{}^*(\boldsymbol{r}) = (P_{\mathrm{A}} + P_{\mathrm{B}})\, p(\boldsymbol{r}). \tag{7}$$

The openness of both fragments indeed implies that their electrons explore the whole molecular distribution, so that they become indistinguishable.

As an illustrative example consider the "stockholder" partitioning,

$$\rho_\alpha{}^{\mathrm{H}}(\boldsymbol{r}) = \rho_\alpha{}^0(\boldsymbol{r})\, [\rho(\boldsymbol{r})/\rho^0(\boldsymbol{r})] \equiv \rho_\alpha{}^0(\boldsymbol{r})\, w(\boldsymbol{r}) = [\rho_\alpha{}^0(\boldsymbol{r})/\rho^0(\boldsymbol{r})]\, \rho(\boldsymbol{r}) \equiv s_\alpha{}^0(\boldsymbol{r})\rho(\boldsymbol{r}),$$
$$\textstyle\sum_\alpha \rho_\alpha{}^{\mathrm{H}}(\boldsymbol{r}) = \rho(\boldsymbol{r}), \tag{8}$$

where $w(\boldsymbol{r})$ and $s_\alpha{}^0(\boldsymbol{r})$ denote the Hirshfeld (H) *enhacement* and *share* factors, respectively. Therefore, in this partition scheme all isolated-atom densities $\{\rho_\alpha{}^0(\boldsymbol{r})\}$ are equally (molecularly) enhanced, and each AIM participates in the molecular "profit" $\rho(\boldsymbol{r})$ proportionally to its promolecular "share" $s_\alpha{}^0(\boldsymbol{r})$.

This division principle was shown to have a strong information theoretic (IT) justification [9-17]. The overall reference distribution,

$$\rho^0(\boldsymbol{r}) = \textstyle\sum_\alpha \rho_\alpha{}^0(\boldsymbol{r}), \qquad \int \rho^0(\boldsymbol{r})\, d\boldsymbol{r} = \int \rho(\boldsymbol{r})\, d\boldsymbol{r} = N, \tag{9}$$

represents the system atomic "promolecule" M^0 consisting of the isolated-atom densities shifted to the molecular atomic positions.

This reference state also defines the associated condensed probabilities $\{P_\alpha{}^0 = N_\alpha{}^0/N\}$ and the subsystem-normalized distributions:

$$\{p_\alpha{}^0(\boldsymbol{r}) = \rho_\alpha{}^0(\boldsymbol{r})/N_\alpha{}^0, \qquad N_\alpha{}^0 = \int \rho_\alpha{}^0(\boldsymbol{r})\, d\boldsymbol{r}\}. \tag{10}$$

For the Hirshfeld fragment α^{H} this (normalized) probability distribution thus reads:

$$p_\alpha{}^{\mathrm{H}}(\boldsymbol{r}) = \rho_\alpha{}^{\mathrm{H}}(\boldsymbol{r})/N_\alpha{}^{\mathrm{H}} = [\rho_\alpha{}^0(\boldsymbol{r})/N_\alpha{}^{\mathrm{H}}]\, w(\boldsymbol{r}) = s_\alpha{}^0(\boldsymbol{r})\, [\rho(\boldsymbol{r})\,/N_\alpha{}^{\mathrm{H}}], \qquad N_\alpha{}^{\mathrm{H}} = \int \rho_\alpha{}^{\mathrm{H}}(\boldsymbol{r})\, d\boldsymbol{r}, \qquad \int p_\alpha{}^{\mathrm{H}}(\boldsymbol{r})\, d\boldsymbol{r} = 1. \tag{11}$$

Its molecular analog,

$$p_\alpha(\boldsymbol{r}) \equiv \rho_\alpha{}^{\mathrm{H}}(\boldsymbol{r})/N = P_\alpha{}^{\mathrm{H}}\, [\rho_\alpha{}^{\mathrm{H}}(\boldsymbol{r})/N_\alpha{}^{\mathrm{H}}] = P_\alpha{}^{\mathrm{H}}\, p_\alpha{}^{\mathrm{H}}(\boldsymbol{r}) = P_\alpha{}^0\, [\rho_\alpha{}^{\mathrm{H}}(\boldsymbol{r})/N_\alpha{}^0] = [P_\alpha{}^0\, p_\alpha{}^0(\boldsymbol{r})]\, w(\boldsymbol{r}), \tag{12}$$

is then normalized to the subsystem condensed probability in the whole system:

$$\int p_\alpha(\boldsymbol{r})\, d\boldsymbol{r} = N_\alpha{}^{\mathrm{H}}/N = P_\alpha{}^{\mathrm{H}}.$$

It fulfills the probability-combination rule of Eq. (2) [see also Eq, (5)]:

$$\textstyle\sum_\alpha p_\alpha(\boldsymbol{r}) = \sum_\alpha P_\alpha{}^{\mathrm{H}}\, p_\alpha{}^{\mathrm{H}}(\boldsymbol{r}) = \sum_\alpha (N_\alpha{}^{\mathrm{H}}/N)\, [\rho_\alpha{}^{\mathrm{H}}(\boldsymbol{r})/N_\alpha{}^{\mathrm{H}}] = [\sum_\alpha \rho_\alpha{}^{\mathrm{H}}(\boldsymbol{r})]/N = \rho(\boldsymbol{r})/N = p(\boldsymbol{r}). \tag{13}$$

Therefore, for the fixed molecular density $\rho(\boldsymbol{r})$ and its promolecular reference $\rho^0(\boldsymbol{r})$, and hence also for the fixed $p(\boldsymbol{r}) = \rho(\boldsymbol{r})/N$ and $p^0(\boldsymbol{r}) = \rho^0(\boldsymbol{r})/N$, the determination of the optimum (Hirshfeld) fragment distributions amounts to finding the best (unbiased) probability distributions of subsystems: the internal (fragment-normalized) "shape" factors

$$\boldsymbol{p}^{\mathrm{H}}(\boldsymbol{r}) = \{p_\alpha{}^{\mathrm{H}}(\boldsymbol{r}) = \rho_\alpha{}^{\mathrm{H}}(\boldsymbol{r})/N_\alpha{}^{\mathrm{H}}, \qquad \int p_\alpha{}^{\mathrm{H}}(\boldsymbol{r})\, d\boldsymbol{r} = 1\} \tag{14}$$

or the molecularly-normalized distributions

$$\boldsymbol{p}(\boldsymbol{r}) = \{p_\alpha(\boldsymbol{r}) = \rho_\alpha{}^{\mathrm{H}}(\boldsymbol{r})/N, \qquad \int p_\alpha(\boldsymbol{r})\, d\boldsymbol{r} = N_\alpha{}^{\mathrm{H}}/N = P_\alpha{}^{\mathrm{H}}\}, \tag{15}$$

which most resemble their respective analogs in the isoelectronic promolecule:

$$N^0 = \int \rho^0(\boldsymbol{r})\, d\boldsymbol{r} = \int \rho(\boldsymbol{r})\, d\boldsymbol{r} = N. \tag{16}$$

3. Information-Theoretic Justification of Stockholder Principle

A reference to Eq. (8) shows that the stockholder pieces $\{\rho_\alpha{}^{\mathrm{H}}(\boldsymbol{r})\}$ of the molecular electron density $\rho(\boldsymbol{r})$ are shaped by the optimum (local) AIM conditional probabilities of finding at $\boldsymbol{r}$ an electron attributed to fragment α, $\boldsymbol{P}^{\mathrm{H}}(\boldsymbol{r}) \equiv \{P(\alpha^{\mathrm{H}}|\boldsymbol{r})\}$, reflected by the subsystem share factors

$$s_\alpha{}^{\mathrm{H}}(\boldsymbol{r}) = \rho_\alpha(\boldsymbol{r})^{\mathrm{H}}/\rho(\boldsymbol{r}) \equiv P(\alpha^{\mathrm{H}}|\boldsymbol{r}) = \rho_\alpha{}^0(\boldsymbol{r})/\rho^0(\boldsymbol{r}) = s_\alpha{}^0({}^{opt.}\boldsymbol{r}) \equiv P(\alpha^0|\boldsymbol{r}). \tag{17}$$

For the given electron position $\boldsymbol{r}$ their maximum silmilarity to the corresponding reference probabilities $\boldsymbol{P}^0(\boldsymbol{r}) \equiv \{P(\alpha^0|\boldsymbol{r})\}$ in the atomic promolecule, eventually amounting to the identity of both probability vectors,

$$\boldsymbol{P}^{\mathrm{H}}(\boldsymbol{r}) = \boldsymbol{P}^0(\boldsymbol{r}), \qquad \textstyle\sum_\alpha P(\alpha^0|\boldsymbol{r}) = \sum_\alpha P(\alpha^{\mathrm{H}}|\boldsymbol{r}) = 1, \tag{18}$$

is assured by the minimum, vanishing value of the *local* entropy-deficiency between the trial $\boldsymbol{P}(\boldsymbol{r}) = \{P(\alpha|\boldsymbol{r})\}$ and promolecular sets of conditional-probability densities,

$$\Delta S[\boldsymbol{P}(\boldsymbol{r})|\boldsymbol{P}^0(\boldsymbol{r})] = \textstyle\sum_\alpha P(\alpha|\boldsymbol{r}) \ln[P(\alpha|\boldsymbol{r})/P(\alpha^0|\boldsymbol{r})] = \mathit{minimum}, \tag{19}$$

subject to the normalization condition $\sum_\alpha P^{opt.}(\alpha|\boldsymbol{r}) = 1$ [see Eq. (18)] of the optimum conditional probabilities [9-11]:

$$\delta\{\Delta S[\boldsymbol{P}(\boldsymbol{r})|\boldsymbol{P}^0(\boldsymbol{r})] - \lambda \textstyle\sum_\alpha P(\alpha|\boldsymbol{r})\}^{opt.} = 0 \qquad \Rightarrow \qquad \boldsymbol{P}^{opt.}(\boldsymbol{r}) = \boldsymbol{P}^0(\boldsymbol{r}). \tag{20}$$

Above λ denotes the Lagrange multiplier enforcing this local normalization constraint.

Indeed, the vanishing partial derivative of the above subsidiary entropy density with respect to the unknown $P(\alpha|\boldsymbol{r})$ gives the following Euler equation:

$$\ln[P^{opt.}(\alpha|\boldsymbol{r})/P(\alpha^0|\boldsymbol{r})] + (1-\lambda) \equiv \ln\{P^{opt.}(\alpha|\boldsymbol{r})/[CP(\alpha^0|\boldsymbol{r})]\} = 0, \qquad C = \exp(\lambda - 1), \tag{21}$$

or

$$P^{opt.}(\alpha|\boldsymbol{r}) = CP(\alpha^0|\boldsymbol{r}) = P(\alpha^0|\boldsymbol{r}) = s_\alpha{}^0(\boldsymbol{r}) = s_\alpha{}^{\mathrm{H}}(\boldsymbol{r}), \tag{22}$$

since from the constraint value

$$\sum_\alpha P^{opt.}(\alpha|\boldsymbol{r}) = C \sum_\alpha P(\alpha^0|\boldsymbol{r}) = C = 1. \tag{23}$$

The optimum (stockholder) densities $\boldsymbol{\rho}^{\mathrm{H}}(\boldsymbol{r}) = \{\rho_\alpha^{\mathrm{H}}(\boldsymbol{r})\}$ of AIM also result from the *integral* entropic principle [9-11, 14, 16, 17], determining the minimum overall information distance between the optimized atomic densities $\boldsymbol{\rho}(\boldsymbol{r}) = \{\rho_\alpha(\boldsymbol{r})\}$ and their known promolecular analogs $\boldsymbol{\rho}^0(\boldsymbol{r}) = \{\rho_\alpha^0(\boldsymbol{r})\}$, subject to the exhaustive division constraint $\sum_\alpha \rho_\alpha(\boldsymbol{r}) = \rho(\boldsymbol{r})$:

$$\delta\{\Delta S[\boldsymbol{\rho}|\boldsymbol{\rho}^0] - \int \lambda(\boldsymbol{r}) \sum_\alpha \rho_\alpha(\boldsymbol{r})\, d\boldsymbol{r}\} = 0 \quad \Rightarrow \quad \boldsymbol{\rho}(\boldsymbol{r}) = \boldsymbol{\rho}^{\mathrm{H}}(\boldsymbol{r}). \tag{24}$$

The stockholder pieces of the molecular electron density also minimize the nonadditive part of the entropy deficiency, between the promolecular (nobonded) and molecular (bonded) atomic densities [9-11]. The Hirshfeld partition rule can be also extended to include the least biased partitioning of the molecular *many*-electron densities [14, 15].

4. Isoelectronic AIM and Mixed States of Atomic Fragments

The molecular and promolecular AIM distributions correspond to the *mixed* quantum states of these atomic subsystems, which cannot be described by single wavefunction [14]. The statistical mixtures of the *pure* quantum states of isolated subsystems are specified by the relevant density operators defined by the corresponding state *probabilities*, e.g., those reflecting the imposed thermodynamic conditions.

In the promolecular ensemble the statistical mixture of atomic wavefunctions must involve the same (condensed) probability P_α^0 for all states contributed by the *free*-atom α^0. In the orbital approximation its ground-state configuration

$$\Psi_\alpha(N_\alpha^0) = \langle \boldsymbol{r}|\alpha^0\rangle = \det(\boldsymbol{\psi}_\alpha^0) \tag{25}$$

is determined by N_α^0 (*singly*-occupied) molecular orbitals (MO):

$$\boldsymbol{\psi}_\alpha^0(\boldsymbol{r}) = \{\psi_s(\boldsymbol{r}; \alpha^0) \equiv \langle \boldsymbol{r}|s(\alpha^0)\rangle, \qquad s = 1, 2, \ldots, N_\alpha^0\}. \tag{26}$$

The *promolecular* MO-ensemble is thus defined by the density operator

$$\mathrm{D}^0 = \mathrm{D}(\mathrm{M}^0) = \sum_\alpha P_\alpha^0\, [(N_\alpha^0)^{-1} \sum_s |s(\alpha^0)\rangle\langle s(\alpha^0)|] \equiv \sum_\alpha |\alpha^0\rangle\, P_\alpha^0\, \langle \alpha^0| \equiv \sum_\alpha P_\alpha^0\, \mathrm{P}(\alpha^0), \tag{27}$$

where

$$\mathrm{P}(\alpha^0) = (N_\alpha^0)^{-1} \sum_s |s(\alpha^0)\rangle\langle s(\alpha^0)| = |\alpha^0\rangle\langle\alpha^0| \tag{28}$$

is the projection operator onto the electronic subspace spanned by the ground-state occupied MO of atom α^0, $|s(\alpha^0)\rangle$ denotes the s-th MO state in the molecularly-placed atom α^0 with $\langle \boldsymbol{r}|s(\alpha^0)\rangle = \psi_s(\boldsymbol{r}; \alpha^0)$ standing for its wavefunction analog. In this position representation D^0 defines the promolecular probability density:

$$\begin{aligned} D^0(\boldsymbol{r}) = \langle \boldsymbol{r}|\mathrm{D}^0|\boldsymbol{r}\rangle &= \sum_\alpha \langle \boldsymbol{r}|\alpha^0\rangle\, P_\alpha^0\, \langle \alpha^0|\boldsymbol{r}\rangle = \sum_\alpha P_\alpha^0\, [(N_\alpha^0)^{-1} \sum_s \langle \boldsymbol{r}|s(\alpha^0)\rangle\langle s(\alpha^0)|\boldsymbol{r}\rangle] \\ &= \sum_\alpha P_\alpha^0\, [(N_\alpha^0)^{-1} \sum_s |\psi_s(\boldsymbol{r}; \alpha^0)|^2] = \sum_\alpha P_\alpha^0\, [\rho_\alpha^0(\boldsymbol{r})/N_\alpha^0] = \sum_\alpha P_\alpha^0\, p_\alpha^0(\boldsymbol{r}) = p^0(\boldsymbol{r}). \end{aligned} \tag{29}$$

Let us now define an analogous ensemble of the promolecular atomic states, which represents the bonded (stockholder) AIM. One first realizes that the Hirshfeld electron distributions $\{\rho_\alpha^{\mathrm{H}}\}$, while conserving the molecular density $\rho(\boldsymbol{r})$ and hence also the overall number of electrons N, give rise to the finite effective electron transfers between the chemically-bonded atoms, since the (*fractional*) AIM occupations $\boldsymbol{N}^{\mathrm{H}} = \{N_\alpha^{\mathrm{H}}\}$ differ from the corresponding (*integer*) numbers of electrons in isolated fragments:

$$N_\alpha^{\mathrm{H}} = \int \rho_\alpha^{\mathrm{H}} d\boldsymbol{r} = N P_\alpha^{\mathrm{H}} \neq N_\alpha^0 = \int \rho_\alpha^0 d\boldsymbol{r} = N P_\alpha^0 \quad \text{or} \quad P_\alpha^{\mathrm{H}} \neq P_\alpha^0. \tag{30}$$

In various chemical considerations one also discusses the integer electron transfers, corresponding to the reference ("formal") oxidations or reductions of atomic or molecular fragments. The atomic occupations then correspond to some hypothetical (integer) numbers of electrons $\{N_\alpha^{(i)}\}$, each conserving the overall electron number in the molecule as a whole: $\sum_\alpha N_\alpha^{(i)} = N$. The densities for such i-th hypothesis can be obtained by a straightforward renormalization scaling of the Hirshfeld distributions:

$$\rho_\alpha^{(i)}(\boldsymbol{r}) = (N_\alpha^{(i)}/N_\alpha^{\mathrm{H}})\, \rho_\alpha^{\mathrm{H}}(\boldsymbol{r}) = N_\alpha^{(i)}\, p_\alpha^{\mathrm{H}}(\boldsymbol{r}), \qquad \int \rho_\alpha^{(i)}(\boldsymbol{r})\, d\boldsymbol{r} = N_\alpha^{(i)}. \tag{31}$$

In particular, by setting $\{N_\alpha^{(i)} = N_\alpha^0\}$ one determines electron densities in the *isoelectronic* (*ie*) stockholder atoms:

$$\rho_\alpha^{ie}(\boldsymbol{r}) = N_\alpha^0\, p_\alpha^{\mathrm{H}}(\boldsymbol{r}) = \rho_\alpha^0(\boldsymbol{r})\, [(N_\alpha^0/N_\alpha^{\mathrm{H}})\, w(\boldsymbol{r})] \equiv \rho_\alpha^0(\boldsymbol{r})\, w_\alpha^{ie}(\boldsymbol{r}), \qquad N_\alpha^{ie} = \int \rho_\alpha^{ie}(\boldsymbol{r})\, d\boldsymbol{r} \equiv N_\alpha^0. \tag{32}$$

The isoelectronic AIM thus conserve the local Hirshfeld probabilities and they equalize the condensed stockholder and promolecular probabilities:

$$\{p_\alpha^{ie}(\boldsymbol{r}) = p_\alpha^{\mathrm{H}}(\boldsymbol{r})\}, \qquad \{P_\alpha^{ie} = P_\alpha^0\}. \tag{33}$$

They generate the overall electron density

$$\rho^{ie}(\boldsymbol{r}) = \sum_\alpha \rho_\alpha^{ie}(\boldsymbol{r}) \tag{34}$$

reflecting the *probability* (shape) polarization in Hirshfeld's AIM, for their conserved electron numbers. They define the associated overall probability distribution

$$p^{ie}(\boldsymbol{r}) = \rho^{ie}(\boldsymbol{r})/N = \sum_\alpha P_\alpha^0\, p_\alpha^{\mathrm{H}}(\boldsymbol{r}). \tag{35}$$

In order to introduce the *molecular* MO-ensemble we refer to Eq. (29). The common, atom-independent enhancement factor $w(\boldsymbol{r})$ for atomic densities of isolated atoms in stockholder distributions, $\rho_\alpha^{\mathrm{H}}(\boldsymbol{r}) = \rho_\alpha^0(\boldsymbol{r})\, w(\boldsymbol{r})$, is seen to imply the atom-dependent enhancements in isoelectronic AIM:

$$\rho_\alpha^{ie}(\boldsymbol{r}) = \rho_\alpha^0(\boldsymbol{r})\, w_\alpha^{ie}(\boldsymbol{r}) \quad \text{or} \quad p_\alpha^{ie}(\boldsymbol{r}) = p_\alpha^0(\boldsymbol{r})\, w_\alpha^{ie}(\boldsymbol{r}) = p_\alpha^{\mathrm{H}}(\boldsymbol{r}). \tag{36}$$

Moreover, the probability densities of the isolated and isoelectronic atoms can be both expressed in terms of their related orbital contributions [see Eq. (29)], due to the singly occupied MO $\{\psi_s(\boldsymbol{r}; \alpha^0)\}$ of Eq. (26) and the (normalized) "enhanced" MO [see Eq. (36)],

$$\psi_s(\boldsymbol{r}; \alpha^{ie}) = \langle \boldsymbol{r}|s(\alpha^{ie})\rangle = R_s^{ie}\, [w_\alpha^{ie}(\boldsymbol{r})]^{1/2}\, \psi_s(\boldsymbol{r}; \alpha^0) \equiv R_s^{ie}\, \varphi_s(\boldsymbol{r}; \alpha^{ie}), \qquad R_s^{ie} = \langle \varphi_s(\alpha^{ie})|\varphi_s(\alpha^{ie})\rangle^{-1/2}, \tag{37}$$

$$p_\alpha^0(\boldsymbol{r}) = (N_\alpha^0)^{-1} \sum_s |\psi_s(\boldsymbol{r}; \alpha^0)|^2 \quad \text{and} \quad p_\alpha^{ie}(\boldsymbol{r}) = (N_\alpha^0)^{-1} \sum_s |\psi_s(\boldsymbol{r}; \alpha^{ie})|^2 = p_\alpha^{\mathrm{H}}(\boldsymbol{r}). \tag{38}$$

These locally scaled MO of isoelectronic bonded atoms ultimately define the MO density operator of the Hirshfeld AIM,

$$\mathrm{D}^{\mathrm{H}} = \mathrm{D}^{\mathrm{H}}(\mathrm{M}) = \sum_\alpha P_\alpha^0\, [\sum_s |s(\alpha^{ie})\rangle\langle s(\alpha^{ie})|] \equiv \sum_\alpha P_\alpha^0\, |\alpha^{ie}\rangle\langle\alpha^{ie}| \equiv \sum_\alpha P_\alpha^0\, \mathrm{P}(\alpha^{ie}), \tag{39}$$

where

$$\mathrm{P}(\alpha^{ie}) = \Sigma_s |s(\alpha^{ie})\rangle\langle s(\alpha^{ie})| = |\alpha^{ie}\rangle\langle\alpha^{ie}| \qquad (40)$$

denotes the projection onto the electronic subspace spanned by the ground-state (singly) occupied MO of atom α^{ie}. The position representation of the density operator D^{H} then represents the molecular probability distribution [see Eq. (35)]:

$$D^{\mathrm{H}}(\boldsymbol{r}) = \langle\boldsymbol{r}|\mathrm{D}^{\mathrm{H}}|\boldsymbol{r}\rangle = \Sigma_\alpha \langle\boldsymbol{r}|\alpha^{ie}\rangle\, P_\alpha^{\;0}\, \langle\alpha^{ie}|\boldsymbol{r}\rangle = \Sigma_\alpha P_\alpha^{\;0}\, [(N_\alpha^{\;0})^{-1}\Sigma_s \langle\boldsymbol{r}|s(\alpha^{ie})\rangle\langle s(\alpha^{ie})|\boldsymbol{r}\rangle]$$
$$= \Sigma_\alpha P_\alpha^{\;0}\, [(N_\alpha^{\;0})^{-1}\, \Sigma_s |\psi_s(\boldsymbol{r};\alpha^{ie})|^2] = \Sigma_\alpha P_\alpha^{\;0}\, p_\alpha^{\;\mathrm{H}}(\boldsymbol{r}) = p^{ie}(\boldsymbol{r}). \qquad (41)$$

To summarize, the interacting molecular fragments are described by the corresponding ensembles of the occupied MO in the ground states of constituent free atoms. This is also true for the embedded substrates in the pure quantum state of the reactive system as a whole. The subsystem physical descriptors are then given by the ensemble-averages of the property operators, determined by partial traces involving the fragment density matrices.

5. Density Matrices of Interacting Subsystems

In describing the mixed states of complexes of interacting subsystems it is useful to apply the density matrix formalism of QM [40, 41]. Consider again the complementary acid(A) and base(B) reactants $\mathrm{X} \in (\mathrm{A}, \mathrm{B})$, in the polarized acceptor-donor reactive system of Section 2,

$$\mathrm{R}^+ = [\mathrm{A}^+(x)\,|\,\mathrm{B}^+(\xi)], \qquad (42)$$

where x and ξ denote their sets of internal coordinates, respectively.

The physical properties of subsystems are represented by the corresponding quantum operators acting on their internal degrees-of-freedom. The mutually-closed fragments of R^+ conserve the (integer) number of electrons in isolated subsystems, $\{N_\mathrm{X}^{\;+} = N_\mathrm{X}^{\;0}\}$, so that their molecular Hamiltonians in the Born-Oppenheoimer approximation,

$$\{\mathrm{H}_\mathrm{X}(N_\mathrm{X})_v \equiv \mathrm{H}_\mathrm{X}(N_\mathrm{X})\}, \qquad (43)$$

are well defined. Here,

$$v(\boldsymbol{r}) = v_\mathrm{A}(\boldsymbol{r}) + v_\mathrm{B}(\boldsymbol{r}), \qquad (44)$$

denotes the molecular external potential, due to the fixed nuclei in both reactants, and the interacting-fragment Hamiltonian $\mathrm{H}_\mathrm{X}(N_\mathrm{X})$ acts on the position variables of the $N_\mathrm{X}^{\;0}$ electrons belonging to X^+. Moreover, since R^+ is assumed to represent an isolated system, it will be described by the specific wavefunction $\psi(x, \xi)$, the *pure* quantum state of the whole R^+.

The mutually-closed reactants in R^+ determine the separate complete sets of the stationary states in subsystems. For example, the fixed-energy states of $\mathrm{H}_\mathrm{A}(N_\mathrm{A}^{\;0}) \equiv \mathrm{H}_\mathrm{A}(x)$,

$$\mathrm{H}_\mathrm{A}(x)\, \varphi_s(x) = E_s(\mathrm{A}^+)\, \varphi_s(x), \qquad (45)$$

are capable of expanding the "molecular" state $\psi(x, \xi)$ of the whole reactive system:

$$\Psi(x, \xi) = \Sigma_s\, \Phi_s(\xi)\, \varphi_s(x), \qquad \Phi_s(\xi) = \int \varphi_s^{\;*}(x)\, \Psi(x, \xi)\, dx. \qquad (46)$$

The quantum operator of the physical property $L(\mathrm{A}) = \mathrm{L}_x$ of subsystem A^+ will act only on variables x. Its average value in the pure state $\psi(x, \xi)$ of the reactive system as a whole then reads:

$$\langle L\rangle_\psi = \iint \psi^*(x, \xi)\, \mathrm{L}_x\, \psi(x, \xi)\, dx\, d\xi = \Sigma_s\Sigma_{s'}\, [\int \Phi_{s'}^{\;*}(\xi)\, \Phi_s(\xi)\, d\xi]\, [\int \varphi_{s'}^{\;*}(x)\, \mathrm{L}_x\, \varphi_s(x)\, dx]$$
$$\equiv \Sigma_s\Sigma_{s'}\, \rho_{s,s'}(\mathrm{A})\, L_{s',s}\, (\mathrm{A}) = \mathrm{tr}_\mathrm{A}[\boldsymbol{\rho}(\mathrm{A})\, \mathbf{L}(\mathrm{A})]. \qquad (47)$$

Here $\boldsymbol{\rho}(\mathrm{A}) = \{\rho_{s',s}(\mathrm{A})\}$ stands for the effective density matrix of subsystem $\mathrm{A}^+(x)$, already integrated over coordinates of electrons in the complementary subsystem $\mathrm{B}^+(\xi)$. The partial trace of the preceding equation thus enables one to calculate the ensemble average of the subsystem quantity $L(\mathrm{A})$ 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 stationary representation $\{\varphi_s(x)\}$ of A^+.

Finally, writing the preceding equation in the subsystem position representation,

$$\langle L\rangle_\psi = \iint \rho_\mathrm{A}(x, x')\, \langle x'|\mathrm{L}_x|x\rangle\, dx\, dx', \qquad (48)$$

where

$$\langle x'|\mathrm{L}_x|x\rangle = \mathrm{L}_x \delta(x' - x), \qquad (49)$$

gives the following expression for the subsystem density matrix:

$$\rho_\mathrm{A}(x, x') = \int \psi^*(x', \xi)\, \psi(x, \xi)\, d\xi = \Sigma_s\Sigma_{s'}\, \rho_{s,s'}(\mathrm{A})\, \varphi_{s'}^{\;*}(x')\, \varphi_s(x)$$
$$\equiv \Sigma_s\Sigma_{s'}\, \rho_{s,s'}(\mathrm{A})\, \Omega_{s',s}(x, x') = \mathrm{tr}_\mathrm{A}[\boldsymbol{\rho}(\mathrm{A})\, \boldsymbol{\Omega}_\mathrm{A}(x, x')]. \qquad (50)$$

These ensemble expectation values of subsystem operators in the mixed quantum states are independent of the applied representation. The corresponding dynamics of the partial density matrix is also determined by the molecular Schrödinger equation.

To conclude, the polarized (interacting) reactants $\{\mathrm{X}^+\}$ in R^+ cannot be described by a single wavefunction, i.e., the *pure* quantum state. They have to be instead characterized by the density matrix reflecting an incoherent mixture of subsystem states, weighted by the ensemble probability factors. The bonded AIM in both polarized fragments $\{\mathrm{X}^+\}$ and the equilibrium parts of the whole (molecular) reactive system

$$\mathrm{R}^* = [\mathrm{A}^*(x)\,\text{¦}\,\mathrm{B}^*(\xi)] \equiv \mathrm{M} \qquad (51)$$

containing the mutually-open substrates $\{\mathrm{X}^*\}$, provide other chemical examples of such entangled subsystems.

6. Conclusion

Several intuitive concepts of chemistry still require more rigorous definitions in the molecular QM. Indeed, the exact semantics of chemical bonds, AIM, reactants and molecular fragments in general, the entangled quantum subsystems, still escapes such an exact description. This paper has argued that such interacting molecular pieces cannot be described by the *pure* quantum states. Instead, they have been shown to be in the *mixed* states, which require an ensemble description invoking density operators and density matrices of subsystems.

The density/probability partition/combination rules have been illustrated using the popular stockholder division scheme of Hirshfeld. Its IT justification, in terms of the constrained minimum principles of local and global entropy-deficiency (information-distance) quantities has been summarized and the relevant MO-ensembles, for the isolated and (isoelectronic) Hirshfeld atoms, respectively, have been identified. The former generates the promolecular electron density while the latter gives rise to the molecular electron distribution. We have also explicitly demonstrated that in the *pure* quantum state of the molecular system as a whole its fragments are in the effective *mixed* states thus requiring an ensemble representation.

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