Information Theoretic Approach to Fluctuations and Electron Flows between Molecular Fragments

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The elements of the information theoretic approach to instantaneous electron distributions between molecular subsystems are developed by following the thermodynamic theory of fluctuations and irreversible processes. The distribution function and information theoretic basis of the stockholder partitioning, defining the equilibrium distributions of electrons among subsystems, are briefly summarized. The nonequilibrium (instantaneous) local entropy deficiency and the state parameters and their associated intensive conjugates in the entropy deficiency representation are introduced using the promolecule-referenced local measures of the information distance (entropy deficiency) of Kullback and Leibler between the instantaneous subsystem electron densities, conserving the overall molecular density and the free or Hirshfeld subsystem electron densities, respectively. Within a local description, the Gaussian distribution function of Einstein's theory is introduced, predicting a local dispersion of the subsystem density to be proportional to the molecular density and the square root of the free subsystem share in the promolecule density. The key concepts of the local irreversible thermodynamics of molecular subsystems are introduced for alternative information theoretic entropy-deficiency representations. They include the corresponding affinities (forces) and the conjugate fluxes (response quantities), which together determine the local entropy deficiency source. The Onsager reciprocity relations are derived and justified through fluctuations.

1. Introduction

The problem of partitioning a given molecular density into pieces representing molecular fragments (e.g., those of the bonded atoms in a molecule) has recently been given an unbiased, information theoretic description, much in the spirit of the phenomenological thermodynamic approach,[1] in terms of bonded fragments, which retain as much as possible the information contained in the free atoms defining the promolecule.[2] It has been demonstrated that, in accordance with the basic proposition of information theory, independently of the information-distance measure applied (e.g., the entropy deficiency (missing information) of Kullback and Leibler[3]), the Hirshfeld[2] stockholder partitioning appears as the entropic equilibrium scheme.[4−7] These stockholder subsystems represent the bonded molecular fragments, which most resemble the free subsystems, and they exhibit appealing local information-distance equalization rules.[3b−7] In such a thermodynamic-like description, the information theory[3,8] provides the local entropy representation,[4,5] complementary to the familiar energy representation emphasized in most of the theories of the electronic structure.

Combining this information theoretic approach with the density functional theory[9,10] results in a thermodynamic-like description of equilibria in molecules and their constituent fragments,[4b,5] covering both the horizontal displacements, from one ground-state density to another and the vertical, internal displacements, for the fixed molecular density. Similar information-distance concepts have been used to extract the covalent and ionic bond multiplicities,[11] to design the molecular similarity criteria,[4a] to define the promoted (polarized) atoms in a molecule,[6] and to relate the surprisal analysis of electron densities in molecules to the familiar density-difference diagrams.[7] The information theory has also been used to define new descriptors of the donor−acceptor systems, which combine both the energy and information entropy derivatives,[5b−d,7] and the Hirshfeld stockholder division rule has been generalized to cover the unbiased partitioning of many-electron densities.[5a]

In chemistry, one is interested not only in the equilibrium distributions of electrons in molecules and their constituent fragments but also in processes characterized by rates. The conceptual structure of such a phenomenological dynamical description of the subsystem density fluctuations, determining their softness characteristics,[10] and instantaneous flows of electrons in molecules, in the spirit of the irreversible thermodynamics,[1] calls for two types of conjugate quantities: affinities, to describe the forces that drive a process, and fluxes, to describe the responses to these forces.

The main purpose of this work is to investigate the elements of such an instantaneous (nonequilibrium) approach to molecules and their subsystems. More specifically, we seek an extension of the previous, equilibrium information theoretic development into the nonequilibrium local-thermodynamic description of molecular subsystems, covering the instantaneous, fluctuating state parameters and providing them an appropriate information theoretic distribution function. The second moments of this distribution will be examined in some detail. In particular, the local dispersion of the instantaneous subsystem densities around the corresponding equilibrium (Hirshfeld) values will be linked to the overall molecular density and the subsystem share in the promolecule density. The square of this dispersion will be shown

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to be related to the subsystem local softness.[10] The elements of the irreversible thermodynamic, continuous description of the molecular-density-conserving flows of electrons between subsystems will be established, including the alternative definitions of affinities and fluxes, which together define the local entropy deficiency source. The corresponding Onsager reciprocity relations[1] will be derived and justified through fluctuations.

2. Distribution Function of Fluctuating State Variables

In ordinary thermodynamics[1] the instantaneous (i) extensive parameters $\{x_\alpha{}^{i}\}$ of systems in contact with the reservoirs (r) appropriate to a given set of the free parameters $\mathbf{x}^{i} \equiv (x_0{}^{i}, x_1{}^{i}, ..., x_s{}^{i})$ undergo continual fluctuations due to transfers between the system and the reservoirs. Their equilibrium values $\{x_\alpha\}$, predicted by the maximum entropy principle, are the average values denoted here by the $\langle\ \rangle$ brackets so that the average value of the deviation $\delta x_\alpha{}^{i} \equiv x_\alpha{}^{i} - x_\alpha$ vanishes by definition:

$$\langle x_\alpha{}^{i}\rangle \equiv x_\alpha \qquad \text{or} \qquad \langle \delta x_\alpha{}^{i}\rangle \equiv \langle x_\alpha{}^{i} - x_\alpha\rangle = 0 \qquad \alpha = 0, 1, 2, ..., s \tag{1}$$

The reservoirs are assumed to be restrictive with respect to the remaining variables $\mathbf{x}^{c} \equiv (x_{s+1}, ..., x_t)$, which are kept constant.

In the thermodynamic theory of fluctuations the average (or the most probable) values of state parameters are determined by the statistical distribution function $W(\mathbf{x})$ of all extensive parameters $\mathbf{x} \equiv (\mathbf{x}^{i}, \mathbf{x}^{c})$, which determines the probability

$$W(\mathbf{x})\, dx_0{}^{i}\, dx_1{}^{i} \ldots dx_s{}^{i} \equiv W(\mathbf{x})\, d\mathbf{x}^{i} = P(d\mathbf{x}^{i}) \tag{2}$$

that simultaneously $x_0{}^{i}$ will be found in the range of $dx_0{}^{i}$, $x_1{}^{i}$ will be found in the range of $dx_1{}^{i}$, etc., and $x_s{}^{i}$ will be found in the range of $dx_s{}^{i}$.

The thermodynamic distribution function $W(\mathbf{x})$ depends on the instantaneous entropy, a function of the system extensive parameters $S^{i}(\mathbf{x}) = S^{i}(\mathbf{x}^{i}, \mathbf{x}^{c})$, which assumes the equilibrium value $S(\mathbf{x})$ when the instantaneous extensive parameters are given their average, equilibrium values:

$$S(\mathbf{x}) \equiv \langle S^{i}(\mathbf{x}^{i}, \mathbf{x}^{c})\rangle = S^{i}(\langle \mathbf{x}^{i}\rangle, \mathbf{x}^{c}) = S^{i}(\mathbf{x}) \tag{3}$$

A separate postulate[1] specifies $W(\mathbf{x})$ as the exponential function of a displacement in the relevant Legendre transform of $S^{i}(\mathbf{x})$, the generalized Massieu function, which is appropriate for the actual reservoirs involved. More specifically, the probability $P(d\mathbf{x}^{i})$ for a system in contact with the reservoirs corresponding to the set $\mathbf{x}^{i}$ is given by

$$W(\mathbf{x}) = \Omega \exp(k_{B}{}^{-1}\{\delta\, [S^{i}(\mathbf{x}) - \sum_{\alpha} f_{\alpha}\, x_{\alpha}{}^{i}]\}) = \Omega \exp(k_{B}{}^{-1}[\delta S^{i}(\mathbf{x}) - \sum_{\alpha} f_{\alpha}\, \delta\, x_{\alpha}{}^{i}]) \tag{4}$$

Here, Ω is the normalizing constant such that

$$\int W(\mathbf{x})\, d\mathbf{x}^{i} = 1 \tag{5}$$

k_B is Boltzmann's constant, $\delta S^{i}(\mathbf{x}) = S^{i}(\mathbf{x}) - S(\mathbf{x})$, the sum is over fluctuating variables $x_\alpha{}^{i} \in \mathbf{x}^{i}$, $\{f_\alpha = f_\alpha{}^{r}\}$ are the system conjugate intensive parameters in the entropy representation, equalized at the corresponding reservoir values $\mathbf{f}^{r}$,

$$\mathbf{f} \equiv (f_0, ..., f_s) = \mathbf{f}^{r} \equiv (f_0{}^{r}, ..., f_s{}^{r}) = \frac{\partial S^{r}(\mathbf{x}^{r})}{\partial \mathbf{x}^{r}} \tag{6}$$

where $S^{r}(\mathbf{x}^{r})$ is the entropy function of the reservoirs, with $\mathbf{x}^{r}$ standing for their state parameters. The displacement function in the exponent of the distribution function of eq 4,

$$\begin{aligned}\delta[S^{i}(\mathbf{x}) - \sum_{\alpha} f_{\alpha} x_{\alpha}{}^{i}] &= [S^{i}(\mathbf{x}) - \sum_{\alpha} f_{\alpha}{}^{r} x_{\alpha}{}^{i}] - [S(\mathbf{x}) - \sum_{\alpha} f_{\alpha}{}^{r} x_{\alpha}] \\ &\equiv S^{i}(\mathbf{f}^{r}, \mathbf{x}^{c}) - S(\mathbf{f}^{r}, \mathbf{x}^{c}) = \delta S^{i}(\mathbf{x}) - \sum_{\alpha} f_{\alpha}\, \delta x_{\alpha}{}^{i}\end{aligned} \tag{7}$$

is defined with respect to the maximum value of the quantity in the square brackets of the preceding equation over the complete ranges of fluctuating variables:

$$S(\mathbf{f}^{r}, \mathbf{x}^{c}) = \max_{i}[S^{i}(\mathbf{x}^{i}, \mathbf{x}^{c}) - \sum_{\alpha} f_{\alpha}{}^{r} x_{\alpha}{}^{i}] = S(\mathbf{x}) - \sum_{\alpha} f_{\alpha}{}^{r} x_{\alpha} \tag{8}$$

Therefore, the quantity defined by eq 8 is no longer a function of the fluctuating extensive parameters $\mathbf{x}^{i}$, being instead solely determined by the corresponding intensive parameters of the reservoirs, $\mathbf{f}^{r}$, and the system-constrained extensive parameters, $\mathbf{x}^{c}$. In fact, it represents the Legendre transform of the equilibrium entropy[1] since the most probable values of $\mathbf{x}^{i}$ and $\mathbf{x}^{i*}$ (i.e., those maximizing W, a monotonically increasing function of the exponent $\delta[S^{i}(\mathbf{x}) - \sum_{\alpha} f_{\alpha} x_{\alpha}{}^{i}]$) are determined by the condition

$$S^{i}(\mathbf{x}^{i}, \mathbf{x}^{c}) - \sum_{\alpha} f_{\alpha}{}^{r} x_{\alpha}{}^{i} = \text{maximum} \tag{9}$$

Hence, the maximum of eq 8 occurs when the fluctuating variables have their equilibrium values, which, for macroscopic systems, are practically identical to the most probable values $\mathbf{x}^{i*}$ and $\langle \mathbf{x}^{i}\rangle = \mathbf{x}^{i*}$ because of the sharply peaked nature of the distribution function. The resulting ratio of the distribution width to the average value is to the inverse ($^1/_2$) power in the extensive parameters. The instantaneous entropy therefore takes the equilibrium value of eq 3, and thus eq 8 defines the Legendre transform of the equilibrium entropy, which corresponds to the replacement of the fluctuating extensive variables $\mathbf{x}^{i}$ by their entropy-intensive conjugates $\mathbf{f} = \mathbf{f}^{r}$ in the list of state parameters:

$$S(\mathbf{f}^{r}, \mathbf{x}^{c}) = S^{i}(\langle \mathbf{x}^{i}\rangle, \mathbf{x}^{c}) - \sum_{\alpha} f_{\alpha}{}^{r}\langle x_{\alpha}{}^{i}\rangle \equiv S[\mathbf{f}^{r}] \tag{10}$$

One also defines the Legendre transform of the instantaneous entropy (i.e., the instantaneous Massieu function)

$$S^{i}(\mathbf{f}^{i}, \mathbf{x}^{c}) = S^{i}(\mathbf{x}^{i}, \mathbf{x}^{c}) - \sum_{\alpha} f_{\alpha}{}^{i} x_{\alpha}{}^{i} \equiv S^{i}[\mathbf{f}^{i}] \tag{11}$$

where the entropic instantaneous intensive parameters are defined as the corresponding partial derivatives of the instantaneous entropy

$$\mathbf{f}^{i} = \frac{\partial S^{i}(\mathbf{x}^{i}, \mathbf{x}^{c})}{\partial \mathbf{x}^{i}} \tag{12}$$

Therefore, the equilibrium condition of eq 9 can be rephrased as follows: the equilibrium values of the unconstrained extensive parameters of a system in contact with reservoirs maximize $S^{i}[\mathbf{f}^{i}]$ at constant $\mathbf{f}^{i} = \mathbf{f}^{r}$.

In thermodynamics, the average values of the state parameters plus the full sets of moments are completely equivalent to the distribution itself.[1] It follows from the form of the distribution function of eq 4 that the thermodynamic fluctuation (second) moment is given by the expression[1]

$$\langle \delta x_\alpha^{\,\mathrm{i}}\, \delta x_\beta^{\,\mathrm{i}}\rangle = \int \delta x_\alpha^{\,\mathrm{i}}\, \delta x_\beta^{\,\mathrm{i}}\, W(\mathbf{x})\, \mathrm{d}\mathbf{x}^{\mathrm{i}} = -k_{\mathrm{B}}\left(\frac{\partial x_\alpha}{\partial f_\beta}\right)_{c(\beta)} = -k_{\mathrm{B}}\left(\frac{\partial x_\beta}{\partial f_\alpha}\right)_{c(\alpha)} \tag{13}$$

where the constraints $c(\beta) = (f_0, ..., f_{\beta-1}, f_{\beta+1}, ...\ f_s, \mathbf{x}^{\mathrm{c}}) \equiv (\mathbf{f}'_\beta, \mathbf{x}^{\mathrm{c}})$ and $c(\alpha) = (\mathbf{f}'_\alpha, \mathbf{x}^{\mathrm{c}})$. In particular, for $\alpha = \beta$, the mean-square deviation $\langle(\delta x_\alpha^{\mathrm{i}})^2\rangle = \langle(x_\alpha^{\mathrm{i}})^2\rangle - x_\alpha^2$ measures the magnitude of fluctuations of the variable x_α^{i}, with the ratio $\langle(\delta x_\alpha^{i})^2\rangle^{1/2}/x_\alpha$ characterizing the "sharpness" of the αth section of the distribution function. The general moment of eq 13, for $\alpha \neq \beta$, similarly reflects the correlation between the fluctuations in x_α^{i} and $x_\beta^{\ \mathrm{i}}$.

In what follows, we shall examine fluctuations in the distribution of electrons in a molecule and its constituent fragments. The molecular system can be considered to be externally closed or open. The former case corresponds to the "frozen" (integer) overall number of electrons $N = \int\rho(\mathbf{r})\, \mathrm{d}\mathbf{r}$ or to the fixed electron density ρ, whereas the latter case represents a system in contact with a macrospopic reservoir of electrons. In the externally open system, its grand canonical ensemble average (fractional) number of electrons, resulting from the integration of the corresponding ensemble average density, exhibits different instantaneous values at a given location in space because of the electron transfer to and from the reservoir.

One can also examine the state of subsystems (i.e., molecular fragments, e.g., the bonded atoms in molecules (AIM), which can also be regarded as externally (or mutually) closed or open. The instantaneous densities of subsystems, $\boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r}) = \{\rho_k^{\mathrm{i}}(\mathbf{r})\}$, giving rise to the fixed molecular electron density, $\rho(\mathbf{r}) = \sum_k \rho_k^{\mathrm{i}}(\mathbf{r})$, and the corresponding instantaneous electron populations, $\mathbf{N}^{\mathrm{i}} = \int\boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r})\, \mathrm{d}\mathbf{r} = \{N_k^{\mathrm{i}}\}$, also fluctuate while preserving the overall density, $\rho(\mathbf{r})$, and number of electrons, $N = \sum_k N_k^{\mathrm{i}}$.

Alternatively, one can treat a small portion of a molecule as a local subsystem, with the corresponding molecular remainder then representing the complementary microscopic reservoir, which is infinitely larger than the local subsystem itself. The small subsystem, chosen mentally to be of constant (infinitesimal) volume, undergoes intrinsic fluctuations in the electron (number) density, and it exhibits the associated fluctuations in the energy density.

3. Equilibrium Distribution of Electrons in Molecular Subsystems

Let us consider the fluctuations exhibited by the instantaneous densities $\boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r})$ and electron populations $\mathbf{N}^{\mathrm{i}}$ of molecular fragments, e.g., AIM, reactants, functional groups, etc., relative to the Hirshfeld densities,[2,4−7] $\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r}) = \{\rho_k^{\mathrm{H}}(\mathbf{r})\}$, and the associated numbers of electrons, $\mathbf{N}^{\mathrm{H}} = \int\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r})\, \mathrm{d}\mathbf{r} = \{N_k^{\mathrm{H}}\}$, characterizing the equilibrium subsystems.[4] These stockholder pieces of a given molecular density $\rho(\mathbf{r})$ are defined by the relations

$$\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r}) = \boldsymbol{\rho}^0(\mathbf{r})\left[\frac{\rho(\mathbf{r})}{\rho^0(\mathbf{r})}\right] \equiv \boldsymbol{\rho}^0(\mathbf{r})\, w(\mathbf{r}) \qquad \rho(\mathbf{r}) = \sum_k \rho_k^{\mathrm{H}}(\mathbf{r}) \qquad \rho^0(\mathbf{r}) = \sum_k \rho_k^{0}(\mathbf{r}) \tag{14}$$

involving the unbiased local enhancement factor, $w(\mathbf{r})$, of the ground-state densities of the free subsystems, $\boldsymbol{\rho}^0(\mathbf{r}) = \{\rho_k^0(\mathbf{r})\}$, common to all constituent fragments. Here, $\rho^0(\mathbf{r})$ is the electron density of the promolecule,[2] consisting of the free subsystem densities shifted to their actual positions in a molecule, which also serves as the reference in diagrams displaying the density difference due to bond formation: $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho^0(\mathbf{r})$.

The unbiased fragment densities of eq 14, obeying Hirshfeld's common sense stockholder principle[2], that each fragment participates in the local molecular "profit" $\rho(\mathbf{r})$ in proportion to its local share in the promolecular "investment" $\rho^0(\mathbf{r})$,

$$D_k^{\ \mathrm{H}}(\mathbf{r}) \equiv \frac{\rho_k^{\ \mathrm{H}}(\mathbf{r})}{\rho(\mathbf{r})} = \frac{\rho_k^{\ 0}(\mathbf{r})}{\rho^0(\mathbf{r})} \equiv D_k^{\ 0}(\mathbf{r}) \tag{15}$$

have a solid basis in the information theory[3,8] since they minimize the entropy deficiency (missing information) of Kullback and Leibler,[3]

$$\begin{aligned}\Delta S^{\mathrm{i}}[\boldsymbol{\rho}^{\mathrm{i}}|\boldsymbol{\rho}^0] &= \sum_k \int \rho_k^{\ \mathrm{i}}(\mathbf{r}) \ln\left[\frac{\rho_k^{\ \mathrm{i}}(\mathbf{r})}{\rho_k^{\ 0}(\mathbf{r})}\right] \mathrm{d}\mathbf{r}\\ &\equiv \sum_k \int \Delta s_k^{\ \mathrm{i}}(\rho_k^{\ \mathrm{i}}(\mathbf{r});\, \rho_k^{\ 0}(\mathbf{r}))\, \mathrm{d}\mathbf{r} \equiv \\ &\int \Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r});\, \boldsymbol{\rho}^0(\mathbf{r}))\, \mathrm{d}\mathbf{r}\end{aligned} \tag{16}$$

or other information-distance measures between the instantaneous (trial) subsystem densities $\boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r})$ and the fixed reference densities $\boldsymbol{\rho}^0(\mathbf{r})$ of the isolated fragments, subject to the local constraint of the exhaustive partitioning, $\rho(\mathbf{r}) = \sum_k \rho_k^{\,i}(\mathbf{r})$,[4−7]

$$\begin{aligned}\min_{\mathrm{i}}\{\Delta S^{\mathrm{i}}[\boldsymbol{\rho}^{\mathrm{i}}|\boldsymbol{\rho}^0] - \int F(\mathbf{r})\, [\sum_k \rho_k^{\ \mathrm{i}}(\mathbf{r}) - \rho(\mathbf{r})]\, \mathrm{d}\mathbf{r}\} &= \Delta S[\boldsymbol{\rho}^{\mathrm{H}}|\boldsymbol{\rho}^0]\\ \equiv \sum_k \int \Delta s_k(\rho_k^{\ \mathrm{H}}(\mathbf{r});\, \rho_k^{\ 0}(\mathbf{r}))\, \mathrm{d}\mathbf{r} &= \\ \int \rho(\mathbf{r}) \ln D(\mathbf{r})\, \mathrm{d}\mathbf{r} \equiv \Delta S[\rho|\rho^0] &\equiv \\ \int \Delta s(\rho(\mathbf{r});\, \rho^0(\mathbf{r}))\, \mathrm{d}\mathbf{r}\end{aligned} \tag{17}$$

where the Lagrange multiplier function $F(\mathbf{r})$ can be determined from the value of the constraint. Thus, given the densities of isolated atoms, which provide a natural reference in chemistry, this minimum-entropy deficiency principle determines the subsystem densities in a molecule as a function of the molecular ground-state density ρ. This is in the spirit of the density functional theory,[9,10] according to which ρ, or the shape function $p = \rho/N$,[12] determines all of the physical properties of the molecular system under consideration. The Hirshfeld pieces of the molecular density were also shown to satisfy some objective criteria of transferability.[13]

The Lagrange multiplier function in eq 17 represents the intersubsystem equalized local intensive parameter,

$$\begin{aligned}F(\mathbf{r}) = 1 + \ln w(\mathbf{r}) &= \frac{\delta\Delta S[\rho|\rho^0]}{\delta\rho(\mathbf{r})} = \frac{\partial\Delta s(\rho(\mathbf{r});\, \rho^0(\mathbf{r}))}{\partial\rho(\mathbf{r})}\\ &= \frac{\partial\Delta s_k(\boldsymbol{\rho}_k^{\ \mathrm{H}}(\mathbf{r});\, \rho_k^{\ 0}(\mathbf{r}))}{\partial\rho_k^{\ \mathrm{H}}(\mathbf{r})}\end{aligned} \tag{18}$$

We have explicitly indicated in the preceding equation that $F(\mathbf{r})$ is the (intensive) entropy-deficiency conjugate of the (extensive) molecular and Hirshfeld densities. Thus, this overall function also determines the corresponding intensive conjugates $\mathbf{F}^{\mathrm{H}}(\mathbf{r})$ of the subsystem densities:

$$\mathbf{F}^{\mathrm{H}}(\mathbf{r}) = \frac{\delta \Delta S[\boldsymbol{\rho}^{\mathrm{H}}|\boldsymbol{\rho}^{0}]}{\delta \boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r})} = \frac{\partial \Delta s(\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r});\, \rho^{0}(\mathbf{r}))}{\partial \boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r})} = F(\mathbf{r})\mathbf{1} \quad (19)$$

where the unit vector $\mathbf{1} = (1, 1, ...)$. In eq 19, the functional derivative with respect to the subsystem density is the partial derivative calculated for the fixed densities of the remaining subsystems. It follows from eq 18 that all of these entropy-deficiency conjugates of the electron densities measure the surprisal function of the overall distribution of electrons in a molecule relative to that in the corresponding promolecule reference:

$$I[\rho(\mathbf{r})|\rho^{0}(\mathbf{r})] = \ln w(\mathbf{r}) \equiv I(\mathbf{r}) \quad (20)$$

It should be observed that eqs 14, 18, and 19 imply that the local values of the subsystem surprisals are equalized for the Hirshfeld partitioning at the corresponding value of the surprisal function of the system as a whole:[4,5,7]

$$I[\rho_k^{\mathrm{H}}(\mathbf{r})|\rho_k^{0}(\mathbf{r})] = \ln\left[\frac{\rho_k^{\mathrm{H}}(\mathbf{r})}{\rho_k^{0}(\mathbf{r})}\right] \equiv I_k^{\mathrm{H}}(\mathbf{r}) = I(\mathbf{r}) \qquad k = 1, 2, ..., m \quad (21)$$

Within the information theoretic thermodynamics of molecular systems and their fragments,[4] the minimum-entropy deficiency principle of eq 17 replaces the familiar maximum-entropy principle of ordinary thermodynamics.[1] (See eqs 8 and 9) Thus, the maximum principle of the generalized Massieu function of eq 8, in which the equilibrium values of the unconstrained parameters in a system in contact with reservoirs characterized by their intensive parameters $\mathbf{f}^{\mathrm{r}}$ maximize $S[\mathbf{f}^{\mathrm{r}}]$ at constant $\mathbf{f}^{\mathrm{i}} = \mathbf{f}^{\mathrm{r}}$, will be replaced in the information theoretic approach by an appropriate extremum principle of the relevant Legendre transform of the entropy deficiency.

For example, eqs 18 and 19 identify the Lagrange multiplier function associated with the local constraint of the exhaustive partitioning as being equal to the local intensive conjugates $\{F_k^{\mathrm{H}}(\mathbf{r})\}$ of the equilibrium (Hirshfeld) subsystem densities (equilibrium extensive variables): $F_k^{\mathrm{H}}(\mathbf{r}) = F(\mathbf{r})$, $k = 1, 2, ..., m$. Therefore, the auxiliary functional of the optimum (Hirshfeld) densities in eq 17 is

$$\begin{aligned}\Delta S[\boldsymbol{\rho}^{\mathrm{H}}|\boldsymbol{\rho}^{0}, \rho] &= \min_{\mathrm{i}}\{\Delta S^{\mathrm{i}}[\boldsymbol{\rho}^{\mathrm{i}}|\boldsymbol{\rho}^{0}] - \int F(\mathbf{r})\rho^{\mathrm{i}}(\mathbf{r})\, d\mathbf{r}\} = \\ &\qquad \Delta S[\rho|\rho^{0}] - \int F(\mathbf{r})\, \rho(\mathbf{r})\, d\mathbf{r} \\ &= \Delta S[\rho|\rho^{0}] - \int \left\{\frac{\delta \Delta S[\rho|\rho^{0}]}{\delta \rho(\mathbf{r})}\right\}\rho(\mathbf{r})\, d\mathbf{r} \equiv \\ &\qquad \Delta S[F|\rho^{0}, \rho] \\ &= \Delta S[\boldsymbol{\rho}^{\mathrm{H}}|\boldsymbol{\rho}^{0}] - \int \{\mathbf{F}^{\mathrm{H}}(\mathbf{r})\}\cdot\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r})\, d\mathbf{r} \\ &= \Delta S[\boldsymbol{\rho}^{\mathrm{H}}|\boldsymbol{\rho}^{0}] - \int \left\{\frac{\delta \Delta S[\boldsymbol{\rho}^{\mathrm{H}}|\boldsymbol{\rho}^{0}]}{\delta \boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r})}\right\}\cdot\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r})\, d\mathbf{r} \equiv \\ &\qquad \Delta S[\mathbf{F}^{\mathrm{H}}|\boldsymbol{\rho}^{0}, \rho] \quad (22)\end{aligned}$$

where the instantaneous overall density $\rho^{\mathrm{i}} = \sum_k \rho_k^{\mathrm{i}}$, replaces the extensive variables, ρ or $\boldsymbol{\rho}^{\mathrm{H}}$, with their intensive conjugates, F or $\mathbf{F}$, in the list of state parameters. As also shown in eq 22, this functional defines the equilibrium Legendre transform of the entropy deficiency: $\Delta S[\boldsymbol{\rho}^{\mathrm{H}}|\boldsymbol{\rho}^{0}, \rho] = \Delta S[F|\rho^{0}, \rho] = \Delta S[\mathbf{F}^{\mathrm{H}}|\boldsymbol{\rho}^{0}, \rho]$.

One could similarly introduce the instantaneous intensive entropy-deficiency parameters defined as the corresponding partial functional derivatives of the instantaneous entropy deficiency of eq 16:

$$\begin{aligned}\mathbf{F}^{\mathrm{i}}(\mathbf{r}) &\equiv \frac{\delta \Delta S^{\mathrm{i}}[\boldsymbol{\rho}^{\mathrm{i}}|\boldsymbol{\rho}^{0}]}{\delta \boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r})} = \frac{\partial \Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r});\, \boldsymbol{\rho}^{0}(\mathbf{r}))}{\partial \boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r})} \\ &= \left\{F_k^{\mathrm{i}}(\mathbf{r}) = \frac{\partial \Delta s_k^{\mathrm{i}}(\rho_k^{\mathrm{i}}(\mathbf{r});\, \rho_k^{0}(\mathbf{r}))}{\partial \rho_k^{\mathrm{i}}(\mathbf{r})} = 1 + \ln\left[\frac{\rho_k^{\mathrm{i}}(\mathbf{r})}{\rho_k^{0}(\mathbf{r})}\right] \equiv 1 + I_k^{\mathrm{i}}(\mathbf{r})\right\} \quad (23)\end{aligned}$$

defining the corresponding Legendre transform

$$\Delta S^{\mathrm{i}}[\boldsymbol{\rho}^{\mathrm{i}}, \mathbf{F}^{\mathrm{i}}|\boldsymbol{\rho}^{0}] = \Delta S^{\mathrm{i}}[\boldsymbol{\rho}^{\mathrm{i}}|\boldsymbol{\rho}^{0}] - \sum_k \int F_k^{\mathrm{i}}(\mathbf{r})\, \rho_k^{\mathrm{i}}(\mathbf{r})\, d\mathbf{r} \equiv \sum_k \Delta s_k^{\mathrm{i}}[F_k^{\mathrm{i}}|\rho_k^{0}, \rho] \quad (24)$$

The equilibrium values of the “intensive” subsystem variables for the Hirshfeld subsystem densities, $\mathbf{F}^{\mathrm{i}}(\mathbf{r}) = \mathbf{F}^{\mathrm{H}}(\mathbf{r}) = F(\mathbf{r})\mathbf{1}$, can be interpreted as resulting from coupling of the molecular fragments to a common Hirshfeld reservoir characterized by the entropic intensity $F(\mathbf{r})$ related to the global molecular surprisal function $I(\mathbf{r})$. This observation stresses the global equilibrium character of the Hirshfeld partitioning with respect to the hypothetical intra- and intersubsystem flows of electrons.[4] The subsystem analogue of eq 10 now reads

$$\Delta S[\mathbf{F}^{\mathrm{H}}|\boldsymbol{\rho}^{0}, \rho] = \Delta S[\boldsymbol{\rho}^{\mathrm{H}}[\mathbf{F}^{\mathrm{H}}]|\boldsymbol{\rho}^{0}, \rho] - \sum_k \int F_k^{\mathrm{H}}(\mathbf{r})\, \rho_k^{\mathrm{H}}(\mathbf{r})\, d\mathbf{r} = \min_{\mathrm{i}} \Delta S^{\mathrm{i}}[\boldsymbol{\rho}^{\mathrm{i}}, \mathbf{F}^{\mathrm{H}}[\rho]|\boldsymbol{\rho}^{0}] \quad (25)$$

Thus, the minimum-entropy deficiency principle of eq 17 can be interpreted as (cf. eqs 8−11)

$$\begin{aligned}\min_{\mathrm{i}}\{\Delta S^{\mathrm{i}}[\boldsymbol{\rho}^{\mathrm{i}}|\boldsymbol{\rho}^{0}] - \sum_k \int F_k^{\mathrm{H}}(\mathbf{r})\, \rho_k^{\mathrm{i}}(\mathbf{r})\, d\mathbf{r}\} &\equiv \\ \min_{\mathrm{i}}\Delta S^{\mathrm{i}}[\boldsymbol{\rho}^{\mathrm{i}}, \mathbf{F}^{\mathrm{H}}[\rho]|\boldsymbol{\rho}^{0}] \\ = \Delta S[\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{F}^{\mathrm{H}})|\boldsymbol{\rho}^{0}] - \sum_k \int F_k^{\mathrm{H}}(\mathbf{r})\, \rho_k^{\mathrm{H}}(\mathbf{r})\, d\mathbf{r} &= \\ \Delta S[\mathbf{F}^{\mathrm{H}}|\boldsymbol{\rho}^{0}, \rho] = -N \quad (26)\end{aligned}$$

In other words, the equilibrium subsystem densities $\{\langle\rho_k^{i}(\mathbf{r})\rangle = \rho_k^{\mathrm{H}}(\mathbf{r})\}$ of a molecular system in contact with the Hirshfeld “reservoir”, exhibiting the entropy deficiency intensity $F(\mathbf{r})$, which forces equalization of the subsystem surprisals at this global surprisal level, minimize $\Delta S^{\mathrm{i}}[\boldsymbol{\rho}^{\mathrm{i}}, \mathbf{F}^{\mathrm{H}}[\rho]|\boldsymbol{\rho}^{0}]$ at fixed $F_k^{\mathrm{i}}(\mathbf{r}) = F_k^{\mathrm{H}}(\mathbf{r}) = F(\mathbf{r})$. This is precisely the minimum principle yielding the generalized Massieu function of eq 25, the Legendre transform of the equilibrium entropy deficiency, in which the subsystem densities have been replaced by the local Hirshfeld intensities in the list of the subsystem state parameters.

The final result of eq 26 directly follows from eqs 14−18 and the overall normalization of the Hirshfeld subsystem densities:

$$\Delta S[\mathbf{F}^{\mathrm{H}}|\boldsymbol{\rho}^{0}, \rho] = -\int \sum_k \rho_k^{\mathrm{H}}(\mathbf{r})\, \mathrm{d}\mathbf{r} = -\int \rho(\mathbf{r})\, \mathrm{d}\mathbf{r} = -N \quad (27)$$

Also, because of the additive character of this Legendre transform (see eq 24), its overall value can be decomposed into the corresponding Hirshfeld subsystem contributions $\Delta s_k[F_k^{\mathrm{H}}|\rho_k^0, \rho]$ equal to the negative value of the corresponding normalization N_k^{H} of the electron density of the "stockholder" molecular fragment:

$$\Delta S\,[\mathbf{F}^{\mathrm{H}}|\boldsymbol{\rho}^{0}, \rho] \equiv \sum_k \Delta s_k[F_k^{\mathrm{H}}|\rho_k^{0}, \rho] = - \sum_k \int \rho_k^{\mathrm{H}}(\mathbf{r})\, \mathrm{d}\mathbf{r} \equiv -\sum_k N_k^{\mathrm{H}} \quad (28)$$

4. Local Description of the Density-Partitioning Problem

The above global development can be given an equivalent, local interpretation by taking all quantities per unit volume and using the integrand $\Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r});\ \boldsymbol{\rho}^{0}(\mathbf{r})) \equiv \Delta s^{\mathrm{i}}(\mathbf{r}) \equiv \sum_k \Delta s_k^{\mathrm{i}}(\mathbf{r})$ of the entropy deficiency functional in the subsystem resolution (eq 16) as a measure of the local subsystem's missing information (entropy deficiency) density. Its equilibrium value is reached for the Hirshfeld densities of molecular fragments when $\langle \Delta s^{\mathrm{i}}(\mathbf{r})\rangle = \Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r});\ \boldsymbol{\rho}^{0}(\mathbf{r})) \equiv \Delta s(\mathbf{r}) \equiv \sum_k \Delta s_k(\mathbf{r})$ and the corresponding entropy deficiency conjugates of the local value of the subsystem electron densities are intersubsystem equalized at the overall intensity value: $\mathbf{F}^{\mathrm{H}}(\mathbf{r}) = \partial \Delta s(\mathbf{r})/\partial \boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r}) = \{F_k^{\mathrm{H}}[\rho;\ \mathbf{r}] \equiv F_k^{\mathrm{H}}(\mathbf{r}) = \partial \Delta s_k(\mathbf{r})/\partial \rho_k^{\mathrm{H}}(\mathbf{r}) = F(\mathbf{r})\}$. The local instantaneous intensities are similarly defined by the partial derivatives of eq 23. The local analogues of the instantaneous Legendre transform of eq 24 and the entropy deficiency Massieu function of eq 25 are

$$\begin{aligned}\Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r}), \mathbf{F}^{\mathrm{i}}(\mathbf{r});\ \boldsymbol{\rho}^{0}(\mathbf{r})) &= \Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r});\ \boldsymbol{\rho}^{0}(\mathbf{r})) - \sum_k F_k^{\mathrm{i}}(\mathbf{r})\, \rho_k^{\mathrm{i}}(\mathbf{r}) \equiv \Delta s^{\mathrm{i}}[\mathbf{F}^{\mathrm{i}}(\mathbf{r})]\\ &\equiv \sum_k \Delta s_k^{\mathrm{i}}(\rho_k^{\mathrm{i}}(\mathbf{r}), F_k^{\mathrm{i}}(\mathbf{r});\ \rho_k^{0}(\mathbf{r})) \equiv \sum_k \Delta s_k^{\mathrm{i}}[F_k^{\mathrm{i}}(\mathbf{r})] = -\sum_k \rho_k^{\mathrm{i}}(\mathbf{r}) = -\rho^{\mathrm{i}}(\mathbf{r}) \quad (29)\end{aligned}$$

$$\begin{aligned}\Delta s(\mathbf{F}^{\mathrm{H}}(\mathbf{r});\ \boldsymbol{\rho}^{0}(\mathbf{r}), \rho(\mathbf{r})) &= \Delta s(\boldsymbol{\rho}^{\mathrm{H}}[\mathbf{F}^{\mathrm{H}}[\rho;\ \mathbf{r}];\ \mathbf{r}];\ \boldsymbol{\rho}^{0}(\mathbf{r})) - \sum_k F_k^{\mathrm{H}}[\rho;\ \mathbf{r}]\, \rho_k^{\mathrm{H}}[\rho;\ \mathbf{r}] \equiv \Delta s[\mathbf{F}^{\mathrm{H}}(\mathbf{r})]\\ &= \Delta s(\rho(\mathbf{r});\ \rho^{0}(\mathbf{r})) - F(\mathbf{r})\, \rho(\mathbf{r}) \equiv \Delta s[F(\mathbf{r})]\\ &= \min_{\mathrm{i}} \Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r}), \mathbf{F}^{\mathrm{H}}[\rho;\ \mathbf{r}];\ \boldsymbol{\rho}^{0}(\mathbf{r})) \equiv \sum_k \Delta s_k(\rho_k^{\mathrm{H}}(\mathbf{r}), F_k^{\mathrm{H}}(\mathbf{r});\ \rho_k^{0}(\mathbf{r}), \rho(\mathbf{r})) \equiv \sum_k \Delta s_k[F_k^{\mathrm{H}}(\mathbf{r})]\\ &= -\sum_k \rho_k^{\mathrm{H}}(\mathbf{r}) = -\rho(\mathbf{r}) \quad (30)\end{aligned}$$

Hence, the density-conserving $\rho^{\mathrm{i}}(\mathbf{r}) = \rho(\mathbf{r})$ instantaneous divisions of a given molecular density $\rho(\mathbf{r})$ give $\Delta s[F(\mathbf{r})] = \Delta s^{\mathrm{i}}[\mathbf{F}^{\mathrm{i}}(\mathbf{r})] = -\rho(\mathbf{r})$.

As indicated above, the subsystem contributions to these local Legendre transforms are also additive. The equilibrium function $\Delta s[\mathbf{F}^{\mathrm{H}}(\mathbf{r})]$ is thus "normalized" to the negative value of the molecular density, with the negative subsystem densities $-\rho_k^{\mathrm{H}}(\mathbf{r}) = -\rho_k^{\mathrm{H}}[\rho;\ \mathbf{r}]$ providing the corresponding subsystem contributions $\Delta s_k[F_k^{\mathrm{H}}(\mathbf{r})]$. It also follows from the preceding two equations that

$$\frac{\partial \Delta s[F(\mathbf{r})]}{\partial F(\mathbf{r})} = -\rho(\mathbf{r}) \qquad \frac{\partial \Delta s[\mathbf{F}^{\mathrm{H}}(\mathbf{r})]}{\partial \mathbf{F}^{\mathrm{H}}(\mathbf{r})} = -\boldsymbol{\rho}^{\mathrm{H}}(\mathbf{r}) \qquad \frac{\partial \Delta s_k^{\mathrm{i}}[F_k^{\mathrm{i}}(\mathbf{r})]}{\partial F_k^{\mathrm{i}}(\mathbf{r})} = -\rho_k^{\mathrm{i}}(\mathbf{r}) \quad (31)$$

where the partial differentiation implies that all remaining variables of the local entropic Legendre transform are held fixed.

To simplify notation, in what follows we shall omit the specification of a given position in space, which specifies a particular local subsystem under consideration: $\rho(\mathbf{r}) = \rho$, $\rho_k^{\mathrm{H}}[\rho;\mathbf{r}] = \rho_k^{\mathrm{H}}[\rho]$, $\Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{i}}(\mathbf{r});\ \boldsymbol{\rho}^{0}(\mathbf{r})) = \Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{i}};\boldsymbol{\rho}^{0})$, $\Delta s_k[F_k^{\mathrm{H}}(\mathbf{r})] = \Delta s_k[F_k^{\mathrm{H}}]$, and so forth.

5. Local Gaussian Distribution Function

It follows from eqs 16 and 30 that the local information distance analogue of the exponent in the thermodynamic distribution function of eq 4,

$$\begin{aligned}-\kappa\{\Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{i}};\ \boldsymbol{\rho}^{0}) - \sum_k F_k^{\mathrm{H}}\, \rho_k^{\mathrm{i}} - \Delta s[\mathbf{F}^{\mathrm{H}}]\} &= -\kappa[\Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{i}};\ \boldsymbol{\rho}^{0}) - \Delta s(\boldsymbol{\rho}^{\mathrm{H}}[\rho];\ \boldsymbol{\rho}^{0}) - \sum_k F_k^{\mathrm{H}}\, (\rho_k^{\mathrm{i}} - \rho_k^{\mathrm{H}})]\\ &\equiv -\kappa\, [\delta \Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{i}};\ \rho, \boldsymbol{\rho}^{0}) - \sum_k F_k^{\mathrm{H}}\, \delta\rho_k^{\mathrm{i}}] = -\kappa \sum_k [\delta \Delta s_k^{\mathrm{i}}(\rho_k^{\mathrm{i}};\ \rho, \rho_k^{0}) - F_k^{\mathrm{H}}\, \delta\rho_k^{\mathrm{i}}] \quad (32)\end{aligned}$$

where the factor $\kappa = \rho^{-1}$ is chosen to make the exponent dimensionless, measures the displacement per electron of the local instantaneous information distance relative to that of the Hirshfeld fragments. As indicated in the last equation, the overall displacement $\delta\Delta s^{\mathrm{i}}$ is additive over the constituent molecular fragment components $\{\delta\Delta s_k^{\mathrm{i}}\}$.

The local information-theoretic analogue of the thermodynamic distribution function of eq 4 thus reads

$$\begin{aligned}W(\boldsymbol{\rho}^{\mathrm{i}}) &= \omega\, \exp\{-\rho^{-1}[\delta \Delta s^{\mathrm{i}}(\boldsymbol{\rho}^{\mathrm{i}};\ \rho, \boldsymbol{\rho}^{0}) - \sum_k F_k^{\mathrm{H}}\, \delta\rho_k^{\mathrm{i}}]\}\\ &= \Pi_k \omega_k\, \exp\{-\rho^{-1}[\delta \Delta s_k^{\mathrm{i}}(\rho_k^{\mathrm{i}};\ \rho, \rho_k^{0}) - F_k^{\mathrm{H}}\, \delta\rho_k^{\mathrm{i}}]\} \equiv \prod_k W_k(\rho_k^{\mathrm{i}}) \quad (33)\end{aligned}$$

where $\{W_k(\rho_k^{\mathrm{i}})\}$ are the respective subsystem distributions and $\omega = \Pi_k \omega_k$ is the overall normalization constant with the subsystem normalization factors $\{\omega_k\}$ such that

$$\int W_k(\rho_k^{\mathrm{i}})\, \mathrm{d}\rho_k^{\mathrm{i}} = 1 \qquad k = 1, 2, ..., m \quad (34)$$

The associated Gaussian distribution of the familiar Einstein method[1] can be obtained be expanding the local instantaneous entropy deficiency Δs^{i} around the equilibrium value $\Delta s|_{\mathbf{0}}$ for $\delta\boldsymbol{\rho}^{\mathrm{i}} \equiv \boldsymbol{\rho}^{\mathrm{i}} - \boldsymbol{\rho}^{\mathrm{H}} = \mathbf{0}$ in powers of the local density displacements $\delta\boldsymbol{\rho}^{\mathrm{i}} = \{\delta\rho_k^{\mathrm{i}}\}$,

$$\delta\Delta s^{\mathrm{i}} = \Delta s^{\mathrm{i}} - \Delta s|_{\mathbf{0}} = \sum_k F_k{}^{\mathrm{i}}|_{\mathbf{0}}\,\delta\rho_k{}^{\mathrm{i}} + \frac{1}{2}\sum_k\sum_l \delta\rho_k{}^{\mathrm{i}}\, s_{kl}{}^{\mathrm{H}}\,\delta\rho_l{}^{\mathrm{i}} + ..., \qquad (35\mathrm{a})$$

where $F_k{}^{\mathrm{i}}|_0 = F_k{}^{\mathrm{H}} = F$ (eq 18) and

$$s_{kl}{}^{\mathrm{H}} = \frac{\partial^2\Delta s}{\partial\rho_k\partial\rho_l}\bigg|_{\mathbf{0}} = \frac{\partial}{\partial\rho_k}\left[1+\ln\left(\frac{\rho_l}{\rho_l{}^0}\right)\right]\bigg|_{\mathbf{0}} = (\rho_k{}^{\mathrm{H}})^{-1}\delta_{kl} = \left[\frac{\rho^0}{(\rho\rho_k{}^0)}\right]\delta_{kl} \qquad (35\mathrm{b})$$

Therefore, if one now neglects the higher-order terms and changes the normalization accordingly, one obtains approximately (see eq 15)

$$\delta\Delta s^{\mathrm{i}} \cong \delta\Delta s^{(2)} = F\sum_k \delta\rho_k{}^{\mathrm{i}} + \frac{1}{2}\sum_k\left[\frac{\rho^0}{(\rho\rho_k{}^0)}\right](\delta\rho_k{}^{\mathrm{i}})^2 = F\delta\rho^{\mathrm{i}} + \frac{1}{2}\sum_k (\rho D_k{}^0)^{-1}(\delta\rho_k{}^{\mathrm{i}})^2 \qquad (36)$$

Substituting this expression into eq 33 finally gives the Gaussian distribution in terms of the relative density displacements $\delta\mathbf{y}^{\mathrm{i}} \equiv \{\delta y_k{}^{\mathrm{i}} = \delta\rho_k{}^{\mathrm{i}}/\rho\}$,

$$W(\delta\mathbf{y}^{\mathrm{i}}) \cong W^{(2)}(\delta\mathbf{y}^{\mathrm{i}}) = \varpi\exp\{-(\rho)^{-1}[\delta\Delta s^{(2)} - \sum_k F_k{}^{\mathrm{H}}\,\delta\rho_k{}^{\mathrm{i}}]\} = \prod_k \varpi_k \exp[-(2D_k{}^0)^{-1}(\delta y_k{}^{\mathrm{i}})^2] \equiv \prod_k W_k{}^{\mathrm{G}}(\delta y_k{}^{\mathrm{i}}) \equiv \prod_k W_k{}^{\mathrm{G}}(\delta\rho_k{}^{\mathrm{i}}) \qquad (37)$$

A comparison between the $W_k{}^{\mathrm{G}}(\delta y_k{}^{i})$ function and the standard normal distribution identifies the local dispersion (spread) of $\rho_k{}^{\mathrm{i}}$ around $\rho_k{}^{\mathrm{H}}$, $\sigma_k{}^{\mathrm{H}} \equiv \sigma[\delta\rho_k{}^{\mathrm{i}}] = \rho(D_k{}^0)^{1/2}$ and the subsystem distribution normalization factor $\varpi_k = (\sigma_k{}^{\mathrm{H}})^{-1}(2\pi)^{-1/2}$. This dispersion of the local value of the instantaneous subsystem density implies the equivalent relative dispersion $\sigma[\delta y_k{}^{i}] = (D_k{}^0)^{1/2} = \sigma[\delta\rho_k{}^{\mathrm{i}}]/\rho$.

The product of the uncorrelated subsystem Gaussian distributions of eq 37 gives correctly the second moments, which are of main physical interest. In particular, it predicts the local dispersion of the subsystem density to be proportional to the molecular density and the square root of the subsystem share in the molecule/promolecule (eq 15). Thus, as intuitively expected, the largest local dispersion is exhibited by the AIM that contributes the most to the local value of molecular density. It has been argued recently[5] that the local softness of the Hirshfeld subsystem is proportional to the global softness of the molecule as a whole and the subsystem share factor $D_k{}^0$. We can therefore conclude that the subsystem local softness reflects the square of the dispersion in the local subsystem density. The predicted expression for the dispersion of the fragment density can also be interpreted as an additional local equalization rule for the relative subsystem dispersions: $\sigma_k{}^{\mathrm{H}}(D_k{}^0)^{-1/2} = \rho$, $k = 1, 2, ..., m$.

The local second moments of the Hirshfeld subsystem densities can be also expressed in the form of eq 13. First, we observe that by using eqs 31 and 32 one can express the derivative

$$\frac{\partial W}{\partial F_k{}^{\mathrm{H}}} = \rho^{-1}\left(\rho_k{}^{\mathrm{i}} + \frac{\partial\Delta s[\mathbf{F}^{\mathrm{H}}]}{\partial F_k{}^{\mathrm{H}}}\right)W = \rho^{-1}(\rho_k{}^{\mathrm{i}} - \rho_k{}^{\mathrm{H}})W = \rho^{-1}\delta\rho_k{}^{\mathrm{i}}\,W \qquad (38)$$

Thus, the diagonal second moment of eq 13 can be written as

$$(\sigma_k{}^{\mathrm{H}})^2 = \langle(\delta\rho_k{}^{\mathrm{i}})^2\rangle = \int(\delta\rho_k{}^{\mathrm{i}})^2 W\,\mathrm{d}\boldsymbol{\rho}^{\mathrm{i}} = \rho\int\delta\rho_k{}^{\mathrm{i}}\left(\frac{\partial W}{\partial F_k{}^{\mathrm{H}}}\right)\mathrm{d}\boldsymbol{\rho}^{\mathrm{i}}$$
$$= \rho\frac{\partial}{\partial F_k{}^{\mathrm{H}}}\left[\int\delta\rho_k{}^{\mathrm{i}}\,W\,\mathrm{d}\boldsymbol{\rho}^{\mathrm{i}}\right] - \rho\int W\left[\frac{\partial(\delta\rho_k{}^{\mathrm{i}})}{\partial F_k{}^{\mathrm{H}}}\right]\mathrm{d}\boldsymbol{\rho}^{\mathrm{i}}$$
$$= \rho\left(\frac{\partial\langle\delta\rho_k{}^{\mathrm{i}}\rangle}{\partial F_k{}^{\mathrm{H}}}\right) + \rho\left(\frac{\partial\rho_k{}^{\mathrm{H}}}{\partial F_k{}^{\mathrm{H}}}\right) = \rho\left(\frac{\partial\rho_k{}^{\mathrm{H}}}{\partial F_k{}^{\mathrm{H}}}\right) = \rho\rho_k{}^{\mathrm{H}} = \rho^2 D_k{}^0 \qquad (39)$$

Here we have used eq 1 and eqs 14, 15, 37, and 39 to calculate the derivatives

$$\frac{\partial(\delta\rho_k{}^{\mathrm{i}})}{\partial F_k{}^{\mathrm{H}}} = -\frac{\partial\rho_k{}^{\mathrm{H}}}{\partial F_k{}^{\mathrm{H}}} = \frac{\partial^2\Delta s[\mathbf{F}^{\mathrm{H}}]}{\partial F_k{}^{\mathrm{H}}\,\partial F_k{}^{\mathrm{H}}} \equiv S_{kk} \qquad (40)$$

$$\frac{\partial\rho_k{}^{\mathrm{H}}}{\partial F_k{}^{\mathrm{H}}} = \rho D_k{}^0 = \rho_k{}^{\mathrm{H}} \qquad k = 1, 2, ..., m \qquad (41)$$

The corresponding expression for the off-diagonal second moment reads

$$\langle\delta\rho_k{}^{\mathrm{i}}\,\delta\rho_l{}^{\mathrm{i}}\rangle = \rho\left(\frac{\partial\rho_k{}^{\mathrm{H}}}{\partial F_l{}^{\mathrm{H}}}\right) = \rho\left(\frac{\partial\rho_l{}^{\mathrm{H}}}{\partial F_k{}^{\mathrm{H}}}\right) = -\rho\left\{\frac{\partial^2\Delta s[\mathbf{F}^{\mathrm{H}}]}{\partial F_k{}^{\mathrm{H}}\,\partial F_l{}^{\mathrm{H}}}\right\} \equiv -\rho S_{kl} = 0 \qquad (42)$$

since the distribution of eq 37 predicts that a positive fluctuation $\delta\rho_k{}^{\mathrm{i}}$ is equally likely to be accompanied by the fluctuations $|\delta\rho_l{}^{\mathrm{i}}|$ and $-|\delta\rho_l{}^{\mathrm{i}}|$; that is, $\delta\rho_k{}^{\mathrm{i}}$ and $\delta\rho_l{}^{\mathrm{i}}$ are uncorrelated.

It should be emphasized that the partial derivatives in eqs 38−42 are calculated for the fixed (intersubsystem-equalized) Hirshfeld intensities of the remaining subsystems. The partial differentiation with respect to $F_k{}^{\mathrm{H}}$ thus corresponds to a thermodynamic description in which the *k*th subsystem is coupled to the separately controlled local reservoir characterized by the intensity $F_k{}^{\mathrm{H}}$. Thus, in the derivative of eq 40, one monitors the response in $\rho_k{}^{\mathrm{H}}$ to a given displacement in $F_k{}^{\mathrm{H}}$, with the remaining local density components being coupled to the common reservoir of the initial equilibrium.

To further simplify notation, in what follows we shall drop the upper index i indicating the instantaneous quantity: $\delta\rho_k{}^{\mathrm{i}} = \delta\rho_k$, $\delta\Delta s^{\mathrm{i}} = \delta\Delta s$, and so forth. The trial density ρ_k of a entropy/information variational principle could be also interpreted as the nonequilibrium instantaneous density of subsystem *k*.

6. Affinities, Fluxes, and Reciprocity Relations

Following the conceptual structure of the phenomenological irreversible thermodynamics,[1] we require two types of quantities: affinities, to describe the thermodynamic forces that drive a process, and fluxes, mesuring the responses to these forces. The fluxes vanish when the affinities vanish, and nonzero affinities lead to nonzero fluxes. The rates of irreversible processes are characterized by the relationship between fluxes and affinities. Clearly, specific definitions of such quantities are expected to depend on the measure of the information distance (entropy deficiency) used in the information entropy representation. The identification of the local affinities for a molecular system and its fragments will be carried out by considering the rate of the local production of the entropy deficiency in a continuous system.

As we have already indicated in eqs 16 and 17, one defines the entropy deficiency in a nonequilibrium system by postulating, as in the irreversible thermodynamics,[1] that the functional dependence of the local instantaneous information distance density on the local instantaneous parameter is taken to be identical to the dependence in the Hirshfeld equilibrium.

There are two classes of changes in the electronic structure of interest in chemistry: the so-called vertical displacement redistributes electrons among subsystems while preserving the density of the system as a whole, and the horizontal displacement represents a transition from one ground-state density to another.[5] The former case, to which we limit the present analysis, corresponds to the fixed overall density and thus to the fixed electronic energy and overall missing information relative to the promolecule reference; only the energies of the embedded subsystems[4b] and the subsystem entropy deficiencies change as a result of such vertical variations in the electronic structure of molecular fragments. The latter case, representing a more general change of the system as a whole, would require additional extensive state variables representing the shift in the system's overall entropy deficiency, giving rise to the associated information-theoretic temperature,[4b] measured by the energy conjugate of the global entropy deficiency.

Let us first examine the subsystem affinities $\{\mathscr{F}_k = (\mathscr{F}_{k\alpha}, \alpha = x, y, z), k = 1, 2, ..., m\} \equiv \{\mathscr{F}_{\mathrm{t}}\}$ (i.e., generalized thermodynamic forces of subsystems that drive the process of local change in the subsystem-resolved electronic structure). As in the irreversible thermodynamics, we introduce affinities as gradients of the intensive parameters that are appropriate for a given entropy deficiency representation. In this section, we consider the illustrative example of the Kullback–Leibler[3] measure of the missing information (eq 16). To have forces that identically vanish at the equilibrium (Hirshfeld) partitioning of a given (fixed) molecular density, we define affinities relative to the Hirshfeld equilibrium as gradients of the local displacements in the subsystem intensities, which are conjugates of the density displacements

$$\delta F_k(\mathbf{r}) \equiv F_k(\mathbf{r}) - F_k^{\mathrm{H}}(\mathbf{r}) = \ln\left[\frac{\rho_k(\mathbf{r})}{\rho_k^{\mathrm{H}}(\mathbf{r})}\right] = \frac{\partial \Delta S[\boldsymbol{\rho}|\boldsymbol{\rho}^0]}{\partial \rho_k(\mathbf{r})} - \frac{\partial \Delta S[\boldsymbol{\rho}^{\mathrm{H}}|\boldsymbol{\rho}^0]}{\partial \rho_k^{\mathrm{H}}(\mathbf{r})} \equiv \frac{\partial(\delta \Delta S[\boldsymbol{\rho}|\boldsymbol{\rho}^{\mathrm{H}}])}{\partial[\delta \rho_k(\mathbf{r})]} \qquad (43a)$$

$$\mathscr{F}_k = \nabla \delta F_k = \nabla\left[\ln\left(\frac{\rho_k}{\rho_k^{\mathrm{H}}}\right)\right] = \nabla\left[\ln\left(\frac{\rho_k}{\rho_k^{0}}\right) - \ln\left(\frac{\rho_k^{\mathrm{H}}}{\rho_k^{0}}\right)\right] = \frac{(\nabla \rho_k)}{\rho_k} - \frac{(\nabla \rho_k^{\mathrm{H}})}{\rho_k^{\mathrm{H}}} \qquad (43b)$$

Here, the local affinity $(\nabla \rho_k^{\mathrm{H}})/\rho_k^{\mathrm{H}}$ associated with the *k*th Hirshfeld molecular fragment is

$$\frac{(\nabla \rho_k^{\mathrm{H}})}{\rho_k^{\mathrm{H}}} = \frac{(\nabla \rho_k^{0})}{\rho_k^{0}} + \frac{(\nabla w)}{w} = \frac{(\nabla \rho)}{\rho} + \frac{(\nabla D_k^{0})}{D_k^{0}} \qquad (44)$$

where the share factor contribution is

$$\frac{(\nabla D_k^{0})}{D_k^{0}} = \frac{(\nabla \rho_k^{0})}{\rho_k^{0}} - \frac{(\nabla \rho^{0})}{\rho^{0}} \qquad (45)$$

The responses to these forces are measured by the local subsystem fluxes characterized by the rates of change of the local extensive parameters (subsystem densities ρ^{i} and their sum ρ). As in the irreversible thermodynamics of continuous systems, they are defined here as components of the corresponding local vector current densities of electrons: $\{\mathbf{J}_k = (J_{k\alpha}, \alpha = x, y, z), k = 1, 2, ..., m\} \equiv \{J_r\}$ and $\mathbf{J} = \sum_k \mathbf{J}_k$. The magnitude and direction of each vector reflect the amount and direction, respectively, of the corresponding electron flow across a unit area in unit time. The instantaneous local current density $\mathbf{J}_s = \mathbf{J}_s[\rho]$ of the entropy deficiency transported through a unit area per unit time is then given by a combination of the subsystem electron flows

$$\mathbf{J}_s = \sum_k \delta F_k\, \mathbf{J}_k = \sum_k \ln\left(\frac{\rho_k}{\rho_k^{\mathrm{H}}}\right) \mathbf{J}_k \qquad (46)$$

suggested by the differential of $\Delta S[\boldsymbol{\rho}|\boldsymbol{\rho}^{\mathrm{H}}]$ (see eq 43a),

$$\mathrm{d}\delta\Delta s = \sum_k \frac{\partial(\delta \Delta S[\boldsymbol{\rho}|\boldsymbol{\rho}^{\mathrm{H}}])}{\partial[\delta \rho_k(\mathbf{r})]}\, \mathrm{d}(\delta \rho_k) = \sum_k \delta F_k\, \mathrm{d}(\delta \rho_k) \qquad (47)$$

We now seek to write the rate of the local production of the entropy deficiency density,

$$\delta \Delta s \equiv \Delta s[\boldsymbol{\rho}] - \Delta s[\boldsymbol{\rho}^{\mathrm{H}}] \qquad (48)$$

relative to the Hirshfeld value of eq 17, $\Delta s[\boldsymbol{\rho}^{\mathrm{H}}] = \rho \ln w$. A displacement in the local entropy deficiency source

$$\delta\sigma = \sigma[\boldsymbol{\rho}] - \sigma[\boldsymbol{\rho}^{\mathrm{H}}] \equiv \frac{\mathrm{d}(\delta \Delta s)}{\mathrm{d}t} \qquad (49)$$

is then equal to the rate of a local increase of the entropy deficiency per unit volume, $\partial(\delta\Delta s)/\partial t$, minus the entropy leaving the region, $-\nabla \cdot \mathbf{J}_s$. This statement summarizes the continuity of the missing information:

$$\frac{\mathrm{d}(\delta \Delta s)}{\mathrm{d}t} \equiv \delta\sigma = \frac{\partial(\delta \Delta s)}{\partial t} + \nabla \cdot \mathbf{J}_s \qquad (50)$$

Moreover, since the extensive parameters can be neither produced nor destroyed, the equation of continuity for the displacement $\delta\rho_k = \rho_k - \rho_k^{\mathrm{H}}$ of the *k*th subsystem electron density and that for the overall density become

$$0 = \frac{\partial(\delta \rho_k)}{\partial t} + \nabla \cdot \mathbf{J}_k \qquad k = 1, 2, ..., m \qquad \text{and} \qquad 0 = \frac{\partial(\delta \rho)}{\partial t} + \nabla \cdot \mathbf{J} \qquad (51)$$

Therefore, combining the continuity equations (50 and 51) with eq 46 gives the familiar expression[1] for the displacement of the entropy deficiency production relative to the Hirshfeld level in terms of the products of forces and fluxes,

$$\delta\sigma = \sum_k \mathscr{F}_k \cdot \mathbf{J}_k \equiv \sum_r \mathscr{F}_r J_r \qquad (52)$$

since from eqs 43a, 47, and 51

$$\sum_k \ln\left(\frac{\rho_k}{\rho_k{}^{\mathrm{H}}}\right)\nabla\cdot\mathbf{J}_k = -\frac{\partial(\delta\Delta s)}{\partial t}$$

For the Markoffian system (with no dynamical "memory"), to which we restrict this analysis, each local flux depends on all relative intensities $\mathbf{F} - \mathbf{F}^{\mathrm{H}} = \{\delta F_k = \ln(\rho_k/\rho_k{}^{\mathrm{H}})\}$ and affinities $\{\mathcal{F}_t\}$

$$J_r = J_r(\{\mathcal{F}_t\}, \{\delta F_k\}) \tag{53}$$

and it vanishes, by definition, when all affinities vanish. The Hirshfeld AIM do resemble free atoms to a high degree.[6,7] However, this type of memory of the fragment free origin in the separated subsystem limit is automatically embedded in the entropy deficiency functional of eq 16 through the reference densities.

Expanding J_r in powers of the affinities and neglecting the third-order and higher-order terms gives the linear effect of all affinities on the rth flux

$$J_r = \sum_t \mathcal{F}_t L_{tr} \tag{54}$$

in terms of the kinetic coefficients $\{L_{tr} = L_{tr}(\{\delta F_k\})\}$,

$$\mathbf{L} \equiv \left\{\mathbf{L}_{kl} \equiv \left(\frac{\partial \mathbf{J}_l}{\partial \mathcal{F}_k}\right)_{\mathbf{0}}\right\} \equiv \left\{L_{tr} = \left(\frac{\partial J_r}{\partial \mathcal{F}_t}\right)_{\mathbf{0}}\right\} \tag{55}$$

calculated for the equilibrium (Hirshfeld) subsystems for which all affinities vanish identically, $\delta\mathbf{F}^{\mathrm{H}} = \mathbf{0}$, and thus $\{\mathcal{F}_k = \nabla(\delta F_k{}^{\mathrm{H}}) = \mathbf{0}\}$. The representative coefficient L_{tr} measures the local linear effect of the tth affinity on the rth flux. Combining eqs 52 and 54 gives the for the relative entropy deficiency source the quadratic function of affinities:

$$\delta\sigma = \sum_r \sum_t \mathcal{F}_t L_{tr} \mathcal{F}_r \tag{56}$$

In the absence of an externally applied magnetic field, the reciprocity theorem of Onsager[1] holds for the coupled local molecular subsystems:

$$L_{tr} = L_{rt} \tag{57}$$

That is, in the local linear Markoff process involving a network of electron flows between molecular fragments, the linear effect of the tth affinity on the rth flux is the same as that of the rth affinity on the local tth flux. This symmetry law reflects the Maxwell (cross-differentiation) relation. More specifically, in accordance with eq 52,

$$J_r = \left[\frac{\partial(\delta\sigma)}{\partial \mathcal{F}_r}\right]_{\mathbf{0}} \tag{58}$$

so that by using eq 56 we can write

$$L_{tr} = \left(\frac{\partial J_r}{\partial \mathcal{F}_t}\right)_{\mathbf{0}} = \frac{1}{2}\left[\frac{\partial^2(\delta\sigma)}{\partial \mathcal{F}_t \partial \mathcal{F}_r}\right]_{\mathbf{0}} = \frac{1}{2}\left[\frac{\partial^2(\delta\sigma)}{\partial \mathcal{F}_r \partial \mathcal{F}_t}\right]_{\mathbf{0}} = \left(\frac{\partial J_t}{\partial \mathcal{F}_r}\right)_{\mathbf{0}} = L_{rt} \tag{59}$$

These Onsager reciprocity relations can be justified through fluctuations using the time symmetry of physical laws.[1] Consider again the molecular subsystems in the initial equilibrium and the spontaneous fluctuations $\delta\boldsymbol{\rho} = \boldsymbol{\rho} - \boldsymbol{\rho}^{\mathrm{H}}$ of the local extensive parameters $\boldsymbol{\rho}$ around the corresponding Hirshfeld values $\boldsymbol{\rho}^{\mathrm{H}}$. The correlation moment $\langle\delta\rho_k\,\delta\rho_l(\tau)\rangle$, where $\delta\rho_l$ is observed at time τ after $\delta\rho_k$, must remain unchanged if we replace τ by $(-\tau)$. Hence, taking into account that only relative time between the two correlated densities is significant,

$$\langle\delta\rho_k\,\delta\rho_l(\tau)\rangle = \langle\delta\rho_k(-\tau)\,\delta\rho_l\rangle = \langle\delta\rho_k(\tau)\,\delta\rho_l\rangle \tag{60}$$

Subtracting $\langle\delta\rho_k\,\delta\rho_l\rangle$ from each side of this equation and dividing by τ gives in the limit $\tau \to 0$ the associated relation involving time derivatives of the instantaneous densities of subsystems:

$$\left\langle\delta\rho_k\,\delta\left(\frac{\mathrm{d}\rho_l}{\mathrm{d}t}\right)\right\rangle = \left\langle\delta\left(\frac{\mathrm{d}\rho_k}{\mathrm{d}t}\right)\delta\rho_l\right\rangle \tag{61}$$

Hence, assuming the linear dynamical process of eq 54 for a decay of the fluctuation $\delta(\mathrm{d}\rho_k/\mathrm{d}t)$ through the phenomenological equations

$$\delta\left(\frac{\mathrm{d}\rho_k}{\mathrm{d}t}\right) = \sum_l \delta F_l \mathcal{L}_{lk} \qquad k = 1, 2, ..., m \tag{62a}$$

where $\delta F_k = F_k - F_k{}^{\mathrm{H}}$ (see eqs 18 and 23) and

$$\mathcal{L}_{lk} = \frac{\partial\left[\delta\left(\frac{\mathrm{d}\rho_k}{\mathrm{d}t}\right)\right]}{\partial(\delta F_l)} \equiv \frac{\partial \mathcal{J}_k}{\partial(\delta F_l)} \tag{62b}$$

gives

$$\sum_r \mathcal{L}_{rl}\langle\delta\rho_k\,\delta F_r\rangle = \sum_r \mathcal{L}_{rk}\langle\delta F_r\,\delta\rho_l\rangle \tag{63}$$

Next, from the Hirshfeld distribution function of eq 33, one obtains (see also eq 38)

$$-\rho\left[\frac{\partial W}{\partial(\delta\rho_k)}\right] = W\,\delta F_k \tag{64}$$

Hence, by a straightforward integration by parts of the correlation moment of eq 63,

$$\begin{aligned}\langle\delta\rho_k\,\delta F_r\rangle &= \int\delta\rho_k W\,\delta F_r\,\mathrm{d}(\delta\boldsymbol{\rho}) = -\rho\int\delta\rho_k\left[\frac{\partial W}{\partial(\delta\rho_r)}\right]\mathrm{d}(\delta\boldsymbol{\rho}) \\ &= \rho\int W\left[\frac{\partial(\delta\rho_k)}{\partial(\delta\rho_r)}\right]\mathrm{d}(\delta\boldsymbol{\rho}) = \rho\,\delta_{rk}\int W\,\mathrm{d}(\delta\boldsymbol{\rho}) = \rho\delta_{rk}\end{aligned} \tag{65}$$

Finally, inserting the preceding equation in eq 63 gives the subsystem Onsager theorem in the absence of magnetic fields: $\mathcal{L}_{kl} = \mathcal{L}_{lk}$.

It should be realized that the modified definition of the local affinities $\{\delta F_k\}$ (eq 43a) and fluxes (eq 62b) $\{\mathcal{J}_k = \delta(\mathrm{d}\rho_k/\mathrm{d}t) = \mathrm{d}(\delta\rho_k)/\mathrm{d}t\}$, since $\rho_k{}^{\mathrm{H}}$ in $\delta\rho_k = \rho_k - \rho_k{}^{\mathrm{H}}$ is stationary, which we have used in the above derivation, gives rise to the modified set of kinetic coefficients $\{\mathcal{L}_{lk}\}$, which differs from $\mathbf{L}$ of eq 55. These conjugate forces and responses define the corresponding local entropy production (from eq 47):

$$\delta\sigma = \frac{\mathrm{d}(\delta\Delta s)}{\mathrm{d}t} = \sum_k \delta F_k \mathcal{J}_k \tag{66}$$

Let us reexamine the KL entropy deficiency between the current (instantaneous) densities of subsystems $\boldsymbol{\rho}$ and their equilibrium (Hirshfeld) densities $\boldsymbol{\rho}^{\mathrm{H}}$:

$$\Delta S[\boldsymbol{\rho}|\boldsymbol{\rho}^{\mathrm{H}}] = \sum_k \int \rho_k \ln(\rho_k/\rho_k^{\mathrm{H}})\, \mathrm{d}\mathbf{r} \equiv \sum_k \int \Delta s_k(\mathbf{r}|\rho_k^{\mathrm{H}})\, \mathrm{d}\mathbf{r} \equiv \int \Delta s(\mathbf{r}|\boldsymbol{\rho}^{\mathrm{H}})\, \mathrm{d}\mathbf{r} \quad (67)$$

It can be transformed into an explicit functional of displacements $\{\delta F_k\}$ in the local intensities of eq 43a

$$\Delta S[\boldsymbol{\rho}|\boldsymbol{\rho}^{\mathrm{H}}] = \sum_k \int \rho_k \left[\ln\left(\frac{\rho_k}{\rho_k^{\;0}}\right) - \ln\left(\frac{\rho_k^{\;\mathrm{H}}}{\rho_k^{\;0}}\right)\right] \mathrm{d}\mathbf{r} = \sum_k \int \rho_k (F_k - F_k^{\;\mathrm{H}})\, \mathrm{d}\mathbf{r} \equiv \sum_k \int \rho_k\, \delta F_k\, \mathrm{d}\mathbf{r} \quad (68)$$

which gives rise to the associated subsystem local intensities

$$F_k(\mathbf{r}|\rho_k^{\;\mathrm{H}}) = \frac{\delta \Delta S[\boldsymbol{\rho}|\boldsymbol{\rho}^{\mathrm{H}}]}{\delta \rho_k} = \ln\left[\frac{\rho_k}{\rho_k^{\;\mathrm{H}}}\right] + 1 \equiv \delta F_k + 1 \qquad k = 1, 2, ..., m \quad (69)$$

The second-order Taylor expansion of $\Delta s(\mathbf{r}|\boldsymbol{\rho}^{\mathrm{H}})$ in powers of $\delta\boldsymbol{\rho} = \boldsymbol{\rho} - \boldsymbol{\rho}^{\mathrm{H}} = \{\delta\rho_k\}$ (cf. eqs 35a and 35b) around the equilibrium densities $\{\rho_k = \rho_k^{\mathrm{H}}\}$ for which $\{\delta F_k = 0\}$ and thus $\{F_k(\mathbf{r}|\rho_k^{\mathrm{H}})|_0 = 1\}$ gives

$$\begin{aligned}\Delta s(\mathbf{r}|\boldsymbol{\rho}^{\mathrm{H}}) &\cong \sum_k \left[F_k(\mathbf{r}|\rho_k^{\;\mathrm{H}})\Big|_{\mathbf{0}} + \frac{1}{2}\sum_l s_{kl}(\mathbf{r}|\boldsymbol{\rho}^{\mathrm{H}})\, \delta\rho_l(\mathbf{r})\right]\delta\rho_k(\mathbf{r}) \\ &= \sum_k \delta\rho_k(\mathbf{r}) + \frac{1}{2}\sum_k [\rho_k^{\;\mathrm{H}}(\mathbf{r})]^{-1}[\delta\rho_k(\mathbf{r})]^2 \\ &= \delta\rho(\mathbf{r}) + \frac{1}{2}\sum_k \frac{[\delta\rho_k(\mathbf{r})]^2}{\rho_k^{\;\mathrm{H}}(\mathbf{r})} \\ &\equiv \Delta s^{(2)}(\mathbf{r}|\boldsymbol{\rho}^{\mathrm{H}}) \equiv \sum_k \Delta s_k^{\;(2)}(\mathbf{r}|\rho_k^{\;\mathrm{H}}) \end{aligned} \quad (70)$$

since $\Delta s(\mathbf{r}|\boldsymbol{\rho}^{\mathrm{H}})|_{\mathbf{0}} = \mathbf{0}$ and $s_{kl}(\mathbf{r}|\boldsymbol{\rho}^{\mathrm{H}}) = \{[\partial^2 \Delta s(\mathbf{r}|\boldsymbol{\rho}^{\mathrm{H}})/\partial\rho_k(\mathbf{r})\partial\rho_l(\mathbf{r})]_{\mathbf{0}}\} = [\rho_k^{\mathrm{H}}(\mathbf{r})]^{-1}\delta_{kl} = s_{kl}^{\mathrm{H}}$ (eq 35b). Thus, one recovers the local Gaussian distribution of Einstein's quadratic approach (cf. eq 37) approximating the exact Hirshfeld distribution function of eq 33:

$$W^{\mathrm{G}}(\delta\boldsymbol{\rho}|\boldsymbol{\rho}^{\mathrm{H}}) = \prod_k W_k^{\;\mathrm{G}}(\delta\rho_k|\rho_k^{\;\mathrm{H}}) \quad (71a)$$

$$\begin{aligned} W_k^{\;\mathrm{G}}(\delta\rho_k|\rho_k^{\;\mathrm{H}}) &= \varpi_k \exp\{-\rho^{-1}[\Delta s_k^{\;(2)}(\mathbf{r}|\rho_k^{\;\mathrm{H}}) - F_k(\mathbf{r}|\rho_k^{\;\mathrm{H}})|_0\, \delta\rho_k\} \\ &= \varpi_k \exp\{-(2\rho_k^{\;\mathrm{H}}\rho)^{-1}[(\delta\rho_k)^2]\} \\ &= \varpi_k \exp\left\{-(2D_k^{\;0})^{-1}\left[\left(\frac{\delta\rho_k}{\rho}\right)^2\right]\right\} \end{aligned} \quad (71b)$$

At this point, instead of expanding the KL information distance $\delta\Delta s = \Delta s(\mathbf{r}|\boldsymbol{\rho}^{\mathrm{H}})$ (eqs 5a and 70), one could expand in powers of $\delta\rho$ the density

$$\Delta s^{L}(\mathbf{r}|\mathbf{F}^{\mathrm{H}}) = \sum_k \rho_k(\mathbf{r}) \left\{\ln\left[\frac{\rho_k(\mathbf{r})}{\rho_k^{\;0}(\mathbf{r})}\right] - F_k^{\;\mathrm{H}}(\mathbf{r})\right\} = \Delta s(\mathbf{r}|\boldsymbol{\rho}^{\mathrm{H}}) - F(\mathbf{r})\, [\sum_k \rho_k(\mathbf{r})] \quad (72)$$

of the Legendre transform $\Delta S[\boldsymbol{\rho}, \mathbf{F}^{\mathrm{H}}|\boldsymbol{\rho}^0] \equiv \int \Delta s^{L}(\mathbf{r}|\mathbf{F}^{\mathrm{H}})\, \mathrm{d}\mathbf{r}$ itself (see eq 26). A reference to the constrained variational principle of eqs 17, 25, and 26 (see also eqs 18 and 19) indicates that its linear terms must identically vanish since $\partial\Delta s^{L}/\partial\rho_k(\mathbf{r})|_{\mathbf{0}} = \delta F_k|_{\mathbf{0}} = 0$. Thus, truncating the series at the second order term gives (see eq 35b)

$$\delta\Delta s^{\mathrm{L}}(\mathbf{r}|\mathbf{F}^{\mathrm{H}}) \equiv \Delta s^{\mathrm{L}}(\mathbf{r}|\mathbf{F}^{\mathrm{H}}) - \Delta s^{\mathrm{L}}(\mathbf{r}|\mathbf{F}^{\mathrm{H}})|_0 \cong \frac{1}{2}\sum_k \sum_l s_{kl}^{\;\mathrm{H}}\, \delta\rho_k\, \delta\rho_l = \frac{1}{2}\sum_k (\rho_k^{\;\mathrm{H}})^{-1}(\delta\rho_k)^2 \geq 0 \quad (73)$$

As we have already remarked before, the specific form of the relative entropy source (eqs 52, 56, and 66) will depend on the adopted measure of the entropy deficiency density, all of them predicting the unbiased Hirshfeld partitioning as the equilibrium scheme. But even for a given choice of the information distance, an identification of affinities and fluxes is not unique. We have identified in the local entropy production expression of eq 52 the specific choice of these quantities, which closely follows that adopted in the irreversible thermodynamics of continuous systems. However, in eqs 62a, 62b, and 66, the displacement in the local intensity relative to the Hirshfeld value (eq 43a]) rather then its gradient (eq 43b) has been used as an alternative definition of a local thermodynamic force driving the flows $\{\mathcal{J}_k\}$.

As an additional illustration of this dependence, let us consider the rate of the Legendre-transformed density $\delta\Delta s^{\mathrm{L}}$. Differentiating eq 73 gives

$$\frac{\mathrm{d}[\delta\Delta s^{L}]}{\mathrm{d}t} \equiv \delta\Sigma = \sum_k \left[\frac{\delta\rho_k}{\rho_k^{\;\mathrm{H}}}\right]\left[\frac{\mathrm{d}(\delta\rho_k)}{\mathrm{d}t}\right] \equiv \sum_k \mathcal{F}_k \mathcal{J}_k \quad (74)$$

since ρ_k^{H} is stationary. For the kth subsystem in a molecule, this expression identifies yet another pair of affinities $\mathcal{F}_k$ measuring the Hirshfeld-referenced relative density displacement and the conjugated flux $\mathcal{J}_k$ of eq 62b. Clearly, this new entropy deficiency source gives rise to yet another set of kinetic coefficients: $\{\mathcal{L}_{kl} = \partial\mathcal{J}_l/\partial\mathcal{F}_k\}$.

Therefore, a choice of affinities and fluxes, even within a given entropy deficiency representation, is by no means unique. It depends on the selected functional form of the information distance density. As we have seen, the specific identification of these parameters also affects the explicit form of the resulting kinetic coefficients and reciprocity relations.

The equilibrium distribution of electrons among constituent subsystems represents the statistical equilibrium (i.e., the average effect over instantaneous fluctuations in the subsystem densities $\delta\boldsymbol{\rho}(\delta\mathbf{F})$ preserving the overall density ρ. Clearly, these fluctuations also affect the displacements of the local instantaneous intensities $\delta\mathbf{F} = \delta\mathbf{F}(\delta\boldsymbol{\rho})$. Therefore, as a final example of the nonuniqueness of the local information-theoretic development, one could consider the entropy deficiency as a functional of forces $\delta\mathbf{F}$ of eqs 43a and 47 rather than of subsystem densities $\boldsymbol{\rho} = \boldsymbol{\rho}(\delta\mathbf{F})$ or their displacements, e.g., $\delta\Delta S[\delta\mathbf{F}] = \Delta S[\boldsymbol{\rho}(\delta\mathbf{F})|\boldsymbol{\rho}^{\mathrm{H}}] = \sum_k \int \rho_k\ \delta F_k\ \mathrm{d}\mathbf{r} \equiv \int \delta\Delta s(\delta\mathbf{F})\ \mathrm{d}\mathbf{r}$. The Legendre transform $\Delta S[\boldsymbol{\rho}(\delta\mathbf{F}), \mathbf{F}^{\mathrm{H}}|\boldsymbol{\rho}^0] \equiv \int \Delta s^{\mathrm{L}}(\delta\mathbf{F}^{\mathrm{H}})\, \mathrm{d}\mathbf{r}$ or its fluctuation $\delta\Delta S[\boldsymbol{\rho}(\delta\mathbf{F}),$

$\mathbf{F}^{\mathrm{H}}|\boldsymbol{\rho}^0] \equiv \int \delta\Delta s^{\mathrm{L}}(\delta\mathbf{F}^{\mathrm{H}})\,\mathrm{d}\mathbf{r}$ (eq 73) can be similarly treated as functionals of displacements in local intensities.

The dependence of the instantaneous densities of subsystems on their conjugate intensities follows from eq 43a,

$$\rho_{k=}\rho_k^{\mathrm{H}}\exp(\delta F_k) \equiv \rho_k^{\mathrm{H}} + \delta\rho_k \qquad \text{or}$$
$$\delta\rho_k = \rho_k^{\mathrm{H}}[\exp(\delta F_k) - 1] = \rho_k^{\mathrm{H}}\left[\delta F_k + \frac{1}{2}(\delta F_k)^2 + ...\right] \tag{75}$$

and hence $\partial(\delta\rho_k)/\partial(\delta F_k) = \rho_k$.

As an illustrative example, consider the symmetrized information distance of Kullback[3b] defining the divergence

$$\delta\Delta S^{\mathrm{K}}[\boldsymbol{\rho}] = \Delta S\,[\boldsymbol{\rho}, \boldsymbol{\rho}^{\mathrm{H}}] \equiv \Delta S[\boldsymbol{\rho}|\boldsymbol{\rho}^{\mathrm{H}}] + \Delta S[\boldsymbol{\rho}^{\mathrm{H}}|\boldsymbol{\rho}]$$
$$= \sum_k \int \delta\rho_k\, \delta F_k\, \mathrm{d}\mathbf{r} \equiv \sum_k \int \delta\Delta s_k^{\mathrm{K}}(\rho_k)\, \mathrm{d}\mathbf{r} \equiv$$
$$\int \delta\Delta s^{\mathrm{K}}(\boldsymbol{\rho})\, \mathrm{d}\mathbf{r} \tag{76}$$

Substituting the expansion of eq 75 into eq 76 gives the corresponding expansion of the subsystem divergence density:

$$\delta\Delta s_k^{\mathrm{K}}(\rho_k) = \rho_k^{\mathrm{H}}\left[(\delta F_k)^2 + \frac{1}{2}(\delta F_k)^3 + ...\right] \cong$$
$$\frac{1}{2}\sum_k \sum_l g_{kl}\, \delta F_k\, \delta F_l$$
$$g_{kl} = \left[\frac{\partial^2(\delta\Delta s^{\mathrm{K}})}{\partial(\delta F_k)\,\partial(\delta F_l)}\right]_{\mathbf{0}} = 2\rho_k^{\mathrm{H}}\,\delta_{kl} > 0 \tag{77a}$$

The above quadratic expansion demonstrates that this function indeed exhibits a stable equilibrium at $\delta F_k = 0$ (i.e., for the Hirshfeld partitioning of the molecular electron density. The local $\delta\Delta s_k^{\mathrm{K}}$ conjugate of δF_k is defined by the derivative (see eqs 75 and 77a)

$$\frac{\partial(\delta\Delta s_k^{\mathrm{K}})}{\partial(\delta F_k)} = \delta\rho_k + \rho_k\, \delta F_k \cong \sum_l g_{kl}\, \delta F_l = 2\rho_k^{\mathrm{H}}\, \delta F_k \equiv X_k \tag{77b}$$

The expression for the local divergence source relative to the Hirshfeld value thus reads

$$\delta\sigma^{\mathrm{K}} = \frac{\mathrm{d}(\delta\Delta s^{\mathrm{K}})}{\mathrm{d}t} = \sum_k \left[\frac{\partial(\delta\Delta s_k^{\mathrm{K}})}{\partial(\delta F_k)}\right]\left[\frac{\mathrm{d}(\delta F_k)}{\mathrm{d}t}\right] \equiv \sum_k j_k X_k \tag{78}$$

Therefore, in this divergence $\delta\mathbf{F}$ representation the rates of change in local intensities, $\{j_k \equiv \mathrm{d}(\delta F_k)/\mathrm{d}t\}$, determine the relevant Kullback fluxes, whereas the $\delta\mathbf{F}$-dependent parameters $\mathbf{X}$ of eq 77b, proportional to the corresponding Hirshfeld density values, play the role of the conjugate affinities.

Clearly, one could also derive the corresponding relations for the directed divergence measure of the information distance, $\delta\Delta S[\delta\mathbf{F}] = \Delta S[\boldsymbol{\rho}(\delta\mathbf{F})|\boldsymbol{\rho}^{\mathrm{H}}]$, treating the relative subsystem intensities $\delta\mathbf{F}$ as independent state parameters.[14]

8. Conclusions

In information theory, the free-subsystem-referenced variational principle of the entropy deficiency, subject to the auxiliary conditions of the exhaustive partitioning of the molecular density at each point in space, leads to the stockholder electron densities of molecular fragments, which mark the entropy-stable equilibrium state in the subsystem resolution. The resulting overlapping Hirshfeld pieces of the molecular electron distribution exhibit equalized chemical potentials, remove exactly the nonadditivity of the overall entropy deficiency, and exhibit several information density equalization rules, which make them attractive concepts for a chemical interpretation.[4−7]

With the present instantaneous development, we have explored the local thermodynamic analogies in the nonequilibrium information-theoretic description of the vertical processes in molecular subsystems, which preserve the density of the system as a whole. The alternative representations of such a local approach, corresponding to different measures of the missing information or different choices of independent state parameters, have been examined, and the corresponding affinities (forces) and fluxes (responses) determining the relevant local entropy deficiency source have been identified in close analogy to the phenomenological irreversible thermodynamics.[1] For the linear dynamical processes in a molecule (Markoffian system), they imply the local reciprocity rules, analogues of the familiar Onsager relations,[1] which reflect basic symmetries between the linear effects of the subsystem affinities on fluxes. Therefore, the thermodynamic analogies in the entropic description of vertical processes in molecular subsystems can indeed be extended to the nonequilibrium, instantaneous electron distributions and irreversible processes covering both density fluctuations relative to the (stationary) Hirshfeld values and electron flows between constituent fragments. The freedom of choosing alternative state parameters is also reminiscent of that in ordinary thermodynamics.

This and previous works show that the complementary quantities of the entropy deficiency, based on the Shannon entropy/information measure, provide a solid basis for extracting a chemical interpretation from the available molecular electron densities in terms of atoms, functional groups, reactants, and so forth. The entropic concepts can also be used to probe chemical bond multiplicities (subsystem connectivities) in different molecular environments.[11] With the present development, the Hirshfeld subsystems, previously regarded as static entities, can now also be viewed as the averages of the instantaneous (dynamic) entities, with the distribution of local fluctuations being related to the relevant missing information density in the thermodynamic-like fashion. This opens the possibility of extending the range of applications of the information-theoretic treatment of the submolecular processes to the realm of nonequilibrium states of subsystems (e.g., the electronic structure reorganization in a chemical reaction). In other words, this analysis establishes a theoretical framework for an eventual dynamical indexing of the nonequilibrium reactivity phenomena.

Clearly, the vertical, submolecular reality in the subsystem resolution, so important to the language of chemistry, cannot be directly validated experimentally since it is not an observable. It can be verified only indirectly by the demonstrated close analogy to the phenomenological thermodynamics. Nevertheless, consistent chemical interpretations call for a theoretical framework introducing the causality relations between perturbations and responses of molecular subsystems, paralleling the familiar structure of the ordinary thermodynamics. With this development, we have established basic conceptual ingredients of such an information-theoretic approach, filling a gap of the instantaneous density fluctuations, which are always present in open molecular subsystems. These fluctuations are the key ingredient of many chemical concepts (e.g., the chemical softness and Fukui function[10,15]).

The information-theoretic outlook on the electronic structure of molecular systems introduces a novel entropy representation of molecular systems, which we have shown to be vital for a local thermodynamic interpretation of chemical processes. With this development, the whole experience of the ordinary thermodynamics can thus be employed in treating a variety of subtle processes in chemistry.

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