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Information Theory Thermodynamics of Molecules and Their Hirshfeld Fragments

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The Hirshfeld stockholder partitioning of a molecular density into subsystem densities, e.g., of atoms-in-molecules, is derived from the Fisher entropy for locality (intrinsic accuracy) referenced to the isolated atom densities. This complements the previous derivation using the entropy deficiency of Kullback and Leibler, thereby strongly suggesting that the Hirshfeld result is independent of the information measure applied to assimilate the reference atomic information. Several properties of such subsystems are examined. It is shown that they represent equilibrium, stable pieces of the molecular density, which minimize and reduce to zero the nonadditivity of the missing information relative to the isolated atom reference. The equilibrium criteria for the optimum partitioning in both the entropy and energy representations are derived and interpreted in terms of local entropies of subsystems and their related "temperatures" of information. Generalized variational principles in the entropy and energy representations are proposed, which link the entropy of the information theory with energetical parameters of molecular systems. The associated information temperature becomes infinite, when a single ground-state density is the density of interest.

1. Introduction

The dominant perspective in chemical thought is that of molecules as combinations of atoms and functional groups connected by chemical bonds. All such chemical (bonded) subsystems may be considered to be only slightly perturbed in comparison to the corresponding separated subsystems, i.e., when the complementary molecular environments are missing. Chemical atoms are usually only weakly deformed by the polarization and charge transfer associated with the formation of chemical bonds, with a change in the bonding pattern affecting mainly the valence shell of atoms comprising a molecule. It is therefore appealing for interpretative purposes to invoke the criterion of the maximum similarity between the bonded *atoms-in-molecules* (AIM; open subsystems) and the corresponding isolated atoms (or ions) of the periodic table of elements.

As we have recently demonstrated,[1] the information theory[2−9] can be used to assimilate in the most unbiased manner the information content of the appropriate free atom densities, in the partitioning of a molecular density into atomic densities. Using the Kullback−Leibler (KL)[7] minimum missing information (entropy deficiency) principle produces the Hirshfeld[10] ("stockholder") AIM densities as the pieces of the molecular density optimally most resembling the densities of the corresponding isolated atoms. A similar information-theoretic approach gives solutions to the problem of assessing similarity between molecules and their fragments and to the problem of determining the bond multiplicities in a molecule.[11]

The Hirshfeld atom, which exhibits the minimum information distance to its free atom reference, possesses, like its free analogue, a single cusp in its electron density, linked to the effective atomic number of the nucleus.[12] Hirshfeld atoms overlap, and each of them extends over the whole space. One would hope to find that the Hirshfeld partitioning is unique, when the *separated atom limit* is adopted as a reference, being independent of the specific information measure adopted in the entropy extremum principle. In the present paper, we shall examine this question by using the Fisher information for locality called intrinsic accuracy.[8] We demonstrate that it also leads to the Hirshfeld subsystem densities. Moreover, it is shown that it gives rise to additivity of the missing information functional.

The unique character of the stockholder partitioning prompts us here to further examine some of the "thermodynamical" properties of the Hirshfeld subsystems. In particular, we shall elucidate the equilibrium and stable character of such open AIM.

It is essential to note that all divisions of the fixed, ground-state molecular density, say of AB, $\rho = \rho_A + \rho_B$, must be carried out for constant energy of the molecule as a whole, because by the Hohenberg−Kohn theorem of the *density functional theory* (DFT)[13,14] the density fixes the system energy $E = E_v[\rho]$. Therefore, determining the optimum partitioning of ρ by the information-entropy extremum principle calls to mind the familiar maximum entropy principle of classical thermodynamics.[15] We further explore these thermodynamical analogies in the present work, by interpreting the equilibrium principles in both the entropy and energy representations in terms of the information-theoretic entropy densities and the associated local information "temperatures" of subsystems, much in the spirit of earlier thermodynamical transcriptions of DFT.[16]

2. Hirshfeld Partitioning of Molecular Density and the Minimum Entropy Deficiency Principle

The KL[7] referenced information entropy functional of the (normalized) trial probability distribution $p(\vec{r})$ relative to the reference distribution $p_o(\vec{r})$

$$\Delta S^{KL}[p|p_o] = \int p(\vec{r}) \ln\left[\frac{p(\vec{r})}{p_o(\vec{r})}\right] d\vec{r} \equiv S^{KL}[p] \geq 0 \quad (1)$$

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called the missing information or entropy deficiency, measures the information "distance" between p and p_o. The corresponding principle of the minimum entropy deficiency[3,7] represents a systematic procedure for assimilating in the most unbiased manner the information contained in the relevant constraints imposed on the trial distribution $p(\vec{r})$, when searching for the p most resembling the reference distribution p_o.[1,5,6]

The logarithmic part of the integrand in eq 1

$$I[p|p_o] = \ln\left[\frac{p(\vec{r})}{p_o(\vec{r})}\right] \tag{2}$$

called surprisal, provides a local measure of the information contained in p with reference to p_o. The information entropy defined without a reference

$$S[p] = \int p(\vec{r}) \ln[p(\vec{r})]\, d\vec{r} \tag{3}$$

is called the Shannon[2] entropy of the distribution $p(\vec{r})$.

In what follows, we explicitly consider a molecule AB, consisting of two complementary subsystems A and B, e.g., AIM. Generalization to an arbitrary number of subsystems is trivial. To treat the classical problem of partitioning the molecular density $\rho = \rho_A + \rho_B$ into subsystem densities, one defines the entropy deficiency functional[1]

$$\Delta S^{KL}[\rho_A\rho_B|\rho_A^o\rho_B^o] = \sum_{\alpha=A,B} \Delta S^{KL}[\rho_\alpha|\rho_\alpha^o] \equiv \sum_{\alpha=A,B} S_\alpha^{KL}[\rho_\alpha] \equiv S^{KL}[\rho_A,\rho_B] \tag{4}$$

where $\{\rho_\alpha^o\}$ are the separated fragment or other reference densities, and imposes the local constraint of the exhaustive allocation of ρ to ρ_A and ρ_B:

$$\rho(\vec{r}) = \rho_A(\vec{r}) + \rho_B(\vec{r}) \tag{5}$$

Then, the principle of minimum entropy deficiency

$$\delta\{S^{KL}[\rho_A,\rho_B] - \int \lambda(\vec{r})[\rho_A(\vec{r}) + \rho_B(\vec{r})]\, d\vec{r}\} = 0 \tag{6}$$

where $\lambda(\vec{r})$ is the associated Lagrange multiplier function to be determined from the constraint of eq 5, gives[1] the Hirshfeld subsystems:[10]

$$\rho_\alpha^H(\vec{r}) = \rho_\alpha^o(\vec{r})\left[\frac{\rho(\vec{r})}{\rho^o(\vec{r})}\right] \equiv \rho_\alpha^o(\vec{r})\, D(\vec{r}) \equiv w_\alpha^H(\vec{r})\, \rho(\vec{r}) \tag{7}$$

Here $\rho^o = \Sigma_{\alpha=A,B}\ \rho_\alpha^o$ stands for the "promolecule" density consisting of the isolated fragment densities shifted to their actual positions in the molecule. The universal factor $D(\vec{r})$ determines the local proportionality of the subsystem density to the reference density, whereas the local fragment share $w_\alpha^H(\vec{r})$ is the fraction of ρ_α^o in ρ^o.

Now consider the *mixing* missing information functional

$$\Delta S_M^{KL}[\rho_A\rho_B|\rho_A^o\rho_B^o] = \Delta S^{KL}[\rho_A\rho_B|\rho_A^o\rho_B^o] - \Delta S^{KL}[\rho|\rho^o] \tag{8}$$

where the last term is the information distance between the molecular and promolecule densities. This functional provides a measure of the nonadditive part of the missing information, $-\Delta S_M^{KL} = S^{KL}[\rho] - S_A^{KL}[\rho_A] - S_B^{KL}[\rho_B]$, thus indeed reflecting the net effect of mixing the atomic densities in a molecule. Transforming the functional of eq 8 gives (see eq 7)

$$\Delta S_M^{KL} = \sum_{\alpha=A,B} \int \rho_\alpha \ln\left[\frac{\rho_\alpha}{\rho_\alpha^o\left(\dfrac{\rho}{\rho^o}\right)}\right] d\vec{r} = \sum_{\alpha=A,B} \Delta S^{KL}[\rho_\alpha|\rho_\alpha^H] \equiv \Delta S^{KL}[\rho_A\rho_B|\rho_A^H\rho_B^H] \geq 0 \tag{9}$$

i.e., the entropy deficiency of arbitrary subsystem densities $\{\rho_\alpha\}$ relative to the corresponding Hirshfeld densities. The equality sign in eq 9 holds only for $\rho_\alpha = \rho_\alpha^H$, $\alpha = A,B$.

The strong conclusion is that the stockholder partitioning goes uniquely with vanishing nonadditivity of the entropy deficiency, when isolated fragment densities are used as reference. It also follows from eq 9 that any deviation of the subsystem densities from the equilibrium Hirshfeld ones must result in an increase of the entropy deficiency, thus proving the information theoretic stability of the optimum subsystem pieces of the molecular density, with respect to all virtual displacements of the molecular fragment densities preserving ρ.

To be more explicit, consider displacements $\{[d\rho_\alpha]_\rho\}$ which represent changes in the amount of charge transfer between subsystems and their internal polarization. Then, for the Hirshfeld division of ρ, the missing information is stable relative to all such hypothetical displacements

$$\sum_{\alpha=A,B} \int \left.\frac{\delta \Delta S^{KL}}{\delta \rho_\alpha(\vec{r})}\right|_{\{\rho_\alpha^H\}} [d\rho_\alpha(\vec{r})]_\rho\, d\vec{r} = 0, \quad \text{global equilibrium;} \tag{10}$$

$$\sum_{\alpha=A,B} \int \left.\frac{\delta^2 \Delta S^{KL}}{\delta \rho_\alpha(\vec{r})\delta \rho_\alpha(\vec{r})}\right|_{\{\rho_\alpha^H\}} [d\rho_\alpha(\vec{r})]_\rho^{\,2} \geq 0, \quad \text{global stability,} \tag{11}$$

where the equality sign implies $\{d\rho_\alpha = 0\}$.

The KL functional of eq 4 consists of two terms:

$$\Delta S^{KL} = \sum_{\alpha=A,B} \int \rho_\alpha \ln \rho_\alpha\, d\vec{r} - \sum_{\alpha=A,B} \int \rho_\alpha \ln \rho_\alpha^o\, d\vec{r} = S_{deloc}^{KL}[\rho_A,\rho_B] - S_{loc}^{KL}[\rho_A\rho_B|\rho_A^o\rho_B^o] \tag{12}$$

The first, unreferenced term, S_{deloc}^{KL}, yielding the total Shannon information of the subsystem densities, by itself would make the optimum densities of subsystems perfectly delocalized; we therefore call it the *delocalization component* of the missing information functional. The delocalization effect of the S_{deloc}^{KL} functional is manifest in the entropy extremum principle:

$$\delta\{S_{deloc}^{KL}[\rho_A,\rho_B] - \int \phi(\vec{r})[\rho_A(\vec{r}) + \rho_B(\vec{r})]\, d\vec{r}\} = 0 \tag{13}$$

having the perfectly delocalized, equidensity solutions, given by the locally unbiased fractions of ρ:

$$\rho_\alpha^{del}(\vec{r}) = \rho(\vec{r})/2 \qquad \alpha = A,B \tag{14}$$

It is only owing to the second, reference-dependent, *localization component*, S_{loc}^{KL}, that the Hirshfeld atoms become very much like their free analogues.

3. Optimum Subsystem Densities from the Referenced Intrinsic Accuracy Principle

The question naturally arises: Is the optimum partitioning dependent on the specific information measure used, or will other measures produce different optimum solutions to the partitioning problem? We examine this question by turning to another information functional of the parametric probability density $p(\vec{r}|\theta)$ depending upon the parameter θ

$$\mathrm{I}^{\mathrm{F}}(\theta) = \int p(\vec{r}|\theta)\left[\frac{\partial \ln p(\vec{r}|\theta)}{\partial \theta}\right]^2 \mathrm{d}\vec{r} = \int \frac{\left[\frac{\partial p(\vec{r}|\theta)}{\partial \theta}\right]^2}{p(\vec{r}|\theta)}\,\mathrm{d}\vec{r} \tag{15}$$

introduced by Fisher.[8] For the special case when θ is a parameter of locality

$$p(\vec{r}|\vec{\theta}) = p(\vec{r} + \vec{\theta}) \equiv p(\vec{r}\,') \tag{16}$$

the Fisher information becomes ($\partial/\partial\vec{r} = \nabla$)

$$\mathrm{I}^{\mathrm{F}}(\vec{\theta} = \vec{0}) = \int p(\vec{r})\left[\frac{\partial \ln p(\vec{r})}{\mathrm{d}\vec{r}}\right]^2 \mathrm{d}\vec{r} = \int \frac{\left(\frac{\partial p(\vec{r})}{\partial \vec{r}}\right)^2}{p(\vec{r})}\,\mathrm{d}\vec{r} \equiv \mathrm{I}^{\mathrm{F}}[p] \tag{17}$$

This functional defines the so-called *intrinsic accuracy*[17] of $p(\vec{r})$, providing a measure of the "narrowness" of the probability distribution. Because the Shannon (KL) information represents the "spread" of $p(\vec{r})$, the simple Shannon and simple Fisher measures provide complementary characteristics of the probability distribution. Intrinsic accuracy itself, just as the Shannon information $S^{\mathrm{KL}}_{\mathrm{deloc}}$, on minimization produces the perfectly delocalized pieces of the molecular density of eq 14. This can be verified using the variational principle (compare eq 13):

$$\delta\{\mathrm{I}^{\mathrm{F}}_{\mathrm{deloc}}[\rho_{\mathrm{A}},\rho_{\mathrm{B}}] - \int \varphi(\vec{r})[\rho_{\mathrm{A}}(\vec{r}) + \rho_{\mathrm{B}}(\vec{r})]\,\mathrm{d}\vec{r}\} = 0 \tag{18}$$

where $\varphi(\vec{r})$ is the Lagrange multiplier function for the constraint of eq 5 and

$$\mathrm{I}^{\mathrm{F}}_{\mathrm{deloc}}[\rho_{\mathrm{A}},\rho_{\mathrm{B}}] = \mathrm{I}^{\mathrm{F}}[\rho_{\mathrm{A}}] + \mathrm{I}^{\mathrm{F}}[\rho_{\mathrm{B}}] \tag{19}$$

To generate localized subsystem densities, one has to include the separated subsystem reference in the Fisher entropy, which then introduces the necessary "penalty" entropy when the AIM densities deviate from the reference. Following the KL generalization[7] of Shannon's entropy, we propose the referenced generalization of the Fisher function of eq 15

$$\Delta\mathrm{I}^{\mathrm{F}}[p(\vec{r}|\theta)|p_{\mathrm{o}}(\vec{r}|\theta)] = \int p(\vec{r}|\theta)\left\{\frac{\partial \ln[p(\vec{r}|\theta)/p_{\mathrm{o}}(\vec{r}|\theta)]}{\partial \theta}\right\}^2 \mathrm{d}\vec{r} \tag{20}$$

or in the locality form (eq 17)

$$\Delta\mathrm{I}^{\mathrm{F}}[p|p_{\mathrm{o}}] = \int p(\vec{r})\left\{\frac{\partial}{\partial \vec{r}}\ln\left[\frac{p(\vec{r})}{p_{\mathrm{o}}(\vec{r})}\right]\right\}^2 \mathrm{d}\vec{r} = \int p_{\mathrm{o}}\left(\frac{p}{p_{\mathrm{o}}}\right)\left[\frac{\partial \ln(p/p_{\mathrm{o}})}{\partial \vec{r}}\right]^2 \mathrm{d}\vec{r} \tag{21}$$

To test the localization performance of eq 20, we may consider the simplest variational principle

$$\delta\{\Delta\mathrm{I}^{\mathrm{F}}[p|p_{\mathrm{o}}] - \xi \int p(\vec{r})\} = 0 \tag{22}$$

where the Lagrange multiplier ξ is associated with the constraint of p normalization: $\int p\,\mathrm{d}\vec{r} = 1$. The corresponding Euler equation

$$-\left(\frac{\mathrm{d}\ln R(\vec{r})}{\mathrm{d}\vec{r}}\right)^2 - \xi = 0 \tag{23}$$

where $R(\vec{r}) \equiv p(\vec{r})/p_{\mathrm{o}}(\vec{r})$, gives

$$\ln R = \sqrt{-\xi}\int \mathrm{d}\vec{r}, \quad \xi \le 0 \tag{24}$$

Thus, a finite value of $R(\vec{r})$ can only be obtained when $\xi = 0$, $\ln R(\vec{r}) = 0$, or $p(\vec{r}) = p_{\mathrm{o}}(\vec{r})$. The same solution follows when one substitutes $\Delta S^{\mathrm{KL}}[p|p_{\mathrm{o}}]$ for $\Delta I^{\mathrm{F}}[p|p_{\mathrm{o}}]$ in eq 22.[1] This verifies the localization effect of the functional of eq 20, required to produce localized subsystem densities in the molecular density partitioning problem. We call the referenced Fisher's functional of eq 20 the *Fisher missing information* (entropy deficiency) or the *Fisher information distance* between p and p_{o}.

Following the analysis of the preceding section, one again identifies the proper *localization part* of the ΔI^{F} functional as the difference

$$-I^{\mathrm{F}}_{\mathrm{loc}}[p|p_{\mathrm{o}}] = \Delta I^{\mathrm{F}}[p|p_{\mathrm{o}}] - I^{\mathrm{F}}_{\mathrm{deloc}}[p] = 2\int p\left(\frac{\partial \ln p}{\partial \vec{r}}\right)\left(\frac{\partial \ln p_{\mathrm{o}}}{\partial \vec{r}}\right)\mathrm{d}\vec{r} - \int p\left(\frac{\partial \ln p_{\mathrm{o}}}{\partial \vec{r}}\right)^2 \mathrm{d}\vec{r} \tag{25}$$

where $I^{F}_{\mathrm{deloc}}[p] \equiv I^{\mathrm{F}}[p]$ stands for the reference-independent intrinsic accuracy of eq 17.

Let us now go back to the partitioning of the AB density ρ into ρ_{A} and ρ_{B} (eq 5), which can be rewritten in terms of functions $\{R_{\alpha} = \rho_{\alpha}/\rho^{\mathrm{o}}_{\alpha}\}$ of the relative subsystem densities:

$$\rho(\vec{r}) = \rho^{\mathrm{o}}_{\mathrm{A}}(\vec{r})\,R_{\mathrm{A}}(\vec{r}) + \rho^{\mathrm{o}}_{\mathrm{B}}(\vec{r})\,R_{\mathrm{B}}(\vec{r}) \tag{26}$$

Implementing the principle of the minimum of Fisher's entropy deficiency for locality

$$\delta\{\Delta I^{\mathrm{F}}[\rho_{\mathrm{A}}\rho_{\mathrm{B}}|\rho^{\mathrm{o}}_{\mathrm{A}}\rho^{\mathrm{o}}_{\mathrm{B}}] + \int h(\vec{r})[\rho_{\mathrm{A}}(\vec{r}) + \rho_{\mathrm{B}}(\vec{r})]\,\mathrm{d}\vec{r}\} = 0 \tag{27}$$

where $\Delta I^{\mathrm{F}}[\rho_{\mathrm{A}}\ \rho_{\mathrm{B}}|\rho^{\mathrm{o}}_{\mathrm{A}}\rho^{\mathrm{o}}_{\mathrm{B}}] = \Delta I^{\mathrm{F}}[\rho_{\mathrm{A}}|\rho^{\mathrm{o}}_{\mathrm{A}}] + \Delta I^{\mathrm{F}}[\rho_{\mathrm{B}}|\rho^{\mathrm{o}}_{\mathrm{B}}] \equiv S^{\mathrm{F}}[\rho_{\mathrm{A}},\rho_{\mathrm{B}}] \equiv I_{\mathrm{A}}{}^{\mathrm{F}}[\rho_{\mathrm{A}}] + I_{\mathrm{B}}{}^{\mathrm{F}}[\rho_{\mathrm{B}}]$ and $h(\vec{r})$ is the local Lagrange multiplier associated with the exhaustive partitioning constraint of eq 26, gives the following equation for the optimum subsystem densities:

$$\sum_{\alpha=\mathrm{A,B}}\left\{\rho^{\mathrm{o}}_{\alpha}(\vec{r})\left[-\left(\frac{\partial \ln R_{\alpha}(\vec{r})}{\partial \vec{r}}\right)^2 + h(\vec{r})\right]\delta\rho_{\alpha}(\vec{r})\right\} = 0 \tag{28}$$

Hence

$$R_{\mathrm{A}}(\vec{r}) = R_{\mathrm{B}}(\vec{r}) = R(\vec{r}) = \exp\left[\int_{-\infty}^{\vec{r}} h^{1/2}(\vec{r}\,')\,\mathrm{d}\vec{r}\,'\right], \quad h(\vec{r}) \ge 0 \tag{29}$$

Now, the function $R(\vec{r})$ automatically follows from eq 26 (see also eq 7)

$$R(\vec{r}) = \rho(\vec{r})/\rho^{\mathrm{o}}(\vec{r}) = D(\vec{r}) \tag{30}$$

and

$$h = \left[\left(\frac{\partial \rho}{\partial \vec{r}}\right)/\rho - \left(\frac{\partial \rho^{\mathrm{o}}}{\partial \vec{r}}\right)/\rho^{\mathrm{o}}\right]^2 \ge 0 \tag{31}$$

We therefore again find the Hirshfeld subsystem densities of eq 7 as the optimum solutions of the Fisher's entropy deficiency principle of eq 27. Because the same partitioning follows from the KL entropy deficiency measure, one may conjecture that the stockholder partitioning scheme is unique in the information theory, being independent of the particular form of the entropy functional used, provided the same reference to the isolated fragments is made. Additional support for this conclusion comes from the independent axiomatic approach by Ayers[18] to the same problem.

4. Stability of the Hirshfeld Subsystems

We now discuss in some detail the global stability criterion of eq 11 in the AB system. To examine the behavior of the ΔS^{KL} functional of eq 4 relative to displacements of ρ_α from $\rho_\alpha{}^{\mathrm{H}}$, $\alpha = \mathrm{A,B}$, we impose the second local constraint of the fixed density difference

$$d(\vec{r}) = \rho_{\mathrm{A}}(\vec{r}) - \rho_{\mathrm{B}}(\vec{r}) \tag{32}$$

in addition to the molecular density preservation eq 5. Notice that $\rho(\vec{r})$ and $d(\vec{r})$ uniquely determine $\rho_{\mathrm{A}} = (\rho + d)/2$ and $\rho_{\mathrm{B}} = (\rho - d)/2$, so there is no need for any optimization. It can be verified that, among all trial $\{\rho_\alpha(d)\}$, uniquely specified by d for the fixed ρ, the Hirshfeld densities indeed provide the minimum information distance relative to the reference densities (see eq 7):

$$\begin{aligned}\min_{\{\rho_\alpha\}\to\rho} \Delta S^{\mathrm{KL}}[\{\rho_\alpha\}|\{\rho_\alpha^{\mathrm{o}}\}] &= \min_{\{\rho_\alpha(d)\}} \Delta S^{\mathrm{KL}}[\rho,d] = \Delta S^{\mathrm{KL}}[\{\rho_\alpha^{\mathrm{H}}\}|\{\rho_\alpha^{\mathrm{o}}\}] \\ &= \int \rho^{\mathrm{o}}(\vec{r})\, D(\vec{r}) \ln D(\vec{r})\, \mathrm{d}\vec{r} = \Delta S^{\mathrm{KL}}[\rho|\rho^{\mathrm{o}}]\end{aligned} \tag{33}$$

where $\Delta S^{\mathrm{KL}}[\{\rho_\alpha[\rho,d]\}|\{\rho_\alpha^{\mathrm{o}}\}] = \Delta S^{\mathrm{KL}}[\rho,d]$. Indeed, functional differentiation of $\Delta S^{\mathrm{KL}}[\rho,d]$ with respect to $d(\vec{r})$, for the fixed ρ, gives the optimum $d(\vec{r})$ satisfying the following equation:

$$\left(\frac{\delta \Delta S^{\mathrm{KL}}[\rho,d]}{\delta d(\vec{r})}\right)_\rho = \ln\left\{\frac{[\rho(\vec{r}) - d(\vec{r})]\rho_{\mathrm{B}}^{\mathrm{o}}(\vec{r})}{[\rho(\vec{r}) - d(\vec{r})]\rho_{\mathrm{A}}^{\mathrm{o}}(\vec{r})}\right\} = 0 \tag{34}$$

or $\rho_{\mathrm{A}}/\rho_{\mathrm{B}} = \rho_{\mathrm{A}}^{\mathrm{o}}/\rho_{\mathrm{B}}^{\mathrm{o}}$ and $d = D[\rho_{\mathrm{A}}^{\mathrm{o}} - \rho_{\mathrm{B}}^{\mathrm{o}}] = d^{\mathrm{H}}$, which is the Hirshfeld result. Moreover

$$\left(\frac{\delta^2 \Delta S^{\mathrm{KL}}[\rho,d]}{\delta d(\vec{r}) \delta d(\vec{r})}\right)_\rho \Big|_{d^H} = 2\left[\frac{\rho^{\mathrm{o}}(\vec{r})}{\rho(\vec{r})}\right] > 0 \tag{35}$$

thus satisfying the stability criterion of eq 11:

$$(\delta^2 \Delta S^{\mathrm{KL}}[\rho,d])_\rho|_{d^H} = \int \frac{\rho^{\mathrm{o}}(\vec{r})}{\rho(\vec{r})}[d(\vec{r}) - d^{\mathrm{H}}(\vec{r})]^2\, \mathrm{d}\vec{r} \geq 0 \tag{36}$$

with equality only for $d = d^{\mathrm{H}}$.

The above inequality is a manifestation of a general property of the KL entropy function, because the assimilation of the additional constraint of eq 32 cannot result in a decrease of the information distance in comparison to that corresponding to a single constraint of eq 5. This is because the second constraint actually restricts the range of trial distributions to a single pair of ρ_{A} and ρ_{B} consistent with the first constraint.

Let us now consider another, global constraint, in addition to eq 5, of the single subsystem density normalization, say for $\alpha = \mathrm{A}$:

$$\int \rho_{\mathrm{A}}(\vec{r})\, \mathrm{d}\vec{r} = N_{\mathrm{A}} \tag{37}$$

in the entropy deficiency minimum principle of eq 6:

$$\delta\{S^{\mathrm{KL}}[\rho_{\mathrm{A}},\rho_{\mathrm{B}}] - \int \bar{\lambda}(\vec{r})[\rho_{\mathrm{A}}(\vec{r}) + \rho_{\mathrm{B}}(\vec{r})]\, \mathrm{d}\vec{r} - \lambda_{\mathrm{A}} \int \rho_{\mathrm{A}}(\vec{r})\, \mathrm{d}\vec{r}\} = 0 \tag{38}$$

The solutions of the corresponding Euler equations are

$$\rho_{\mathrm{A}}(\vec{r}) = \rho_{\mathrm{A}}^{\mathrm{o}}(\vec{r}) \exp[\zeta(\vec{r}) + \lambda_{\mathrm{A}}] \equiv \rho_{\mathrm{A}}^{\mathrm{o}}(\vec{r}) \exp[\zeta(\vec{r})]\chi \tag{39}$$

$$\rho_{\mathrm{B}}(\vec{r}) = \rho_{\mathrm{B}}^{\mathrm{o}}(\vec{r}) \exp[\zeta(\vec{r})] \tag{40}$$

where $\zeta(\vec{r}) = \lambda(\vec{r}) - 1$ can be obtained from eq 5:

$$\zeta(\vec{r}) = \ln\left\{\frac{\rho(\vec{r})}{[\chi\rho_{\mathrm{A}}^{\mathrm{o}}(\vec{r}) + \rho_{\mathrm{B}}^{\mathrm{o}}(\vec{r})]}\right\} \tag{41}$$

The global Lagrange multiplier can then be determined from the second constraint of eq 37, which gives the equation

$$\chi \int \frac{\rho(\vec{r})\rho_{\mathrm{A}}^{\mathrm{o}}(\vec{r})}{\chi\rho_{\mathrm{A}}^{\mathrm{o}}(\vec{r}) + \rho_{\mathrm{B}}^{\mathrm{o}}(\vec{r})}\, \mathrm{d}\vec{r} = N_{\mathrm{A}} \tag{42}$$

to be solved numerically for $\chi \equiv \exp(\lambda_{\mathrm{A}})$.

These solutions define the subsystem densities most resembling the reference densities and reproducing the specified subsystem numbers of electrons:

$$\rho_\alpha = \rho_\alpha(N_{\mathrm{A}},N_{\mathrm{B}}), \quad \alpha = \mathrm{A,B} \tag{43}$$

thus uniquely determining the entropy deficiency as a function of the specified number of electrons in each subsystem:

$$\Delta S^{\mathrm{KL}}[\rho_\alpha(N_{\mathrm{A}},N_{\mathrm{B}})|\rho_{\mathrm{A}}^{\mathrm{o}}\rho_{\mathrm{B}}^{\mathrm{o}}] = \Delta S^{\mathrm{KL}}[N_{\mathrm{A}}N_{\mathrm{B}}|\rho_{\mathrm{A}}^{\mathrm{o}}\rho_{\mathrm{B}}^{\mathrm{o}}] \tag{44}$$

Again, a stability inequality holds (see eq 33):

$$\Delta S^{\mathrm{KL}}[N_{\mathrm{A}}N_{\mathrm{B}}|\rho_{\mathrm{A}}^{\mathrm{o}}\rho_{\mathrm{B}}^{\mathrm{o}}] \geq \Delta S^{\mathrm{KL}}[N_{\mathrm{A}}^{\mathrm{H}}N_{\mathrm{B}}^{\mathrm{H}}|\rho_{\mathrm{A}}^{\mathrm{o}}\rho_{\mathrm{B}}^{\mathrm{o}}] \tag{45}$$

where $N_\alpha^{\mathrm{H}} = \int \rho_\alpha{}^{\mathrm{H}}\, \mathrm{d}\vec{r}$, $\alpha = \mathrm{A,B}$. This result demonstrates the stable character of the equilibrium (Hirshfeld) subsystems with respect to intersubsystem charge transfer.

5. Chemical Potential Equalization

5.1. External Equilibrium Condition. Let the molecular density ρ be the ground-state density for the AB system. The equalization of the local chemical potential $\mu(\vec{r})$ of this equilibrium distribution of electrons in AB as a whole[14,19,20] requires that

$$\mu(\vec{r}) = \mu[\rho;\vec{r}] \equiv \frac{\delta E_v[\rho]}{\delta\rho(\vec{r})} = \mu \equiv \frac{\partial \bar{E}_v(N)}{\partial N} \tag{46}$$

where[13,14]

$$E_v[\rho] = \int v\rho\, \mathrm{d}\vec{r} + F[\rho] = \bar{E}_v(N) \tag{47}$$

is the system electronic energy, uniquely determined by ρ or by the external potential due to the nuclei, $v(\vec{r}) = v_{\mathrm{A}}(\vec{r}) + v_{\mathrm{B}}(\vec{r})$

$= v[\rho;\vec{r}]$, and the overall number of electrons, $N[\rho] = \int \rho(\vec{r})\,\mathrm{d}\vec{r}$. Here, $F[\rho] = \langle \psi[\rho]|\hat{F}|\psi[\rho]\rangle$ generates the sum of the electronic kinetic and repulsion energies, $\hat{F} = \hat{T}_e + \hat{V}_{ee}$, for the ground-state $\psi[\rho]$; $\mu = \mu[\rho] = \tilde{\mu}[N,v]$ stands for the system *global chemical potential*; and $v_\alpha(\vec{r})$ denotes the external potential generated by the nuclei in the A or B subsystem.

Equation 46 directly follows from the DFT variational principle for open systems[13,19]

$$\delta\{E_v[\rho] - \mu N[\rho]\} = 0, \quad \text{or}\ \mu = \frac{\partial \bar{E}_v(N)}{\partial N} \tag{48}$$

which can be written in the equivalent form

$$\int \left(\frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} - \mu\right) \delta\rho(\vec{r}) = 0, \quad \text{or}\ \mu(\vec{r}) = \mu \tag{49}$$

Above and throughout the paper, functional differentiation with respect to the electron densities is carried out for constant external potential. In these equilibrium conditions, $\int \delta\rho(\vec{r})\,\mathrm{d}\vec{r} = \mathrm{d}N \neq 0$, so that a change in the molecular density originates from an infinitesimal outflow (inflow) of electrons from (to) AB, involving a hypothetical electron reservoir. We therefore call eq 46 the *external equilibrium criterion* for AB as a whole.

Let us now turn to the density partitioning of eq 5, which divides N electrons of AB into N_A and N_B electrons in subsystems. Let us express the molecular electronic energy as the equivalent functional of subsystem densities

$$E_v[\rho] = E_v[\rho_A + \rho_B] = \epsilon_v[\rho_A,\rho_B] \tag{50}$$

This allows one to define the *subsystem local chemical potentials*

$$\mu_\alpha(\vec{r}) \equiv \left(\frac{\delta \epsilon_v[\rho_A,\rho_B]}{\delta \rho_\alpha(\vec{r})}\right)_{\rho_{\beta\neq\alpha}} = \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})}\left(\frac{\delta \rho(\vec{r})}{\delta \rho_\alpha(\vec{r})}\right)_{\rho_{\beta\neq\alpha}} = \mu(\vec{r}) \tag{51}$$

Thus, the local subsystem chemical potentials are equal to the global local chemical potential, which is equalized at the global chemical potential level, $\mu = \mu[\rho] = \mu(\vec{r}) = \mu_\alpha(\vec{r})$. Such external derivatives cannot discriminate, therefore, between alternative divisions of the molecular density.

Moreover, expressing the energy as a function of N_A and N_B, $E_v[\rho] = \bar{\epsilon}_v(N_A,N_B)$, allows one to define the *global subsystem chemical potentials* $\{\mu_\alpha\}$ (see eq 46):

$$\begin{aligned}\mu_\alpha \equiv \left(\frac{\partial \bar{\epsilon}_v(N_A,N_B)}{\partial N_\alpha}\right)_{N_{\beta\neq\alpha}} &= \int \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})}\left(\frac{\partial \rho(\vec{r})}{\partial N_\alpha}\right)_{N_{\beta\neq\alpha}} \mathrm{d}\vec{r} \\ &= \mu\left(\frac{\partial \int \rho(\vec{r})\,\mathrm{d}\vec{r}}{\partial N_\alpha}\right)_{N_{\beta\neq\alpha}} = \mu\left(\frac{\partial N}{\partial N_\alpha}\right)_{N_{\beta\neq\alpha}} = \mu\end{aligned} \tag{52}$$

also equalized at the global chemical potential level. Thus, for each subsystem, $\mu_\alpha = \mu_\alpha(\vec{r}) = \mu$.

It follows from eq 7 that any external displacement of the molecular density $\delta\rho(\vec{r})$ is uniquely partitioned into $\{\delta\rho^H_\alpha(\vec{r})\}$ displacements of the subsystem densities

$$\frac{\mathrm{d}\rho^H_\alpha(\vec{r})}{\mathrm{d}\rho(\vec{r})} = w^H_\alpha(\vec{r}), \quad \alpha = A,B \tag{53}$$

Therefore, defining the Hirshfeld energy functional, $\epsilon_v[\rho^H_A[\rho], \rho^H_B[\rho]] \equiv E_v[\rho]$, one obtains the corresponding subsystem partial functional derivative, called the *Hirshfeld chemical potential*

$$\mu^H_\alpha(\vec{r}) \equiv \frac{\delta \epsilon_v[\rho^H_A,\rho^H_B]}{\delta \rho^H_\alpha(\vec{r})} = \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})}\,\frac{d\rho(\vec{r})}{d\rho^H_\alpha(\vec{r})} = \frac{\mu}{w^H_\alpha(\vec{r})} \equiv \mu^H_\alpha[\rho;\vec{r}], \quad \alpha = A,B \tag{54}$$

which is not equalized throughout the space. Also, combining eqs 46 and 54 gives

$$\mu^H_\alpha(\vec{r})\delta\rho^H_\alpha(\vec{r}) = \mu\delta\rho(\vec{r}), \quad \alpha = A,B \tag{55}$$

We note that any shift in $\delta\rho^H_A$ implies an associated shift in $\delta\rho^H_B$, so that $\delta\rho^H_A + \delta\rho^H_B = \delta\rho$. This is in contrast to the functional derivatives of eq 51, probing the energy response to a local change of one subsystem for the fixed (embedding) density of the other subsystem.

5.2. Internal Equilibrium Condition. In the partitioning problem of eq 5, ρ and d (eq 32) uniquely specify subsystem densities, both equilibrium and nonequilibrium: $\rho_\alpha = \rho_\alpha(\rho,d)$, $\alpha = A,B$. Consider the externally closed AB system, consisting of the two mutually open subsystems A and B. The fixed ρ constraint, $d\rho(\vec{r}) = 0$, then implies a local relation between virtual, intersubsystem density displacements

$$(\delta\rho_A(\vec{r}))_\rho = -(\delta\rho_B(\vec{r}))_\rho \tag{56}$$

or

$$(\delta d(\vec{r}))_\rho = 2[\delta\rho_A(\vec{r})]_\rho = -\,2[\delta\rho_B(\vec{r})]_\rho \tag{57}$$

Consider now the in situ (charge transfer) functional derivative of the molecular energy density functional in the subsystem resolution (eq 50), $\epsilon_v[\{\rho_\alpha(\rho,d)\}] \equiv \epsilon_v[\rho,d]$, for constant ρ:

$$\begin{aligned}\left(\frac{\delta \epsilon_v[\rho,d]}{\delta d(\vec{r})}\right)_\rho &= \sum_{\alpha=A,B}\left(\frac{\delta \epsilon_v[\rho_A,\rho_B]}{\delta \rho_\alpha(\vec{r})}\right)_{\rho_{\beta\neq\alpha}}\left(\frac{\partial \rho_\alpha(\vec{r})}{\partial d(\vec{r})}\right)_\rho \\ &= \frac{1}{2}[\mu_A(\vec{r}) - \mu_B(\vec{r})] = 0\end{aligned} \tag{58}$$

where we have used eqs 51, 56, and 57 to identify derivatives in the chain rule. Thus, because $\mu_A(\vec{r}) = \mu_B(\vec{r}) = \mu$, the internal equilibrium condition is automatically satisfied for any $d(\vec{r})$, as for all alternative partitionings of the ground-state ρ into ρ_A and ρ_B.

The foregoing analysis of the external and internal equilibrium criteria shows that the chemical potential (electronegativity) quantities cannot be used to identify the equilibrium partitioning of the molecular ground-state density. Their failure to discriminate among alternative division schemes is because the electronic energy $E_v[\rho]$ is the same for all partitionings: $\delta_v[\rho,d] = E_v[\rho]$. This indicates a clear need for entropic parameters to characterize the states of subsystems in AB. We shall examine this in more detail in Section 6 below.

5.3. Energy Partitioning and Subsystems-in-Molecules. Although the energy $E_v[\rho]$ of AB as a whole is conserved for all partitionings of eq 5, the energy of an embedded subsystem $\alpha = A,B$ in AB, in the presence of the other subsystem $\beta \neq \alpha$, changes as a result of the intersubsystem charge transfer. Here we examine the subtle problem of the partitioning of the molecular energy of eq 47 into the subsystem energies for a given partitioning of ρ into ρ_A and ρ_B.

Consider first the energy $E_\alpha[\rho_\alpha]$, which depends solely on the single subsystem density. For this purpose, we partition the universal Hohenberg−Kohn functional $F[\rho] = F[\rho_A + \rho_B]$ of eq 47 into the additive, $F^a[\rho_A, \rho_B] = F[\rho_A] + F[\rho_B]$, and nonadditive, $F^n[\rho_A, \rho_B] = F[\rho] - F^a[\rho_A,\rho_B]$, contributions:

$$F[\rho] = F^a[\rho_A,\rho_B] + F^n[\rho_A,\rho_B] \tag{59}$$

The nonadditive part must vanish at infinite separation between subsystems, $\lim_{(RAB\to\infty)} F^n[\rho_A, \rho_B] = 0$, because by the size-consistency requirement

$$\lim_{R_{AB}\to\infty} E[\rho] = E_A[\rho_A] + E_B[\rho_B] \tag{60}$$

and

$$\lim_{R\to\infty} \int \rho v \, \mathrm{d}\vec{r} = \sum_{\alpha=A,B} \int \rho_\alpha v_\alpha \, \mathrm{d}\vec{r} \tag{61}$$

This partitioning of $F[\rho]$ gives

$$E_\alpha[\rho_\alpha] = \int v(\vec{r})\rho_\alpha(\vec{r}) \, \mathrm{d}\vec{r} + F[\rho_\alpha], \quad \alpha = A,B \tag{62}$$

Because of the nonvanishing $F^n[\rho_A,\rho_B]$ for the overlapping densities of subsystems at finite separations, the energy of the embedded α (in the presence of β) would appear to be best defined as

$$\epsilon_\alpha[\rho_A,\rho_B] = E_\alpha[\rho_\alpha] + F^n[\rho_A,\rho_B] \tag{63}$$

The total electronic energy can now be expressed as (see eq 50)

$$\begin{aligned} E_v[\rho] &= \epsilon_A[\rho_A,\rho_B] + E_B[\rho_B] = E_A[\rho_A] + \epsilon_B[\rho_A,\rho_B] \\ &\equiv \epsilon_v[\rho_A,\rho_B] \end{aligned} \tag{64}$$

This gives for the local subsystem chemical potential of eq 51

$$\begin{aligned} \mu_\alpha(\vec{r}) &= \left(\frac{\delta\epsilon_\alpha[\rho_A,\rho_B]}{\delta\rho_\alpha(\vec{r})}\right)_{\rho_{\beta\neq\alpha}} = \frac{\delta E_\alpha[\rho_\alpha]}{\delta\rho_\alpha(\vec{r})} + \left(\frac{\delta F^n[\rho_A,\rho_B]}{\delta\rho_\alpha(\vec{r})}\right)_{\rho_{\beta\neq\alpha}} \\ &\equiv {\mu_\alpha}^\alpha(\vec{r}) + {\mu_\alpha}^e(\vec{r}) = \mu_\alpha[\rho_\alpha,\rho_\beta;\vec{r}], \quad \alpha = A,B \end{aligned} \tag{65}$$

where ${\mu_\alpha}^\alpha(\vec{r}) = v(\vec{r}) + \delta F[\rho_\alpha]/\delta\rho_\alpha(\vec{r})$ is the contribution due to ρ_α alone and ${\mu_\alpha}^e(\vec{r})$ is the corresponding embedding (e) correction due to ρ_β. The subsystem chemical potential equalization $\mu_\alpha(\vec{r}) = \mu_\alpha = \mu$ (Section 5.1) then implies that ${\mu_\alpha}^e(\vec{r})$ must cancel out the local dependence of ${\mu_\alpha}^\alpha(\vec{r})$. The internal equilibrium criterion of Section 5.2 directly follows from the condition of preservation of $E_v[\rho_A + \rho_B] = E_v[\rho]$ with respect to all density preserving virtual flows of electrons between subsystems, $d\rho_A + d\rho_B = 0$ (see also eq 58):

$$\begin{aligned} d\epsilon_v[\rho_A,\rho_B] &= \sum_{\alpha=A,B} \int \mu_\alpha(\vec{r}) \, d\rho_\alpha(\vec{r}) \, \mathrm{d}\vec{r} \\ &= \int d\rho_A(\vec{r})[\mu_A(\vec{r}) - \mu_B(\vec{r})] \, \mathrm{d}\vec{r} \\ &= \int d\rho_B(\vec{r})[\mu_B(\vec{r}) - \mu_A(\vec{r})] \, \mathrm{d}\vec{r} = 0 \end{aligned} \tag{66}$$

We would like to remark now that in the DFT for subsystems[18,21] one absorbs the effect of embedding, because of the presence of the complementary subsystem, into the subsystem effective external potentials $\{v_\alpha^{\mathrm{eff}}(\vec{r}) = v_\alpha^{\mathrm{eff}}[v,\{\rho_\alpha\}; \vec{r}]\}$, so that the embedded subsystem energy (eq 63) assumes the global-like form (see eq 47):

$$\epsilon_\alpha[\rho_\alpha,\rho_\beta] = \int v_\alpha^{\mathrm{eff}}(\vec{r})\rho_\alpha(\vec{r}) \, d\vec{r} + F[\rho_\alpha] = \bar{E}_{v_\alpha^{\mathrm{eff}}}(N_\alpha), \quad \alpha = A,B \tag{67}$$

Hence, the equation for the subsystem chemical potential becomes

$$\mu_\alpha(\vec{r}) = \left(\frac{\delta\epsilon_\alpha[\rho_\alpha,\rho_\beta]}{\delta\rho_\alpha(\vec{r})}\right)_{\rho_{\beta\neq\alpha}} = v_\alpha^{\mathrm{eff}}(\vec{r}) + \frac{\delta F[\rho_\alpha]}{\delta\rho_\alpha(\vec{r})} \tag{68}$$

which also is of the form of the global ground-state Euler equation (see eq 49):

$$\mu(\vec{r}) = \mu = v(\vec{r}) + \frac{\delta F[\rho]}{\delta\rho(\vec{r})} \tag{69}$$

It follows from the chemical potential electronegativity (χ) equalization $\mu_A(\vec{r}) = \mu_B(\vec{r}) = \mu = -\chi$ (Section 5.1), the partitioning of eq 64, and eqs 67 and 69, that

$$v_\alpha^{\mathrm{eff}}(\vec{r}) = v_\alpha(\vec{r}) + \left[v_{\beta\neq\alpha}(\vec{r}) + \left(\frac{\delta F^n[\rho_\alpha,\rho_\beta]}{\delta\rho_\alpha(\vec{r})}\right)_{\rho_{\beta\neq\alpha}}\right] \tag{70}$$

and

$$\frac{\delta F[\rho]}{\delta\rho(\vec{r})} = \frac{\delta F[\rho_\alpha]}{\delta\rho_\alpha(\vec{r})} + \left(\frac{\delta F^n[\rho_\alpha,\rho_\beta]}{\delta\rho_\alpha(\vec{r})}\right)_{\rho_{\beta\neq\alpha}} \tag{71}$$

An algorithm for determining the subsystem effective external potential from the embedding density of the complementary molecular environment has been proposed by Ayers,[18] in the spirit of the Zhao−Morrison−Parr (ZMP) procedure.[22]

The above analysis indicates that the subsystem density ρ_α is the ground-state density for the effective external potential v_α^{eff}:

$$\rho_\alpha(\vec{r}) = \rho_\alpha[v_\alpha^{\mathrm{eff}};\vec{r}] \tag{72}$$

Equation 70 also demonstrates that for constant subsystem external potentials $\{v_\alpha\}$, and thus also v, the effective potential is a functional of the subsystem densities

$$v_\alpha^{\mathrm{eff}}(\vec{r}) = v_\alpha^{\mathrm{eff}}[\rho_A,\rho_B;\vec{r}] \tag{73}$$

Therefore, by the Hohenberg−Kohn theorem[13] and its multicomponent generalization,[23] a given partitioning $\rho = \rho_A + \rho_B$ of the molecular electronic density is uniquely identified by the corresponding subsystem effective external potentials:

$$[\rho_A,\rho_B] \leftrightarrow [v_A^{\mathrm{eff}},v_B^{\mathrm{eff}}] \tag{74}$$

Moreover, the equilibrium (Hirshfeld) electronic densities of subsystems are uniquely identified by the minimum of the missing entropy functional $\Delta S[\rho_A\rho_B|\rho_A^o\rho_B^o] = S[\rho_A,\rho_B]$, e.g., $S^{KL}[\rho_A,\rho_B]$ or $S^F[\rho_A,\rho_B]$ (Section 3). Therefore, the following mapping exists between information-distance entropies, Hirshfeld densities of subsystems, the associated effective external potentials, and subsystem energies:

$$S[\rho_A^H,\rho_B^H] \leftrightarrow [\rho_A^H,\rho_B^H] \leftrightarrow [v_{A,H}^{eff},v_{B,H}^{eff}] \leftrightarrow [\epsilon_\alpha^H,\epsilon_\beta^H] \tag{75}$$

where $v_{\alpha,H}^{eff} \equiv v_\alpha^{eff}[\rho_A^H,\rho_B^H;\vec{r}]$ and $\epsilon_\alpha^H \equiv \epsilon_\alpha[\rho_A^H,\rho_B^H]$, $\alpha = A,B$. Note, however, that the subsystem energies as defined by eq 67 do not sum to the total energy (see eq 64).

This mapping and eq 67 provide a vital link between the energies of equilibrium subsystems and their information entropies. This connection between the information entropy and the optimum partitioning of the molecular density, through the effective external potentials, facilitates a "thermodynamic" approach to subsystems-in-molecules, which we will explore in the next section.

We also observe that, by manipulating the effective external potentials, one can interpret v-representable densities of any (nonequilibrium) partitioning of ρ, $\{\rho_\alpha\}$, as comprising the ground-state densities for some $\{v_\alpha^{eff}\}$. Such external potentials can therefore be viewed as thermodynamic "constraints" associated with the particular division of ρ. The basic problem of "thermodynamics" behind such a partitioning procedure is the determination of the equilibrium state (i.e., Hirshfeld partitioning) that eventually results after the removal of such internal constraints in a closed composite system, characterized by the fixed molecular electronic density ρ. The molecular external potential $v = v_A + v_B$ effectively determines the molecular "volume", in which electrons are "confined". Similarly, the subsystem effective external potentials $\{v_\alpha^{eff}\}$ can be considered as molecular analogues of the thermodynamic volumes of subsystems. Therefore, their energy conjugates, $\{[\partial\epsilon_\alpha/\partial v_\alpha^{eff}(\vec{r})]_{\rho^A,\rho^B} = \rho_\alpha(\vec{r})\}$ (see eq 67), are reminiscent of the thermodynamical pressures of subsystems. Similarly, the functional derivative $[\delta E_v[\rho]/\delta v(\vec{r})]\rho = \rho(\vec{r})$, represents the molecular analogue of the local "pressure" of the composite system, associated with the "volume" related external potential v.

We call attention to the fact that a search for the external potential $v[\rho]$, which matches a given density ρ through the ground-state relations of eqs 72 and 73, calls for the universal Legendre transform functional[24-26] $F[\rho] = \max_v[E_v[\rho] - \int \rho v \, d\vec{r}]$. For the v-representable densities, this search is equivalent to the Levy construction.[27]

6. Elements of the Local "Thermodynamical" Description of the Equilibrium Partitioning of Molecular Densities

As has been shown in the preceding section, a given exhaustive partitioning of the ground-state density $\rho = \rho[N,v]$ into ρ_A and ρ_B, $\rho = \rho_A + \rho_B$, does not affect the energy of the composite system as a whole, $E_v[\rho]$, while directly influencing the embedded subsystem energies $\{\epsilon_\alpha[\rho_A,\rho_B]\}$ and the missing information functional $S[\rho_A,\rho_B]$. The equilibrium partitioning into Hirshfeld subsystem densities, $\{\rho_\alpha^H\}$, gives rise to a unique minimum value of the missing information $S[\{\rho_\alpha^H\}]$ for the assumed references $\{\rho_\alpha^o\}$, which also determine the promolecule density ρ^o. Any assumed subsystem densities determine uniquely the effective subsystem potentials $\{v_\alpha^{eff}[\rho_A,\rho_B;\vec{r}]\}$, for which they are the ground-state densities. Therefore, the search for the optimum partitioning can be also interpreted as a search in the subsystem effective external potential space.

We now attempt a phenomenological description of the subsystem equilibrium (Hirshfeld) densities in the spirit of a previous "thermodynamical" interpretation of DFT.[16] To formulate a basis for such a local "thermodynamical" transcription of the Hirshfeld partitioning scheme, we will follow the axiomatic approach of Callen.[15] We first present the molecular equivalents of Callen's first three postulates and develop their implications. We also comment upon properties of the state parameters of molecular subsystems.

Equilibrium Partitionings. *Postulate I. Among all possible partitionings of* ρ*'s into* ρ_A *and* ρ_B*, for the chosen references* $\{\rho_\alpha^o\}$ *and* ρ^o*, there exist particular divisions (called equilibrium ones), that are characterized completely by* ρ *and the reference densities.*

Indeed, $\{\rho_\alpha^H = \rho_\alpha^o[\rho/\rho^o] = \rho_\alpha^H[\rho, \rho^o, \rho_\alpha^o]\}$ give rise to ρ, which by the Hohenberg−Kohn theorems determines external potential $v = v[\rho]$ and the system number of electrons $N = N[\rho]$. We have clearly proved in the preceding sections the stable equilibrium character of the Hirshfeld subsystems. Also, because the Hirshfeld subsystem densities determine $S[\rho_A^H,\rho_B^H]$ and $\{\epsilon_\alpha[\rho_A^H,\rho_B^H]\}$, the equilibrium entropy deficiency and subsystem energies are unique functionals of the molecular and reference densities.

In the equilibrium "thermodynamics", one is interested in changes of subsystems, from one equilibrium partitioning, with $(\rho, \rho^o, \{\rho_\alpha^o\})$, to another, with $(\rho', \rho^{o\prime}, \{\rho_\alpha^{o\prime}\})$. All such displacements involve a shift in the molecular ground-state density and, thus, also a change in the external potential (e.g., due to a shift in nuclear positions in space) and the associated reference ρ^o.

Minimum Entropy Deficiency and Entropy Density. *Postulate II. There exists a function (called the information entropy deficiency S) of the extensive subsystem parameters* $\{\rho_\alpha\}$ *of any composite system AB, defined for all equilibrium (Hirshfeld) partitionings of* ρ *and having the following property. The values assumed by* $\{\rho_\alpha\}$ *in the absence of internal constraints* $\{v_\alpha^{eff}[[\rho_\alpha]; \vec{r}]\}$ *are those that minimize S over the manifold of constrained equilibrium states.*

We have already demonstrated this property of the missing information functional $S = S^{KL}[\rho_A,\rho_B]$ in Sections 2 and 4. The given nonequilibrium partitionings can always be considered as representing ground-state subsystem densities for the corresponding effective external potentials $\{v_\alpha^{eff}\}$, representing the internal constraints, which identify the given subsystem densities.

The KL[7] entropy deficiency $S = S^{KL}[\rho_A,\rho_B]$ is always nonnegative. This follows from the inequality $\ln x \geq 1 - 1/x$. Hence, $\ln(\rho_\alpha/\rho_\alpha^o) \geq (\rho_\alpha - \rho_\alpha^o)/\rho_\alpha$. Multiplying the last inequality by ρ_α and integrating over all space then gives

$$S^{KL}[\rho_A,\rho_B] \geq \sum_{\alpha=A,B} \int (\rho_\alpha - \rho_\alpha^o) \, d\vec{r} = \int (\rho - \rho^o) \, d\vec{r} = 0 \tag{76}$$

because the molecule and promolecule densities are isoelectronic.

Molecular and subsystem densities can be thought of as strongly nonhomogeneous electron gases. Therefore, for interpretative purposes, one may use the appropriate *local* information-entropy parameters, e.g., the *entropy deficiency density* $s(\vec{r})$ and its additive subsystem contributions, $s(\vec{r}) = \Sigma_{\alpha=A,B}[s_\alpha(\vec{r})]$, as the parameters of state for a current partitioning of ρ. Alternatively, the local entropy densities per electron, $\bar{s}(\vec{r}) = s(\vec{r})/\rho(\vec{r})$ and $\{\bar{s}_\alpha(\vec{r}) = s_\alpha(\vec{r})/\rho_\alpha(\vec{r})\}$, can be used for this purpose.

It should be realized, however, that the densities of the functional $S^{KL}[\rho_A,\rho_B]$ of eq 4 and of its subsystem components can be negative. Therefore, to ensure the positive character of the local missing entropies of information (i.e., the information "distance"), we take, as the basic "thermodynamic" entropy measure, the density of the symmetrized missing entropy of Kullback,[3,18] called *divergence*:

$$S^{\mathrm{K}}[\rho_{\mathrm{A}},\rho_{\mathrm{B}}] = \sum_{\alpha=\mathrm{A,B}} \{\Delta S^{\mathrm{KL}}[\rho_\alpha|\rho_\alpha^{\mathrm{o}}] + \Delta S^{\mathrm{KL}}[\rho_\alpha^{\mathrm{o}}|\rho_\alpha]\}$$

$$= \sum_{\alpha=\mathrm{A,B}} \int (\rho_\alpha - \rho_\alpha^{\mathrm{o}}) \ln\left(\frac{\rho_\alpha}{\rho_\alpha^{\mathrm{o}}}\right) \mathrm{d}\vec{r}$$

$$\equiv \sum_{\alpha=\mathrm{A,B}} \int s_\alpha^{\mathrm{K}}(\vec{r})\, \mathrm{d}\vec{r} \equiv \int s^{\mathrm{K}}(\vec{r})\, \mathrm{d}\vec{r} \geq 0 \quad (77)$$

This represents the unbiased sum of the information distance from ρ_α to ρ_α^{o} and that from ρ_α^{o} to ρ_α, $\alpha = \mathrm{A,B}$. The equality sign in eq 77 requires $\{\rho_\alpha = \rho_\alpha^{\mathrm{o}}\}$. Because $s_\alpha^{\mathrm{K}}(\vec{r})$ is a monotonic increasing function of the local density value, $s_\alpha K(\vec{r}) = s_\alpha^{\mathrm{K}}(\rho_\alpha(\vec{r}))$, the subsystem density state variables $\{\rho_\alpha\}$ can be replaced by the corresponding local entropies $\{s_\alpha^{\mathrm{K}}\}$ as the state parameters defining the current partitioning of ρ. All of this accords with the following:

Postulate III. The entropy deficiency of a composite system S and its density $s^{\mathrm{K}}(\vec{r})$ are additive over the constituent components.

Information "Thermodynamical" Criterion of the Equilibrium Partitioning. One obtains from eq 77 the local dependencies of the set of local subsystem parameters $\{s_\alpha^{\mathrm{K}}(\vec{r})\}$ upon the other set $\{\rho_\alpha(\vec{r})\}$:

$$\frac{\mathrm{d}s_\alpha^{\mathrm{K}}(\vec{r})}{\mathrm{d}\rho_\alpha(\vec{r})} = \left[\frac{\mathrm{d}\rho_\alpha(\vec{r})}{\mathrm{d}s_\alpha^{\mathrm{K}}(\vec{r})}\right]^{-1} = \ln\left(\frac{\rho_\alpha}{\rho_\alpha^{\mathrm{o}}}\right) + \frac{\rho_\alpha - \rho_\alpha^{\mathrm{o}}}{\rho_\alpha} \equiv f_\alpha(\vec{r}) \quad (78)$$

The corresponding partial functional derivatives of the embedded subsystem energies $\{\epsilon_\alpha[\rho_\alpha, \rho_\beta] = \tilde{\epsilon}_\alpha[s_{\mathrm{A}}^{\mathrm{K}},s_{\mathrm{B}}^{\mathrm{K}}]\}$ with respect to the subsystem entropy densities $\{s_\alpha^{\mathrm{K}}(\vec{r})\}$ define the *local information "temperatures"*:

$$\tau_\alpha^{\mathrm{K}} \equiv \left(\frac{\delta\tilde{\epsilon}_\alpha[s_{\mathrm{A}}^{\mathrm{K}},s_{\mathrm{B}}^{\mathrm{K}}]}{\delta s_\alpha^{\mathrm{K}}(\vec{r})}\right)_{\rho_{\beta\neq\alpha}} = \left(\frac{\delta\epsilon_\alpha[\rho_{\mathrm{A}},\rho_{\mathrm{B}}]}{\delta\rho_\alpha(\vec{r})}\right)_{\rho_{\beta\neq\alpha}} f_\alpha^{-1}(\vec{r})$$

$$= \mu_\alpha(\vec{r})/f_\alpha(\vec{r}) = \mu/f_\alpha(\vec{r}) \quad (79)$$

where we have used eq 78 and invoked the chemical potential equalization (see Section 5).

It should be observed that the equilibrium values of the Kullback entropy densities of eq 77 are (see eq 7)

$$s_\alpha^{\mathrm{K,H}}(\vec{r}) \equiv s_\alpha^{\mathrm{K}}[\{\rho_\alpha^{\mathrm{H}}\};\vec{r}] \equiv \rho_\alpha^{\mathrm{o}}(\vec{r})[D(\vec{r}) - 1] \ln D(\vec{r}) \quad (80)$$

Also, the corresponding local information "temperatures" from eqs 78 and 79 are

$$\tau_\alpha^{\mathrm{K,H}}(\vec{r}) = \mu/f_\alpha^{\mathrm{H}}(\vec{r}), \quad \alpha = \mathrm{A,B} \quad (81)$$

where

$$f_\alpha^{\mathrm{H}}(\vec{r}) = \ln D(\vec{r}) + [D(\vec{r}) - 1]/D(\vec{r}) \equiv f(\vec{r}) \quad (82)$$

Equations 81 and 82 imply that

$$\tau_{\mathrm{A}}^{\mathrm{K,H}}(\vec{r}) = \tau_{\mathrm{B}}^{\mathrm{K,H}}(\vec{r}) \quad (83)$$

This is the local information-entropic supplement to the equilibrium criterion in the $\{\rho_\alpha\}$ representation (eqs 51 and 58), i.e., of the subsystem chemical potential equalization. It demands that at each point in space the local information "temperatures" of the mutually open subsystems equalize at the equilibrium partitioning. Notice, however, that, although the subsystem chemical potentials equalize for any trial partitioning, the information temperature equalization takes place only for the equilibrium (Hirshfeld) subsystem densities.

A similar conclusion follows from the corresponding "thermodynamic" interpretation of the variational procedure of eq 6. Suppose that the equilibrium densities of subsystems have been reached. The minimum of the entropy deficiency $S^{\mathrm{KL}}[\rho_{\mathrm{A}}, \rho_{\mathrm{B}}]$ for such optimum division of ρ then demands that a virtual transfer of the electronic density, $\mathrm{d}\rho_{\mathrm{A}}(\vec{r}) = -\mathrm{d}\rho_{\mathrm{B}}(\vec{r})$, will produce no change in $S^{\mathrm{KL}}[\rho_{\mathrm{A}}, \rho_{\mathrm{B}}]$ of the composite system: $\mathrm{d}\Delta S^{\mathrm{KL}} = 0$. Because S^{KL} is an additive sum of the subsystem contributions, the corresponding expression for $\mathrm{d}\Delta S^{\mathrm{KL}}$ gives

$$\mathrm{d}S^{\mathrm{KL}}[\rho_{\mathrm{A}},\rho_{\mathrm{B}}] = \sum_{\alpha=\mathrm{A,B}} \int \frac{\delta S_\alpha{}^{\mathrm{KL}}[\rho_\alpha]}{\delta\rho_\alpha(\vec{r})}\, \mathrm{d}\rho_\alpha(\vec{r})\, \mathrm{d}\vec{r}$$

$$\equiv \int [\bar{\mathrm{s}}_\alpha^{\mathrm{KL}}(\vec{r}) - \bar{\mathrm{s}}_\beta^{\mathrm{KL}}(\vec{r})]\, \mathrm{d}\rho_\alpha(\vec{r})\, \mathrm{d}\vec{r} = 0 \quad (84)$$

where we have introduced the KL entropy deficiency densities of subsystems (see eqs 1−3) per electron

$$\bar{\mathrm{s}}_\alpha^{\mathrm{KL}}(\vec{r}) = \frac{\delta S_\alpha^{\mathrm{KL}}}{\delta\rho_\alpha(\vec{r})} = I[\rho_\alpha|\rho_\alpha^{\mathrm{o}}] + 1, \quad \alpha = \mathrm{A,B} \quad (85)$$

The corresponding information-theoretic condition for equilibrium partitioning therefore requires

$$\bar{\mathrm{s}}_A^{\mathrm{KL}}(\vec{r}) = \bar{\mathrm{s}}_B^{\mathrm{KL}}(\vec{r})$$

$$\text{or} \quad I[\rho_A|\rho_A^{\mathrm{o}}] = I[\rho_B|\rho_B^{\mathrm{o}}]$$

$$\text{or} \quad R_{\mathrm{A}}(\vec{r}) \equiv \frac{\rho_{\mathrm{A}}(\vec{r})}{\rho_{\mathrm{A}}^{\mathrm{o}}(\vec{r})} = \frac{\rho_{\mathrm{B}}(\vec{r})}{\rho_{\mathrm{B}}^{\mathrm{o}}(\vec{r})} \equiv R_{\mathrm{B}}(\vec{r}) \quad (86)$$

Equation 7 shows that this equation is indeed satisfied by the Hirshfeld densities of subsystems, for which

$$R_a^{\mathrm{H}}(\vec{r}) = D(\vec{r}), \quad \alpha = \mathrm{A,B} \quad (87)$$

Let us similarly interpret the entropy deficiency minimum principle of eq 27, for the referenced Fisher entropy. The extremum implies that for the equilibrium densities $\mathrm{d}S^{\mathrm{F}} = 0$, where $\mathrm{d}S^{\mathrm{F}}$ corresponds to an infinitesimal, virtual transfer of density between subsystems $\mathrm{d}\rho_{\mathrm{A}}(\vec{r}) = -\mathrm{d}\rho_{\mathrm{B}}(\vec{r})$. Thus

$$\sum_{\alpha=\mathrm{A,B}} \int \frac{\delta I_\alpha^{\mathrm{F}}}{\delta\rho_\alpha(\vec{r})}\, \mathrm{d}\rho_\alpha(\vec{r})\, \mathrm{d}\vec{r} =$$

$$\int [\bar{\mathrm{s}}_{\mathrm{B}}^{\mathrm{F}}(\vec{r}) - \bar{\mathrm{s}}_{\mathrm{A}}^{\mathrm{F}}(\vec{r})]\, \mathrm{d}\rho_{\mathrm{A}}(\vec{r})\, \mathrm{d}\vec{r} = 0 \quad (88)$$

where the Fisher information density per electron of subsystem α in AB (see eq 21) is

$$\bar{\mathrm{s}}_\alpha^{\mathrm{F}}(\vec{r}) \equiv \left[\frac{\partial \ln R_\alpha(\vec{r})}{\partial\vec{r}}\right]^2 \quad (89)$$

Therefore, the equilibrium again requires that

$$\bar{s}^{\mathrm{F}}_{\mathrm{A}}(\vec{r}) = \bar{s}^{\mathrm{F}}_{\mathrm{B}}(\vec{r}) \quad \text{or} \quad R_{\mathrm{A}}(\vec{r}) = R_{\mathrm{B}}(\vec{r}), \tag{90}$$

which is indeed satisfied by the Hirshfeld densities of eq 7 (see eq 87).

The above local information entropy and temperature transcriptions of the intersubsystem equilibrium criteria of eqs 83, 86, 87, and 90 can be thought of as a "thermodynamical" supplement of the familiar chemical potential equalization principle. Although the latter fails to distinguish the Hirshfeld division as the equilibrium one, the local entropy/temperature criteria uniquely identify this very partitioning as the equilibrium one. Equilibrium requires equalization of the local information content parameters of the mutually open subsystems.

7. Elements of the Information Theoretic "Thermodynamics" in DFT

The aim of the truly "thermodynamic" description just given is to describe changes that accompany a given displacement of the system under consideration, from one equilibrium (ground-state) molecular density $\rho_1 = \rho_1[N_1,v_1]$ to another $\rho_2 = \rho_2[N_2,v_2]$. Such a "horizontal" displacement, along the ground-state surface $\rho_{\mathrm{g.s.}} = \rho[N,v]$ is in contrast to the "vertical" search in the ρ partitioning problem, which we examined earlier, in which ρ is fixed. Such a vertical search is over the effective external potentials of subsystems or, equivalently, their densities, which sum up to a given molecular density.

A given change from one v-representable density ρ to another involves a change in the generalized ground-state density functional for the electronic energy

$$E[\rho] = E_{v[\rho]}[\rho] \equiv \tilde{E}[v[\rho],\rho] \tag{91}$$

in which the external potential changes with ρ in such a way that the current ρ matches the external potential $v[\rho]$, for which ρ is the ground-state density. This energy density functional differs from the Hohenberg–Kohn functional $E_v[\rho]$, the variational principle for which calls for the minimum energy for *fixed* v, not related to the trial density ρ.[13]

To relate the information entropy $S[\rho]$, which could also involve relevant reference densities, to the system energetical parameters, thus introducing the "physics" to the information theoretic problem, one uses the generalized variational principle in the entropy representation:

$$\delta\{S[\rho] - \sum_k \lambda_k I_k[\rho]\} = 0 \tag{92}$$

where λ_k is the Lagrange multiplier associated with the kth constraint $I_k[\rho] = I_k^{\mathrm{o}}$, with $\{I_k[\rho]\}$ including the system energy quantities. Such an application of the information entropy in determining the exchange-correlation part of the effective Kohn–Sham potential[28] has recently been reported by Parr and Wang.[29] The entropy term in this principle represents a "device", which allows one to assimilate in the optimum density ρ the physical information contained in the constraints, and possibly in the reference densities built in the $S[\rho]$ functional itself, in the most unbiased manner possible.

As in the ordinary thermodynamics of open systems, the entropy extremum principle of eq 92 requires the constraint of the fixed number of electrons, $N[\rho] = N^{\mathrm{o}}$. Moreover, to introduce a temperature parameter, usually associated with the constraint of the fixed average energy, as the inverse of its Lagrange multiplier, we also require $E[\rho] = E^{\mathrm{o}}$. The corresponding generalized entropy extremum principle involving these two constraints then reads

$$\delta\left\{S[\rho] - \frac{1}{\bar{T}}E[\rho] + \frac{\bar{\mu}}{\bar{T}}N[\rho]\right\} = 0 \tag{93}$$

where we have identified, by analogy with ordinary thermodynamics

$$\bar{T}^{-1} = (\partial S/\partial E)_N \tag{94}$$

$$-\frac{\bar{\mu}}{\bar{T}} = (\partial S/\partial N)_E \tag{95}$$

as the inverse of the system global information temperature ($\bar{T}$) and the negative ratio of the chemical potential related quantity $\bar{\mu}$ to $\bar{T}$.

To identify the physical meaning of $\bar{\mu}$ we examine the corresponding principle in the energy representation for the fixed entropy $S[\rho] = S^{\mathrm{o}}$

$$\delta\{E[\rho] - \bar{T}S[\rho] - \bar{\mu}N[\rho]\} = 0 \tag{96}$$

Hence

$$\bar{T} = \left(\frac{\partial E}{\partial S}\right)_N \quad \text{and} \quad \bar{\mu} = \left(\frac{\partial E}{\partial N}\right)_S \tag{97}$$

It should be realized, however, that the constant N and constant E constraints do not identify a single ground-state density but rather a whole ensemble of them, because there are many ground-state densities which reproduce the right energy and right number of electrons. The molecular state specified by these constraints is a statistical mixture of all admissible densities, which satisfy the constraints.

When one fixes the molecular density $\rho(\vec{r}) = \rho^{\mathrm{o}}(\vec{r})$ through the corresponding local Lagrange multiplier $\omega(\vec{r})$, one also fixes the energy $E[\rho] = E[\rho^{\mathrm{o}}]$ and the number of electrons $N[\rho] = N[\rho^{\mathrm{o}}]$, thus making the two constraints of eq 93 redundant. For a finite value of $\bar{\mu}$, this implies $\bar{T}[\rho_{\mathrm{o}}] \rightarrow \infty$, because then the two constraint terms in eq 93 vanish identically. In the variational principle of eq 96, the information entropy "penalty" term is multiplied by an infinite Lagrange multiplier,[29] as in the ZMP procedure.[22] The fixed ρ principle of the minimum energy for the fixed entropy reads

$$\delta\{E[\rho] - \int \omega(\vec{r})\rho(\vec{r})\, \mathrm{d}\vec{r}\} = 0 \tag{98}$$

or

$$\left(\frac{\delta E[v[\rho],\rho]}{\delta\rho(\vec{r})}\right)_{\rho=\rho^{\mathrm{o}}} = \omega(\vec{r}) \tag{99}$$

The last two equations must be equivalent to the ground-state Euler eqs 48 and 69, respectively, when the external potential is fixed. Indeed, because $E[\rho] = \int v[\rho;\vec{r}]\rho(\vec{r})\, \mathrm{d}\vec{r} + F[\rho]$

$$\begin{aligned}\left(\frac{\delta E[\rho]}{\delta\rho(\vec{r})}\right)_{\rho=\rho^{\mathrm{o}}} &= v[\rho^{\mathrm{o}};\vec{r}\,] + \frac{\delta F[\rho]}{\delta\rho(\vec{r})}\Big|_{\rho^{\mathrm{o}}} + \int \rho^{\mathrm{o}}(\vec{r}\,)\frac{\delta v[\rho;\vec{r}\,']}{\delta\rho(\vec{r}\,)}\, \mathrm{d}\vec{r}\,' \\ &= \mu[\rho^{\mathrm{o}}] + \int \rho^{\mathrm{o}}(\vec{r}\,)\, \frac{\delta v[\rho;\vec{r}\,']}{\delta\rho(\vec{r}\,)}\, \mathrm{d}\vec{r}\,' = \omega(\vec{r}\,)\end{aligned} \tag{100}$$

Hence, by equating $\delta v[\rho;\vec{r}\,']/\delta\rho(\vec{r}) = 0$ (fixed v functional), as is done in the Hohenberg−Kohn variational principle, one indeed recovers the HK Euler eq 69.

8. Conclusion

It follows from the present and previous analyses of the information-theoretic basis of the Hirshfeld partitioning of the molecular electron densities that the stockholder molecular fragments, e.g., the optimum, unbiased bonded AIM, result from the minimization of the information distance between the AIM densities and those of free atoms defining the promolecule reference. As we have demonstrated in the present work, this result is independent of the two alternative (Shannon or Fisher) referenced entropies, adopted as possible information theoretic measures of this distance. We have also shown that the Hirshfeld fragments exhibit unique equilibrium properties, most conveniently formulated in terms of the interfragment equalization of the alternative indices of the local information content of each AIM density component.

Clearly, the Hirshfeld procedure is reference dependent. However, as recently argued and numerically demonstrated elsewhere,[12] the resulting AIM densities for alternative promolecule choices, e.g., the atomic and ionic references in NaCl, are for all practical purposes the same. This weak dependence of the AIM/fragment densities on the selected promolecule reference is natural in chemistry. As explicitly reflected by the familiar density difference diagrams, chemistry as the science of chemical bonds indeed deals with transitions of constituent atoms from their initial, nonbonded (ground) states of the promolecule to their final bonded state in a molecule. Therefore, the concept of a relevant reference is at the basis of most interpretations in chemistry, so its reappearance in the context of the Hirshfeld partitioning should not come as a surprise. The universal (*standard*) nonbonded reference is that of the *separated* (neutral) *free atoms* in their respective ground states, irrespective of the actual net electric charge and the character of bonds in the molecular system under consideration. Only such a convention represents a truly nonbonded promolecule reference, e.g., in NaCl, because the ionic promolecule, Na^+Cl^-, represents an ionic pair exhibiting a single ionic bond. Notice that this unique, standard choice of the atomic reference is also in agreement with the accepted chemical reference for determining the direction and the amount of charge transfer in molecular systems. Therefore, the reference "ambiguity" problem of the Hirshfeld partitioning is apparent, if one is to conform to the accepted chemical practice. In other words, the Hirshfeld fragments, if they are to be used as tools in the *chemical* theory of electronic structure of molecular systems, must be derived from the unique, standard reference of the free neutral atoms of the periodic table of elements.

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