J Math Chem (2010) 47:667–691
DOI 10.1007/s10910-009-9594-5

ORIGINAL PAPER

Use of non-additive information measures in exploring molecular electronic structure: stockholder bonded atoms and role of kinetic energy in the chemical bond

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Received: 7 July 2009 / Accepted: 17 August 2009 / Published online: 16 September 2009

Abstract The entropic principles of information theory are used for defining molecular fragments. The *additive* and *non-additive* components of the entropy-deficiency and Fisher-information functionals are introduced. The implications of the adopted constraints for predicted in situ charge sensitivities of molecular fragments in donor–acceptor systems are examined and the exhaustive, local partitioning of the molecular electron/probability density into atomic pieces is discussed as an illustration. The alternative information principles using the free-atom references, which define the atomic "promolecule", formulated in terms of the local electron density/probability of bonded atoms and their share/enhancement factors, are shown to give rise the stockholder partitioning of Hirshfeld. It is alternatively characterized by the common (subsystem independent), molecular local enhancements for each bonded atom or by the equality of the molecular and promolecular share factors. This unbiased division is shown to exactly remove the *non-additive* component of the missing-information of electron probabilities; in the *conditional* probability representation the entropy-deficiency of stockholder atoms is shown to generate the exactly vanishing *additive* component. The additivity of information contributions in the hypothetical (*non-interacting*) Kohn-Sham (KS) system in the resolution defined by the KS molecular orbitals (MO) is stressed and their non-additivity in the atomic-orbital (AO) resolution is emphasized. The non-additive Fisher information of the real (*interacting*) molecular system in both the MO and AO resolutions is then examined: the former is linked to the *electron localization function* (ELF) while the latter defines the so called *contragradience* (CG) criterion for localizing chemical bonds in the molecule. The bonding basins of the negative CG density in the valence-shell identify regions of an increased electron delocalization due to formation of the chemical bond. Representative plots of these local probes of the molecular electron distributions are presented and discussed.

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Keywords Contra-gradience bond criterion · Density functional theory · Electron localization function · Information principles for subsystems · Non-additive Fisher information · Stockholder atoms

1 Introduction

In modern *Density Functional Theory* (DFT) [1–5] the ground-state density $\rho(\boldsymbol{r}) = \rho[v(\mathbf{R}); \boldsymbol{r}] \equiv \rho(\boldsymbol{r}; \mathbf{R})$, or in a shortened notation $\rho = \rho[v]$, representing the equilibrium distribution of electrons for the current *Born-Oppenheimer* (BO) external potential $v(\boldsymbol{r})$ due to the system nuclei in their fixed positions $\mathbf{R} = \{\boldsymbol{R}_\alpha\}$ (the atomic units are used throughout), $v(\boldsymbol{r}) = -\sum_\alpha Z_\alpha/|\boldsymbol{r} - \boldsymbol{R}_\alpha|$, where $\{Z_\alpha\}$ denote the nuclear charges, replaces the associated wave function $\Psi = \Psi[v]$ as the system basic state-variable. More specifically, it follows from the celebrated *Hohenberg-Kohn* (HK) theorems [1] that for the non-degenerate electronic state ρ uniquely determines the shape of the system external potential itself, $v = v[\rho]$, and hence the electronic Hamiltonian of the N-electron molecular system,

$$\hat{\mathrm{H}}(N, v) = \sum_{i=1}^{N} v(\boldsymbol{r}_i) + [\hat{\mathrm{T}}(N) + \hat{\mathrm{V}}_{ee}(N)] \equiv \hat{\mathrm{V}}_{ne}(N) + \hat{\mathrm{F}}(N) = \hat{\mathrm{H}}[\rho], \tag{1}$$

and its ground-state wave function, $\Psi[N, v] = \Psi[\rho[v]]$. Here the set $\{\boldsymbol{r}_i\}$ groups the electronic positions, the operator $\hat{\mathrm{V}}_{ne}(N)$ corresponds to the electron-nuclear attraction energy, and $\hat{\mathrm{F}}(N) = \hat{\mathrm{T}}(N) + \hat{\mathrm{V}}_{ee}(N)$ combines the operators of the electronic kinetic energy, $\hat{\mathrm{T}}(N) = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2$, and the Coulomb repulsion energy, $\hat{\mathrm{V}}_{ee}(N) = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} |\boldsymbol{r}_i - \boldsymbol{r}_j|^{-1}$. The equilibrium ($v$-representable) density thus determines the expectation value of the system electronic energy:

$$E_v[\rho[v]] = \int v(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r} + \langle \Psi[\rho[v]]|\hat{\mathrm{F}}|\Psi[\rho[v]]\rangle \equiv V_{ne}[\rho] + F^{\mathrm{HK}}[\rho], \tag{2}$$

which satisfies the variational principle of the second HK theorem:

$$E_v[\rho[v]] \le E_v[\rho'[v']], \qquad v'(\boldsymbol{r}) \neq v(\boldsymbol{r}) + const. \tag{3}$$

To summarize, in this non-degenerate scenario the ground-state density in principle determines the system wave function $\Psi = \Psi[\rho]$ and hence also the expectation value $A[\rho] = \langle \Psi[\rho]|\hat{\mathrm{A}}|\Psi[\rho]\rangle$ of any physical observable $\hat{\mathrm{A}}$, e.g., of the system electronic energy: $E_v[\rho] = \langle \Psi[\rho]|\hat{\mathrm{H}}[\rho]|\Psi[\rho]\rangle$. In other words, the equilibrium electron distribution then carries the *complete* information about the molecular system in question: its electronic structure, trends in chemical reactivity, a pattern of chemical bonds (inter-atomic "*connectivities*"), etc.

However, as argued elsewhere [6–14], the informed decisions about the exhaustive division of the molecular density into pieces describing molecular fragments, $\boldsymbol{\rho}(\boldsymbol{r}; \mathbf{R}) \equiv \{\rho_\alpha(\boldsymbol{r}; \mathbf{R})\}$, in terms of which chemists often formulate their hypotheses, e.g., *Atoms-in-molecules* (AIM), functional groups, the (σ/π)-electron subsystems, reactants, etc.,

$$\rho(\boldsymbol{r};\mathbf{R}) = \sum_{\alpha} \rho_{\alpha}(\boldsymbol{r};\mathbf{R}), \tag{4}$$

can be effected only by using the alternative subsidiary criteria, e.g., topological [15] or information-theoretic [6–14] in character.

The techniques and concepts of the *Information Theory* (IT) of Fisher, Shannon and others [16–23] have indeed been shown to provide novel, efficient tools for tackling diverse problems in the theory of molecular electronic structure. Among other developments, the IT definition of bonded atoms [6–14,24] gives rise to Hirshfeld's [25] "*stockholder*" division of the molecular electron distribution into atomic fragments. In search for the entropic origins of the chemical bond the information content of electronic distributions in molecules has been examined [6,10–14] and the thermodynamic-like description of the electronic "gas" in molecular systems has been developed [6,26–28].

The Shannon theory of communication [19–21] has been successfully applied to probe bonding patterns in molecules within the *Communication Theory of the Chemical Bond* (CTCB) in atomic resolution [6,29–36] and in its orbital formulation, the *Orbital Communication Theory* (OCT) [37–40]. The key concept of this IT approach is the molecular information system, which can be constructed at alternative levels of resolving the electron probabilities into contributions attributed to the underlying (mutually exclusive) fragments determining the channel "inputs" and "outputs". For example, the molecular probability distribution can be resolved into probabilities of finding an electron on the basis-set orbital, AIM, molecular fragment, etc. Such molecular information channels can be generated within both the *local* and *condensed* descriptions of the electronic distribution in the molecule. Such networks describing the probability/information propagation in a molecule can be characterized by the standard quantities developed in IT for real communication devices.

Due to electron delocalization throughout the chemical bonds in a molecule, the transmission of "signals" about the electron-assignment to the underlying units of the resolution in question becomes randomly disturbed, thus exhibiting the communication "noise". Indeed, an electron initially attributed to the given atom/orbital in the channel input (molecular or promolecular) can be later found with a non-zero probability at several locations in the molecular "output". This feature of the electron delocalization is embodied in the conditional probability matrix of the outputs given inputs defining the molecular channel. Both the *one*-electron and *two*-electron approaches have been devised to generate the information networks in molecules. The latter [6,29–36] uses the simultaneous probabilities of two electrons in a molecule, assigned to the input and output, respectively, to determine the conditional probabilities between bonded atoms, while the former [37–42] constructs the orbital-pair probabilities using the familiar superposition principle of quantum mechanics [43]. This development has widely explored the use of the average communication-noise (delocalization, indeterminacy) and information-flow (localization, determinacy) indices as novel descriptors of the overall IT covalency and ionicity, respectively. Both chemical bonds of the molecular system as a whole and the *internal* bonds present in its constituent subsystems as well as the *external*, inter-fragment bonds can be characterized using these communication descriptors.

The *Information Theory* (IT) thus provides an efficient tool for an extraction of the chemical interpretation in terms of molecular fragments from the molecular quantum-mechanical descriptors [6]. The atomic pieces of the molecular electron densities, so important for the chemical epistemology, are in fact Kantian *noumenons* [24] so that an additional (entropy/information) level of the IT variational principles is required for an objective extraction of the chemical interpretation of the known molecular distributions of electrons in terms of bonded-atoms as building blocks of molecules. These atomic fragments are known to retain most of the "information" contained in the free atoms of the periodic table of elements, exhibiting only subtle changes in their valence shells due to the intra-atom "promotion"/hybridization (*polarization*, P) and the inter-atomic *charge transfer* (CT), relative to the atomic "*promolecule*", consisting of the free-atom distributions $\boldsymbol{\rho}^0(\boldsymbol{r}; \mathbf{R}) = \{\rho_\alpha^0(\boldsymbol{r}; \boldsymbol{R}_\alpha)\}$ placed in the molecular locations of constituent atoms. These changes are reflected by the familiar density difference (deformation density),

$$\Delta\rho(\boldsymbol{r}; \mathbf{R}) = \rho(\boldsymbol{r}; \mathbf{R}) - \rho^0(\boldsymbol{r}; \mathbf{R}), \tag{5}$$

where the promolecular electron distribution

$$\rho^0(\boldsymbol{r}; \mathbf{R}) = \sum_\alpha \rho_\alpha^0(\boldsymbol{r}; \mathbf{R}_\alpha). \tag{6}$$

An illustrative case of such IT principles in the Shannon theory, using only the inter-atomic (*non-additive*, bonding) information components, will be discussed in the first part of the present analysis. These information measures are devoid of the intra-atomic (*additive*, non-bonding) information terms thus focusing on the truly bonding effects.

In quantum chemistry the analysis of the physical origins of the chemical bond constitutes one of the primary goals. The familiar virial theorem [44–46] decomposition of the diatomic Born-Oppenheimer potential indicates that for the equilibrium bond length it is the overall (negative) change in its potential component, due to a *contraction* of constituent atoms in the presence of each other, which is ultimately responsible for the net stabilizing (bonding) effect. The associated change in the overall kinetic energy is negative at an earlier stage of the mutual approach by both atoms, when it is dominated by the *longitudinal* contribution associated with the gradient component along the bond axis; it ultimately assumes the destabilizing (antibonding) character at the equilibrium internuclear separation, mainly due to its *transverse* contribution associated with the gradient components in the directions perpendicular to the bond axis [47–51]. This overall virial theorem perspective thus indicates that the kinetic energy constitutes the driving force of the bond-formation process at its early stage.

These variations in the total energy components combine the delicate (truly bonding) inter-atomic effects originating from the stabilizing combinations of *atomic orbitals* (AO) in the occupied *molecular orbitals* (MO), which determine the effective bonding patterns in the molecule, and the accompanying processes of the intra-atomic polarization, which involve both the nonbonding (lone) pairs of both the inner- and outer-shell electrons. Therefore, these energy contributions effectively hide the minute changes in the system valence-shell, which are associated by chemists with the chemical bond concept. Thus, some partitioning of these overall energy contributions is called for in order to separate these subtle bonding phenomena from the associated promotion of bonded atoms. For example, the alternative perspective on variations in the kinetic energy component, say of the covalent-bond in H_2, is to partition it into the (negative) *gradient* component determined for the fixed scaling factor (effective charge of the nuclei) of the separated-atom orbitals, manifesting the bonding combination of AO in MO and the remaining *contraction* contribution, reflecting the optimum scaling of the basis functions. It follows from the classical analysis by Ruedenberg and co-workers [49–51] that the contraction of the atomic electron distributions is possible in molecule due to the relative lowering of the kinetic energy in the bonding region between the two nuclei, as reflected by both the longitudinal and transverse gradient components of the average electronic kinetic energy. Therefore, the whole process of redistributing electrons during formation of the chemical bond can be also regarded as being "catalyzed" by the kinetic energy gradient effect.

Both these perspectives thus emphasize the fundamental role of the kinetic energy in the chemical bond formation process. A similar conclusion follows from the theoretical analysis by Goddard and Wilson [52]. It should be recalled that the expectation value of this energy component is proportional to the system average Fisher information contained in electronic distribution [53–55]. Indeed, the molecular quantum mechanics and IT are related through the Fisher [16–18] (locality) measure of information [55–58], which represents the gradient content of the system wave-function, thus being proportional to the average kinetic energy of electrons. The stationary Schrödinger equation marks the optimum probability amplitude of the Fisher information principle including the constraint of the fixed value of the system potential energy. The *electron localization function* (ELF) [59] has been shown to explore the non-additive part of this information measure in the MO resolution [6,60], while a similar approach in the AO representation [61] generates the so called *contra-gradience* (CG) criterion [55] for localizing chemical bonds in molecules. It is determined by the AO representation of the electronic kinetic-energy operator.

It should be realized that each resolution (4) of the molecular electron density/probability distribution implies the associated division of the molecular (*total*) physical quantity $A[\rho]$ into its *additive*, $A^{\text{add.}}[\boldsymbol{\rho}]$, and *non-additive*, $A^{\text{nadd.}}[\boldsymbol{\rho}]$, contributions:

$$A[\rho] = A^{\text{total}}[\boldsymbol{\rho}] = A^{\text{add.}}[\boldsymbol{\rho}] + A^{\text{nadd.}}[\boldsymbol{\rho}], \quad A^{\text{add.}}[\boldsymbol{\rho}] = \sum_{\alpha} A[\rho_\alpha]. \tag{7}$$

We have indicated above that in the underlying multi-component system $A[\rho]$ becomes the functional of the whole vector of the subsystem densities [62]: $A[\rho] = A^{\text{total}}[\boldsymbol{\rho}]$.

For example, this Gordon-Kim-type division [63] of the kinetic energy functional defines the non-additive contribution which constitutes the basis of the DFT embedding concept of Cortona [64] and Wesołowski [65–67]. Such division can also be used to partition the information quantities themselves [6,13,60,61]. In particular, the inverse of the non-additive Fisher information in the MO resolution [60] has been shown to define the IT-ELF concept, in the spirit of the original Becke and Edgecombe formulation [59], while the related quantity in the AO resolution of the *Self-Consistent*

Field (SCF) MO theory offers the key CG criterion for localization of chemical bonds in molecular systems [55,61].

In the ensuing pages we shall further explore the implications of such non-additive information terms for properties of molecular fragments resulting from the entropic principles of IT and for the electron/bond localization in molecules. The illustrative examples of the IT-ELF plots and the patterns of bonding regions from the CG probe will also be reported.

2 Entropic rules for molecular partitioning and charge sensitivities of reactants

A general form of such information principles [6,54–58] involves some information functional $I[p]$ of the overall electron probability distribution $\rho(\boldsymbol{r})$, the *shape* function of the electron density, $\rho(\boldsymbol{r}) = Np(\boldsymbol{r})$, or functionals $I[\boldsymbol{p}(\pi)]$ of fragment distributions $\boldsymbol{p}(\pi;\boldsymbol{r}) = \{p_\alpha(\boldsymbol{r}) = p(\boldsymbol{r})P(\alpha|\boldsymbol{r})\}$ in the given partitioning π of the molecule, $p(\boldsymbol{r}) = \sum_\alpha p_\alpha(\boldsymbol{r})$; here, $P(\alpha|\boldsymbol{r})$ stands for the conditional probability that an electron found at position $\boldsymbol{r}$ is attributed to fragment α. Alternatively, the functionals of the electron density $I[\rho]$ or of its pieces $\boldsymbol{\rho}(\pi;\boldsymbol{r}) = \{\rho_\alpha(\boldsymbol{r}) = Np_\alpha(\boldsymbol{r})\}$, $I[\boldsymbol{\rho}(\pi)]$, can be employed in the entropic principles. In the local partitioning problems, of dividing the molecular distribution density at the fixed position in space, one accordingly uses the densities of these information functionals: $I(p(\boldsymbol{r}))$, $I(\rho(\boldsymbol{r}))$ or $\{I(\boldsymbol{p}(\pi;\boldsymbol{r}))$ or $I(\boldsymbol{\rho}(\pi;\boldsymbol{r}))\}$.

Above we have indicated that the subsystem distributions of the π division of the whole molecule into fragments defining the associated multi-component system are determined by the partition conditional probabilities $\boldsymbol{P}(\pi|\boldsymbol{r}) = \{P(\alpha|\boldsymbol{r})\}$,

$$\mathbf{P}(\pi|\boldsymbol{r}) = \{P(\alpha|\boldsymbol{r}) = p_\alpha(\boldsymbol{r})/p(\boldsymbol{r}) = \rho_\alpha(\boldsymbol{r})/\rho(\boldsymbol{r})\},$$
$$\rho_\alpha(\boldsymbol{r}) = Np_\alpha(\boldsymbol{r}),\ \sum_\alpha P(\alpha|\boldsymbol{r}) = 1, \tag{8}$$

which are often defined with respect to some overall or fragment reference(s), $q^0(\boldsymbol{r})$ or $\boldsymbol{Q}^0(\pi|\boldsymbol{r}) = \{Q^0(\alpha|\boldsymbol{r})\}$. Therefore, in the conditional probability $P(\alpha|\boldsymbol{r})$, that an electron at $\boldsymbol{r}$ originates from fragment α, the subsystem identity α thus represents the distribution *variable*, while the second, spatial index $\boldsymbol{r}$ constitutes the parameter, as indeed reflected by the normalization condition in the preceding equation.

The entropy/information variational principles then involve the optimization of the subsystem probabilities in the relevant information functional (function), subject to the required normalization and/or physical constraints, e.g., $\left\{F_i[p] = F_i^0\right\}$ or $\left\{G_j[\boldsymbol{P}(\pi)] = G_j^0\right\}$. For example, the overall entropic rules for probabilities in the global and subsystem resolutions read:

$$\delta\left\{I[p] - \sum\nolimits_i \lambda_i F_i[p]\right\} = 0 \quad \text{or} \quad \delta\left\{I[\boldsymbol{p}(\pi)] - \sum_j \mu_j G_j[\boldsymbol{p}(\pi)]\right\} = 0, \tag{9}$$

where λ_i and μ_i are the Lagrange multipliers enforcing the constraints related to the constrained functionals $F_i[p]$ and $G_j[\boldsymbol{P}(\pi)]$, respectively. In the local-partitioning problems the corresponding functional densities replace functionals in the second of the preceding entropy/information principles:

$$\delta\left\{I(\boldsymbol{p}(\pi;\boldsymbol{r}))-\sum_i \mu_j(\boldsymbol{r})G_j(\boldsymbol{p}(\pi;\boldsymbol{r}))\right\}=0 \quad \text{or}$$
$$\delta\left\{I(\boldsymbol{P}(\pi|\boldsymbol{r}))-\sum_j \mu_j(\boldsymbol{r})G_j(\boldsymbol{P}(\pi|\boldsymbol{r}))\right\}=0. \tag{10}$$

These local rules involve the Lagrange-multiplier functions $\{\mu_i(\boldsymbol{r})\}$; the second of them uses the conditional probabilities as local variables, which uniquely determine the associated fragment electron densities $\boldsymbol{\rho}(\pi;\boldsymbol{r})$ and probabilities $\boldsymbol{p}(\pi;\boldsymbol{r})$. These information rules assimilate in the optimum probabilities the relevant constraints and maximize similarities to references involved in the least biased manner possible. The specific values of Lagrange multipliers are subsequently determined from the values of the constraints themselves:

$$\lambda_i=\lambda_i\left(\left\{F_j^0\right\}\right),\quad \mu_j=\mu_j\left(\left\{G_k^0\right\}\right),\quad \mu_j(\boldsymbol{r})=\mu_j\left(\left\{G_k^0(\boldsymbol{r})\right\}\right). \tag{11}$$

It should be observed that the applied references, e.g., those used in the cross-entropy of Kullback and Leibler [6,22,23], represent *soft* information "constraints", since they fix nothing; instead they only generate the overall similarity between the optimized molecular probabilities and their initial distributions in the promolecule. The *hard* constraints in Eqs. (9, 10), enforced by the associated Lagrange multipliers, actually fix in the optimum solutions the associated normalization/physical quantities at their prescribed values.

One should also recall at this point that the selected (hard) constraints of the relevant information principle for determining the optimum, (unbiased) molecular fragments may influence the charge sensitivities of the latter [68]. This is the case when they define the prescribed value X^0 of the *differentiated* state-parameter X, e.g., the subsystem number of electrons $\boldsymbol{X}=\boldsymbol{N}=\left\{N_\alpha=\int\rho_\alpha(\boldsymbol{r})d\boldsymbol{r}\right\}$, in the derivative descriptors $\{\Phi_\alpha(\boldsymbol{r})=\partial\rho_\alpha(\boldsymbol{r})/\partial N_\alpha\}$ defining the *Fukui-function* (FF) indices of molecular fragments [3,68–74]. When the differentiation is carried out with respect to the charge separation between reactants, measured by the amount N_{CT} of CT B→A between the A(acidic) and B(basic) reactants in the *donor–acceptor* (DA) reactive system A—B, $X=N_{\mathrm{CT}}$, the associated derivatives define the reactant contributions $\boldsymbol{\Phi}_{\mathrm{CT}}(\boldsymbol{r})=\left\{\Phi_{\mathrm{CT},\alpha}(\boldsymbol{r})=\partial\rho_\alpha(r)/\partial N_{\mathrm{CT}},\alpha=\mathrm{A},\mathrm{B}\right\}$ to the *charge affinity* of DA system [68–75]: $\Phi_{\mathrm{DA}}(\boldsymbol{r})=\Phi_{\mathrm{CT,A}}(\boldsymbol{r})-\Phi_{\mathrm{CT,B}}(\boldsymbol{r})$.

The equilibrium condition in the energy representation alone, calling for the internal equalization of the chemical potentials (electronegativities) of the mutually-closed subsystems, is insufficient to define the equilibrium partitioning of the electron density of the whole reactive system into densities of the reactants [6]. For their unique, unbiased definition the minimum principle of the (reactant/promolecule)-referenced functional of the entropy-deficiency is required.

Hence the generalized FF indices of these reactant subsystems, measuring the electron-density derivatives of molecular fragments with respect to their overall electron populations or the amount of CT between them, must contain the derivative of the information functional itself with respect to the differentiated electron population parameters, calculated at their prescribed values enforced by the constraints:

$$\partial I(\boldsymbol{N})/\partial N_\alpha = \sum_j \left\{\left[\partial \mu_j(\boldsymbol{N})/\partial N_\alpha\right] G_j(N_\alpha) + \mu_j(N_\alpha)\left[\partial G_j(\boldsymbol{N})/\partial N_\alpha\right]\right\} \quad \text{or}$$

$$\partial I(N_{\mathrm{CT}})/\partial N_{\mathrm{CT}} = \sum_j \left\{\left[\partial \mu_j(N_{\mathrm{CT}})/\partial N_{\mathrm{CT}}\right] G_j(N_{\mathrm{CT}}) + \mu_j(N_{\mathrm{CT}})\left[\partial G_j(N_{\mathrm{CT}})/\partial N_{\mathrm{CT}}\right]\right\}. \tag{12}$$

The relevant chain-rule expressions for the FF and charge-affinity quantities then read:

$$\Phi_\alpha(\boldsymbol{r}) = \left(\frac{\partial \rho_\alpha(\boldsymbol{r})}{\partial I}\right)\left(\frac{\partial I}{\partial N_\alpha}\right) \quad \text{and} \quad \Phi_{\mathrm{CT},\alpha}(\boldsymbol{r}) = \left(\frac{\partial \rho_\alpha(\boldsymbol{r})}{\partial I}\right)\left(\frac{\partial I}{\partial N_{\mathrm{CT}}}\right), \tag{13}$$

where the first factor in these products reflects the dependence of the subsystem density upon the information content for the current values of the electron-population or charge-separation constraints. Indeed, both the information and the constraint parts of the variational principles of Eq. (10), which influence the optimum fragment distributions, should affect the physical properties of the reactants, e.g., their charge sensitivities.

3 Stockholder principle derived from additive and non-additive information measures

As an illustration consider the *local* partitioning problem of Eq. (4), in which the molecular electron/probability density at point $\boldsymbol{r}$ is divided into atomic contributions, π = AIM, in accordance with the conditional probabilities (*share factors*) $\boldsymbol{P}(\mathrm{AIM}|\boldsymbol{r}) = \{P(\alpha|\boldsymbol{r}) = p_\alpha(\boldsymbol{r})/p(\boldsymbol{r}) = \rho_\alpha(\boldsymbol{r})/\rho(\boldsymbol{r})\} \equiv \boldsymbol{P}(\boldsymbol{r})$; here $P(\alpha|\boldsymbol{r})$stands for the probability that electron at $\boldsymbol{r}$ belongs to atom α, etc. It has been shown elsewhere [6–14] that for the purpose of obtaining the optimum probability densities $\boldsymbol{p}(\boldsymbol{r}) = \{p_\alpha(\boldsymbol{r})\}$ of bonded-atoms, $\sum_\alpha p_\alpha(\boldsymbol{r}) = p(\boldsymbol{r})$, which resemble the most the reference distributions $\boldsymbol{p}^0(\boldsymbol{r}) \equiv \{p_\alpha^0(\boldsymbol{r})\}$ of the *free* (separated) *atoms* (FA) defining the promolecular distribution $p^0(\boldsymbol{r}) = \sum_\alpha p_\alpha^0(\boldsymbol{r})$, the most appropriate information measure is the *overall* entropy-deficiency functional of Kullback and Leibler [22,23],

$$\begin{aligned}\Delta S^{\mathrm{add.}}\left[\boldsymbol{p}(\mathrm{AIM})|\boldsymbol{p}^0(\mathrm{FA})\right] &= \sum_\alpha \int p_\alpha(\boldsymbol{r}) \ln\left(\frac{p_\alpha(\boldsymbol{r})}{p_\alpha^0(\boldsymbol{r})}\right) d\boldsymbol{r}\\ &\equiv \sum_\alpha \int \Delta S_\alpha\left(p_\alpha(\boldsymbol{r})|p_\alpha^0(\boldsymbol{r})\right) d\boldsymbol{r}\\ &\equiv \int \Delta S^{\mathrm{add.}}\left(\boldsymbol{p}(\mathrm{AIM};\boldsymbol{r})|\boldsymbol{p}^0(\mathrm{FA};\boldsymbol{r})\right) d\boldsymbol{r},\end{aligned} \tag{14}$$

also called the relative ("cross") entropy, missing information, or the directed divergence. The associated global information principle using the probability normalization constraint,

$$\delta\left\{\Delta S^{\text{add.}}[\boldsymbol{p}(\text{AIM})|\boldsymbol{p}^0(\text{FA})] - \int \mu(\boldsymbol{r})\sum_\alpha p_\alpha(\boldsymbol{r})d\boldsymbol{r}\right\} = 0, \tag{15}$$

then yields [6–9] the Hirshfeld (stockholder) division [25].

The promolecular references also determine the initial conditional probabilities

$$\boldsymbol{P}^0(\text{FA}|\boldsymbol{r}) = \left\{P(\alpha^0|\boldsymbol{r}) = p_\alpha^0(\boldsymbol{r})/p^0(\boldsymbol{r}) = \rho_\alpha^0(\boldsymbol{r})/\rho^0(\boldsymbol{r})\right\} \equiv \boldsymbol{P}^0(\boldsymbol{r}). \tag{16}$$

This local partitioning problem can be alternatively formulated in terms of the missing-information *density* $\Delta S^{add.}(\boldsymbol{p}(\text{AIM};\boldsymbol{r})|\boldsymbol{p}^0(\text{FA};\boldsymbol{r}))$ of Eq. (14), which can be conveniently expressed in terms of the conditional probabilities $\boldsymbol{P}(\boldsymbol{r})$ and $\boldsymbol{P}^0(\boldsymbol{r})$:

$$\begin{aligned}
&\Delta S^{\text{add.}}(\boldsymbol{p}(\text{AIM};\boldsymbol{r})|\boldsymbol{p}^0(\text{FA};\boldsymbol{r}))\\
&\quad = p(\boldsymbol{r})\sum_\alpha\left(\frac{p_\alpha(\boldsymbol{r})}{p(\boldsymbol{r})}\right)\ln\left\{\left[\left(\frac{p_\alpha(\boldsymbol{r})}{p(\boldsymbol{r})}\right)\Big/\left(\frac{p_\alpha^0(\boldsymbol{r})}{p^0(\boldsymbol{r})}\right)\right]\left(\frac{p(\boldsymbol{r})}{p^0(\boldsymbol{r})}\right)\right\}\\
&\quad = p(\boldsymbol{r})\sum_\alpha P(\alpha|\boldsymbol{r})\ln\left[\left(\frac{P(\alpha|\boldsymbol{r})}{P(\alpha^0|\boldsymbol{r})}\right)\left(\frac{p(\boldsymbol{r})}{p^0(\boldsymbol{r})}\right)\right]\\
&\quad = p(\boldsymbol{r})\ln\left(\frac{p(\boldsymbol{r})}{p^0(\boldsymbol{r})}\right) + p(\boldsymbol{r})\sum_\alpha P(\alpha|\boldsymbol{r})\ln\left(\frac{P(\alpha|\boldsymbol{r})}{P(\alpha^0|\boldsymbol{r})}\right)\\
&\quad \equiv \Delta S(p(\boldsymbol{r})|p^0(\boldsymbol{r})) + p(\boldsymbol{r})\Delta S^{\text{add.}}(\boldsymbol{P}(\boldsymbol{r})|\boldsymbol{P}^0(\boldsymbol{r})).
\end{aligned} \tag{17}$$

It should be further observed that in the local partitioning problem the overall distributions $p(\boldsymbol{r})$ and $p^0(\boldsymbol{r})$ as well as the promolecular conditional probabilities of FA, $\boldsymbol{P}^0(\boldsymbol{r})$, are fixed. Therefore, only the molecular conditional probabilities of AIM, $\boldsymbol{P}(\boldsymbol{r})$, are to be determined from the corresponding (entropic) Euler equations, which define the optimum shapes of bonded atoms. The optimized information density for this partition is thus given by

$$\begin{aligned}
\Delta S^{\text{add.}}\left(\boldsymbol{P}(\boldsymbol{r})|\boldsymbol{P}^0(\boldsymbol{r})\right) &= \sum_\alpha \Delta S_\alpha\left(P(\alpha|\boldsymbol{r})|P\left(\alpha^0|\boldsymbol{r}\right)\right),\\
\Delta S_\alpha\left(P(\alpha|\boldsymbol{r})|P\left(\alpha^0|\boldsymbol{r}\right)\right) &= P(\alpha|\boldsymbol{r})\ln\left[P(\alpha|\boldsymbol{r})/P\left(\alpha^0|\boldsymbol{r}\right)\right].
\end{aligned} \tag{18}$$

Moreover, since the conditional probabilities must satisfy the normalization constraint of Eq. (8), the associated information principle must enforce this (local) subsidiary condition through the use of the appropriate Lagrange multiplier $\mu(\boldsymbol{r})$. Therefore, the corresponding (local) rule of the maximum "likeness" of the bonded atoms to their non-bonded analogs reads:

$$\delta \left\{ \Delta S^{\text{add.}}(\boldsymbol{P}(\boldsymbol{r})|\boldsymbol{P}^0(\boldsymbol{r})) - \mu(\boldsymbol{r}) \sum_\alpha P(\alpha|\boldsymbol{r}) \right\} = 0. \tag{19}$$

The associated Euler equations for the optimum conditional probabilities defining the AIM pieces of the molecular electron density thus read:

$$\begin{aligned} &\partial \Delta S^{\text{add.}} \left(\boldsymbol{P}(\boldsymbol{r})|\boldsymbol{P}^0(\boldsymbol{r})\right) / \partial P(\alpha|\boldsymbol{r}) - \mu(\boldsymbol{r}) \\ &= \partial \Delta S_\alpha \left[P(\alpha|\boldsymbol{r}) | P\left(\alpha^0|\boldsymbol{r}\right) \right] / \partial P(\alpha|\boldsymbol{r}) - \mu(\boldsymbol{r}) \\ &= \ln \left[P(\alpha|\boldsymbol{r}) / P\left(\alpha^0|\boldsymbol{r}\right) \right] - [\mu(\boldsymbol{r}) - 1] \\ &\equiv \ln \left[P(\alpha|\boldsymbol{r}) / P\left(\alpha^0|\boldsymbol{r}\right) \right] - \ln C(\boldsymbol{r}) \\ &\equiv \ln \left\{ P(\alpha|\boldsymbol{r}) / \left[C(\boldsymbol{r}) P\left(\alpha^0|\boldsymbol{r}\right) \right] \right\} = 0, \quad \alpha = 1, 2, \ldots \end{aligned} \tag{20}$$

It can be straightforwardly demonstrated [6–14] that these Euler equations indeed give rise to the stockholder partitioning of Hirshfeld (H) [25]. It directly follows from the preceding equation that

$$P(\alpha|\boldsymbol{r})/[C(\boldsymbol{r})P(\alpha^0|\boldsymbol{r})] = 1 \quad \text{or} \quad P(\alpha|\boldsymbol{r}) = C(\boldsymbol{r})P(\alpha^0|\boldsymbol{r}). \tag{21}$$

Using this result in the normalization constraint of conditional probabilities then gives

$$\begin{aligned} \sum_\alpha P(\alpha|\boldsymbol{r}) = C(\boldsymbol{r}) \sum_\alpha P(\alpha^0|\boldsymbol{r}) = C(\boldsymbol{r}) \left[\sum_\alpha \rho_\alpha^0(\boldsymbol{r}) \right] / \rho^0(\boldsymbol{r}) = C(\boldsymbol{r}) = 1 \\ \text{or} \quad \boldsymbol{P}(\boldsymbol{r}) \equiv \boldsymbol{P}^{\text{H}}(\boldsymbol{r}) = \boldsymbol{P}^0(\boldsymbol{r}). \end{aligned} \tag{22}$$

The optimum (local) IT partitioning of the molecular electron density thus reads:

$$\begin{aligned} \rho_\alpha^{\text{H}}(\boldsymbol{r}) = \rho(\boldsymbol{r})[\rho_\alpha^0(\boldsymbol{r})/\rho^0(\boldsymbol{r})] \equiv \rho(\boldsymbol{r})P(\alpha^0|\boldsymbol{r}) = \rho_\alpha^0(\boldsymbol{r})[\rho(\boldsymbol{r})/\rho^0(\boldsymbol{r})] \equiv \rho_\alpha^0(\boldsymbol{r})w(\boldsymbol{r}), \\ \sum_\alpha \rho_\alpha^{\text{H}}(\boldsymbol{r}) = \rho(\boldsymbol{r}). \end{aligned} \tag{23}$$

Here the molecular (sybsystem-independent) *enhacement factor* $w(\boldsymbol{r})$ modifies in the molecule the free-atom density $\rho_\alpha^0(\boldsymbol{r})$ into the associated bonded-atom distribution $\rho_\alpha^H(\boldsymbol{r})$, while the promolecular *share-factor* $P(\alpha^0|\boldsymbol{r})$ determines the participation of αth AIM in $\rho(\boldsymbol{r})$. It also directly follows from Eq. (22) that

$$\Delta S^{\text{add.}} \left(\boldsymbol{P}^{\text{H}}(\boldsymbol{r})|\boldsymbol{P}^0(\boldsymbol{r})\right) = 0. \tag{24}$$

Therefore, the Hirshfeld partitiong exactly eliminates the *additive* part of the free-atom referenced entropy deficiency of the local *conditional* probabilities of bonded atoms relative to the associated promolecular references.

To summarize, the optimum (Hirshfeld) conditional probabilities (share factors), $\boldsymbol{P}^{\mathrm{H}}(\boldsymbol{r}) = \{P(\alpha^{H}|\boldsymbol{r})\}$ are equal to those defining the promolecule, $\boldsymbol{P}^{0}(\boldsymbol{r}) = \{P(\alpha^{0}|\boldsymbol{r})\}$:

$$P(\alpha^{\mathrm{H}}|\boldsymbol{r}) = \rho_{\alpha}^{\mathrm{H}}(\boldsymbol{r})/\rho(\boldsymbol{r}) = p_{\alpha}^{\mathrm{H}}(\boldsymbol{r})/p(\boldsymbol{r}) = P(\alpha^{0}|\boldsymbol{r}) = \rho_{\alpha}^{0}(\boldsymbol{r})/\rho^{0}(\boldsymbol{r}) = p_{\alpha}^{0}(\boldsymbol{r})/p^{0}(\boldsymbol{r}). \tag{25}$$

This equality constitutes the familiar *stockholder rule* [25]: the bonded atom "share" $P(\alpha^{\mathrm{H}}|\boldsymbol{r})$ in the molecular "profit" $\rho(\boldsymbol{r})$ is determined by its share $P(\alpha^{0}|\boldsymbol{r})$ in the promolecular "investment" $\rho^{0}(\boldsymbol{r})$.

One of the remarkable features of this partitioning is that the density of the overall entropy deficiency between the molecular and promolecular electron probability densities [see Eq. (14)], which determines the *total* missing-information functional in the stockholder-AIM resolution,

$$\begin{aligned}\Delta S(p(\boldsymbol{r})|p^{0}(\boldsymbol{r})) &\equiv \Delta S^{\mathrm{total}}(\boldsymbol{p}^{\mathrm{H}}(\boldsymbol{r})|\boldsymbol{p}^{0}(\boldsymbol{r}))\\ &= \Delta S^{\mathrm{add.}}(\boldsymbol{p}^{\mathrm{H}}(\boldsymbol{r})|\boldsymbol{p}^{0}(\boldsymbol{r})) + \Delta S^{\mathrm{nadd.}}\left(\boldsymbol{p}^{\mathrm{H}}(\boldsymbol{r})|\boldsymbol{p}^{0}(\boldsymbol{r})\right),\end{aligned} \tag{26}$$

is exactly equal to its *additive* component:

$$\begin{aligned}\Delta S(p(\boldsymbol{r})|p^{0}(\boldsymbol{r})) &= p(\boldsymbol{r})\ \ln w(\boldsymbol{r}) = \left[\sum_{\alpha} p_{\alpha}^{\mathrm{H}}(\boldsymbol{r})\right]\ \ln\left[p_{\alpha}^{\mathrm{H}}(\boldsymbol{r})/p_{\alpha}^{0}(\boldsymbol{r})\right]\\ &= \sum_{\alpha} p_{\alpha}^{\mathrm{H}}(\boldsymbol{r})\ln\left[w_{\alpha}^{\mathrm{H}}(\boldsymbol{r})\right] \equiv \Delta S^{\mathrm{add.}}\left(p^{\mathrm{H}}(\boldsymbol{r})|p^{0}(\boldsymbol{r})\right),\end{aligned} \tag{27}$$

due to the the common (molecular), unbiased enhancement factor for all bonded atoms,

$$w_{\alpha}^{\mathrm{H}}(\boldsymbol{r}) \equiv p_{\alpha}^{\mathrm{H}}(\boldsymbol{r})/p_{\alpha}^{0}(\boldsymbol{r}) = w(\boldsymbol{r}) = p(\boldsymbol{r})/p^{0}(\boldsymbol{r}), \quad \alpha = 1, 2, \ldots \tag{28}$$

In other words, the equality of Eq. (27) implies that for this particular partitioning the non-additive information distance between the (molecularly-normalized) probability distributions $\boldsymbol{p}^{\mathrm{H}}(\boldsymbol{r})$ of the bonded atoms and those characterizing the free atoms $\boldsymbol{p}^{0}(\boldsymbol{r})$ vanishes identically:

$$\Delta S^{\mathrm{nadd.}}\left(\boldsymbol{p}^{\mathrm{H}}(\boldsymbol{r})|\boldsymbol{p}^{0}(\boldsymbol{r})\right) = 0, \tag{29}$$

and hence also the overall functional $\Delta S^{\mathrm{nadd.}}[\boldsymbol{p}^{\mathrm{H}}|\boldsymbol{p}^{0}] = 0$. The normalization-constrained minimum principle of $\Delta S^{\mathrm{add.}}[\boldsymbol{p}^{\mathrm{H}}|\boldsymbol{p}^{0}]$ thus implies the associated minimum of the (positive) $\Delta S[p|p^{0}] = \Delta S^{\mathrm{total}}[\boldsymbol{p}^{\mathrm{H}}|\boldsymbol{p}^{0}]$.

The stockholder division rule can be thus alternatively defined as the one which exactly eliminates the *non-additive* entropy-deficiency contributions of the fragment (molecularly-normalized, free-atom referenced) probability distributions:

$$\Delta S^{\text{nadd.}}(\boldsymbol{p}(\boldsymbol{r})|\boldsymbol{p}^0(\boldsymbol{r})) = \Delta S^{\text{total}}(\boldsymbol{p}^{\text{H}}(\boldsymbol{r})|\boldsymbol{p}^0(\boldsymbol{r})) - \Delta S^{\text{add.}}(\boldsymbol{p}^{\text{H}}(\boldsymbol{r})|\boldsymbol{p}^0(\boldsymbol{r})) = 0. \quad (30)$$

Finally, the information-distance density $\Delta S^{\text{add.}}[\boldsymbol{p}(\text{AIM}; \boldsymbol{r})|\boldsymbol{p}^0(\text{FA}; \boldsymbol{r})]$ of Eq. (13) can be alternatively expressed in terms of the unknown (variational) enhancement factors $\boldsymbol{w}(\boldsymbol{r}) = \{w_\alpha(\boldsymbol{r}) = p_\alpha(\boldsymbol{r})/p_\alpha^0(\boldsymbol{r})\}$ of bonded atoms:

$$\Delta S^{\text{add.}}(\boldsymbol{p}(\text{AIM}; \boldsymbol{r})|\boldsymbol{p}^0(\text{FA}; \boldsymbol{r})) = \sum_\alpha p_\alpha^0(\boldsymbol{r}) w_\alpha(\boldsymbol{r}) \ln w_\alpha(\boldsymbol{r}) \equiv \Delta S^{\text{add.}}(\boldsymbol{w}(\boldsymbol{r})). \quad (31)$$

The associated local information principle for determining these enhancements must then involve $\Delta S^{\text{add.}}(\boldsymbol{w}(\boldsymbol{r}))$ as the relevant information density and the constraint of the exhaustive partitioning,

$$\sum_\alpha p_\alpha(\boldsymbol{r}) = \sum_\alpha p_\alpha^0(\boldsymbol{r}) w_\alpha(\boldsymbol{r}) = p(\boldsymbol{r}), \quad (32)$$

enforced by the Lagrange multiplier $\xi(\boldsymbol{r})$:

$$\delta\{\Delta S^{\text{add.}}(\boldsymbol{w}(\boldsymbol{r})) - \xi(\boldsymbol{r}) \sum_\alpha p_\alpha^0(\boldsymbol{r}) w_\alpha(\boldsymbol{r})\} \equiv \delta\Omega(\boldsymbol{w}(\boldsymbol{r})) = 0. \quad (33)$$

The partial differentiations of this auxiliary function of the subsystem enhancements then give the associated Euler equations for the optimum $\boldsymbol{w}(\boldsymbol{r})$:

$$\begin{aligned} \frac{\partial\Omega(\boldsymbol{w}(\boldsymbol{r}))}{\partial w_\alpha(\boldsymbol{r})} &= p_\alpha^0(\boldsymbol{r})\{\ln w_\alpha(\boldsymbol{r}) - [\xi(\boldsymbol{r}) - 1]\} \\ &\equiv p_\alpha^0(\boldsymbol{r})[\ln w_\alpha(\boldsymbol{r}) - \ln D(\boldsymbol{r})] = 0, \quad \alpha = 1, 2, \ldots, \end{aligned} \quad (34)$$

and hence $w_\alpha(\boldsymbol{r}) = D(\boldsymbol{r})$. Finally, from the local value of the constraint one recovers the equalization of all local enhancement factors of AIM at the molecular enhancement $w(\boldsymbol{r})$ value, which marks the stockholder partitioning [Eq. (28)]:

$$\begin{aligned} &\sum_\alpha p_\alpha^0(\boldsymbol{r}) w_\alpha(\boldsymbol{r}) = D(\boldsymbol{r}) \sum_\alpha p_\alpha^0(\boldsymbol{r}) = D(\boldsymbol{r}) p^0(\boldsymbol{r}) = p(\boldsymbol{r}) \quad \text{or} \\ &D(\boldsymbol{r}) = w_\alpha^{\text{H}}(\boldsymbol{r}) = w(\boldsymbol{r}). \end{aligned} \quad (35)$$

4 Non-additivities in the Kohn-Sham limit

In the *Kohn-Sham* (KS) limit [2] of DFT, referring to the hypothetical system involving the non-interacting electrons, which give rise to the same ground-state electron density $\rho = \rho[v]$ as in the real (interacting) system, the electron density is expressed as the sum of contributions from N-lowest (occupied) KS spin-orbitals: $\rho(\boldsymbol{r}) = \sum_k |\varphi_k(\boldsymbol{r})|^2 = \sum_k \rho_k(\boldsymbol{r})$. The non-interacting subsystems are thus identified by the subsets $\{\boldsymbol{\varphi}_\alpha\}$ of these orbitals $\boldsymbol{\varphi} \equiv \{\boldsymbol{\varphi}_\alpha\} = \{\varphi_k\}, k = 1, 2, \ldots, N$, defining the associated electron densities:

$$\rho_\alpha(\boldsymbol{r}) = \sum_{l \in \alpha} |\varphi_l(\boldsymbol{r})|^2. \tag{36}$$

They determine specific partition schemes of the molecular density in this non-interacting limit, $\pi = \{\boldsymbol{\varphi}_\alpha\}$, $\rho(\boldsymbol{r}) = \sum_\alpha \rho_\alpha(\boldsymbol{r})$, with the ultimate division into N independent MO components $\{\rho_k\}$.

It should be realized that for the fixed external potential the $V_{ne}[\rho]$ energy contribution is additive with respect to the density partitioning, so that the only source of non-additivity in the electronic energy is due to the complementary functional $F^{\mathrm{HK}}[\rho]$ of Eq. (2). However, since the electronic repulsion is switched off in the hypothetical KS system, the only source of the energy non-additivity is then due to the non-interacting (s) kinetic energy:

$$\begin{aligned} T_s[\rho] = T_s^{\mathrm{total}}[\boldsymbol{\varphi}] &= -\frac{1}{2}\sum_{k=1}^{N}\int \varphi_k^*(\boldsymbol{r})\Delta\varphi_k(\boldsymbol{r})d\boldsymbol{r} \equiv \sum_{k=1}^{N} T_k[\varphi_k] \\ &= \frac{1}{2}\sum_{k=1}^{N}\int \nabla\varphi_k^*(\boldsymbol{r}) \cdot \nabla\varphi_k(\boldsymbol{r})d\boldsymbol{r} = \frac{1}{8} I_s^{\mathrm{F}}[\rho], \end{aligned} \tag{37}$$

where we have introduced the KS functional $I_s^{\mathrm{F}}[\rho]$ for the overall Fisher information in the probability-amplitude representation for the N-component system, in which each occupied KS spin-orbital determines the separable piece of the electron density [16–18,54,55],

$$I_s^{\mathrm{F}}[\rho] = I_s^{\mathrm{F,total}}[\boldsymbol{\varphi}] = 4\sum_{k=1}^{N}\int |\nabla\varphi_k(\boldsymbol{r})|^2 d\boldsymbol{r} \equiv \sum_{k=1}^{N} I_{k,k}^{\mathrm{F}}[\varphi_k], \tag{38}$$

and $I_k^{\mathrm{F}}[\varphi_k] = 8T_k[\varphi_k]$. It should be observed that each fragment of Eq. (36) exhibits in this limit the fragment kinetic energy given by the sum of $\{T_k[\varphi_k]\}$ components corresponding to the subsystem KS-orbitals,

$$T_\alpha[\rho_\alpha] = \sum_{l \in \alpha} T_l[\varphi_l]. \tag{39}$$

Therefore, in the KS limit the total and kinetic energies are exactly additive in the MO resolution. Indeed, the KS orbitals constitute the independent (stationary) states of each MO component of the non-interacting system, so that the probability-current and the Fisher-information/kinetic energy non-additivities exactly vanish. This is no longer the case in the (orthogonalized) AO/basis-function resolution, $\boldsymbol{\chi} = \{\chi_1, \ldots, \chi_m\}$, in terms of which MO are expressed, $\boldsymbol{\varphi} = \boldsymbol{\chi}\mathbf{C}^{\mathrm{KS}}$; here $(m \times N)$ rectangular matrix $\mathbf{C}^{\mathrm{KS}} = \langle\boldsymbol{\chi}|\boldsymbol{\varphi}\rangle$ groups the expansion coefficients of these MO linear combinations of AO (LCAO MO). Indeed, the expectation value of the kinetic energy is then given by the trace of the product of the non-diagonal matrices grouping the *Charge-and-Bond-Orders* (CBO),

$$\boldsymbol{\gamma}^{\mathrm{KS}} = \langle \boldsymbol{\chi} | \left(\sum_{k=1}^{N} |\varphi_k\rangle\langle\varphi_k| \right) |\chi\rangle = \langle \boldsymbol{\chi} | \boldsymbol{\phi} \rangle \langle \boldsymbol{\phi} | \boldsymbol{\chi} \rangle = \mathbf{C}^{\mathrm{KS}} \mathbf{C}^{\mathrm{KS}\dagger} = \left\{ \gamma_{u,w}^{\mathrm{KS}} \right\}, \tag{40}$$

the AO representation of the projection operator onto all (ground-state occupied) KS MO, and the associated AO matrix elements of the kinetic energy operator,

$$\mathbf{T} = \left\langle \boldsymbol{\chi} \middle| \hat{\mathrm{T}} \middle| \boldsymbol{\chi} \right\rangle = \left\{ T_{u,w} = -\frac{1}{2} \left\langle \chi_u \middle| \Delta \middle| \chi_w \right\rangle \right\}, \tag{41}$$

$$T_s[\rho] = T_s^{\mathrm{total}}[\boldsymbol{\chi}] = \mathrm{tr}\left(\boldsymbol{\gamma}^{\mathrm{KS}} \mathbf{T} \right). \tag{42}$$

This expression and the associated *additive* component in the AO resolution,

$$T_s^{\mathrm{add.}}[\boldsymbol{\chi}] = \sum_{u=1}^{m} \gamma_{u,u}^{\mathrm{KS}} T_{u,u}, \tag{43}$$

give rise to the associated AO *non-additive* kinetic energy,

$$T_s^{\mathrm{nadd.}}[\boldsymbol{\chi}] = \sum_{u=1}^{m} \sum_{v=1}^{m} \gamma_{u,v}^{\mathrm{KS}} \left(1 - \delta_{v,u}\right) T_{v,u} = 2 \sum_{u=1}^{m-1} \sum_{v=u+1}^{m} \gamma_{u,v}^{\mathrm{KS}} T_{v,u}. \tag{44}$$

It is proportional to the corresponding non-additive Fisher information at this resolution level [55,61], measuring the CG functional of the non-interacting system:

$$I_s^{\mathrm{F,nadd.}}[\boldsymbol{\chi}] = 4 \sum_{u=1}^{m} \sum_{w=1}^{m} \int \gamma_{u,w}^{\mathrm{KS}} (1 - \delta_{u,w}) \nabla \chi_w^*(\boldsymbol{r}) \cdot \nabla \chi_u(\boldsymbol{r}) d\boldsymbol{r} \equiv \int f_s^{\mathrm{nadd.}}(\boldsymbol{r}) d\boldsymbol{r}$$
$$\equiv 2 \int \bar{f}_s^{\mathrm{nadd.}}(\boldsymbol{r}) d\boldsymbol{r} = 8 T_s^{\mathrm{nadd.}}[\boldsymbol{\chi}]. \tag{45}$$

Here, $\bar{f}_s^{\mathrm{nadd.}}(\boldsymbol{r})$ denotes the non-additive Fisher information (CG) density per electron pair of the hypothetical KS system. Its interacting-system analog $\bar{f}^{\mathrm{nadd.}}(\boldsymbol{r})$ in the SCF MO theory has been previously designed as a useful tool for locating the chemical bonds in molecules [55,61].

5 Non-additive Fisher-information in electron-localization function

In the real (interacting) molecular systems there is no additivity of $F^{\mathrm{HK}}[\rho]$ and $T[\rho]$ in both the MO and AO resolutions. Consider, e.g., the non-additivities in the Fisher [16–18] local measure of the information content in the given, normalized probability density $p(\boldsymbol{r}) = \psi^2(\boldsymbol{r}), \int p(\boldsymbol{r})d\boldsymbol{r} = 1$, where $\psi(\boldsymbol{r})$ stands for the (real) probability amplitude:

$$I^{\mathrm{F}}[p] \equiv \int f(\boldsymbol{r})d\boldsymbol{r} = \int p(\boldsymbol{r})[\nabla \ln p(\boldsymbol{r})]^2 d\boldsymbol{r} = \int \frac{|\nabla p(\boldsymbol{r})|^2}{p(\boldsymbol{r})} d\boldsymbol{r} = 4\int |\nabla\psi(\boldsymbol{r})|^2 \equiv I^{\mathrm{F}}[\psi]. \tag{46}$$

It characterizes the distribution "sharpness" (localization, determinacy) and provides a complementary descriptor of the probability distribution to the global Shannon [19] entropy,

$$I^S[p] \equiv -\int p(\boldsymbol{r})\ln p(\boldsymbol{r})d\boldsymbol{r}, \tag{47}$$

which reflects the distribution "spread" (delocalization, indeterminacy).

In the spin-resolved DFT one examines the energy functionals of spin densities $\{\rho_\sigma(\boldsymbol{r})\}$, for the spin-like electrons occupying the $\left\{\boldsymbol{\psi}_\sigma = \{\psi_i^\sigma\}\right\}$ MO,

$$\rho_\sigma(\boldsymbol{r}) = \sum_{i\in\sigma}^{\text{occd.}} \left[\psi_i^\sigma(\boldsymbol{r})\right]^2. \tag{48}$$

The kinetic energy density in this MO resolution,

$$\tau_\sigma(\boldsymbol{r}) = \sum_{i\in\sigma} |\nabla\psi_i^\sigma(\boldsymbol{r})|^2, \tag{49}$$

is thus proportional to the sum of *additive* Fisher information densities in the amplitude representation:

$$\tau_\sigma(\boldsymbol{r}) = \frac{1}{4} f_\sigma^{\text{add.}}(\boldsymbol{r}). \tag{50}$$

The leading term of the Taylor expansion of the spherically averaged (Hartree-Fock) conditional pair-probability of finding in distance s from the reference electron of spin σ at position $\boldsymbol{r}$ the other spin-like electron then reads [59],

$$P_c^{\sigma\sigma}(s|\boldsymbol{r}) = \frac{1}{3} D_\sigma(\boldsymbol{r})s^2 + \cdots, \tag{51}$$

where

$$D_\sigma(\boldsymbol{r}) = \tau_\sigma(\boldsymbol{r}) - \frac{|\nabla\rho_\sigma(\boldsymbol{r})|^2}{4\rho_\sigma(\boldsymbol{r})} = -\frac{1}{4}[f_\sigma^{\text{total}}(\boldsymbol{r}) - f_\sigma^{\text{add.}}(\boldsymbol{r})] = -\frac{1}{4} f_\sigma^{\text{nadd.}}(\boldsymbol{r}) \geq 0. \tag{52}$$

We have explicitly indicated above that the function $D_\sigma(\boldsymbol{r})$ defined in the preceding equation can be identified as being proportional to the negative non-additive component of the Fisher information in this spin-resolved MO resolution [6,61].

The appropriately calibrated *square* of its inverse, known as ELF [59], has been successfully used as the probe of the electron localization in molecules [59,60,76,77]. A somewhat improved behavior is observed in the DFT-tailored simple inverse of this function, known as IT-ELF [60]. In Fig. 1 we have compared the perspective views of these functions for N_2, NH_3, PH_3 and B_2H_6. These ELF functions convincingly validate the use of this local probe as an indicator of the localization of the valence electrons in the bonding and non-bonding (lone-pair) regions of these illustrative molecular systems. Indeed in the homonuclear diatomic N_2 one detects in both plots the typical accumulation of electrons between the nuclei due to the formation of the triple N≡N bond and the accompanying increase in the localization of the lone pair electrons in the non-bonding regions of both atoms, a clear manifestation of the accompanying *sp* hybridization. The three localized N–H bonds are also clearly visualized in both NH_3 panels of Fig. 1; a similar ELF patterns are detected in the PH_3 part of the figure. The final B_2H_6 plots are also seen to successfully locate the bonding electrons of the four terminal B–H bonds.

6 Contra-gradience probe of chemical bonds

The non-additive Fisher information density in the AO resolution (Eq. 45), defined for the singly occupied *spin*-orbitals $\boldsymbol{\psi} = \boldsymbol{\chi}\mathbf{C} = \{\psi_k, k = 1, 2, \ldots, N\}$ of the real (interacting) molecular system, e.g., those from the SCF MO or KS calculations, reads:

$$I^{\mathrm{F,nadd.}}[\boldsymbol{\chi}] = 4\sum_{k=1}^{m}\sum_{l=1}^{m}\int \gamma_{k,l}\left(1-\delta_{k,l}\right)\nabla\chi_l^*(\boldsymbol{r})\cdot\nabla\chi_k(\boldsymbol{r})d\boldsymbol{r} \equiv \int f^{\mathrm{nadd.}}(\boldsymbol{r})d\boldsymbol{r}$$
$$\equiv 2\int \bar{f}^{\mathrm{nadd.}}(\boldsymbol{r})d\boldsymbol{r} = 8T^{\mathrm{nadd.}}[\boldsymbol{\chi}]. \tag{53}$$

where

$$\boldsymbol{\gamma} = \langle\boldsymbol{\chi}|\left(\sum_{k=1}^{N}|\psi_k\rangle\langle\psi_k|\right)|\chi\rangle = \langle\boldsymbol{\chi}|\boldsymbol{\psi}\rangle\langle\boldsymbol{\psi}|\boldsymbol{\chi}\rangle = \mathbf{C}\mathbf{C}^\dagger = \left\{\gamma_{u,\,w}\right\}. \tag{54}$$

Its density per electronic pair, $\bar{f}^{\mathrm{nadd.}}(\boldsymbol{r})$, has been recently advocated [55,61] as a sensitive probe of the presence of chemical bonds, with the bonding regions being associated with the largest (valence) $\bar{f}^{\mathrm{nadd.}}(\boldsymbol{r}) < 0$ basins between atoms. The surrounding $\bar{f}^{\mathrm{nadd.}}(\boldsymbol{r}) > 0$ (*anti*-bonding) valence regions and the core regions of the negative $\bar{f}^{\mathrm{nadd.}}(\boldsymbol{r})$ then exhibit the familiar electron reorganization (promotion) effects on the constituent atoms, e.g., the valence AO hybridization, core polarization by the valence electrons, etc.

An extensive numerical analysis of the applicability of this CG probe of chemical bonds [61], reporting its implementation within the standard SCF MO calculations

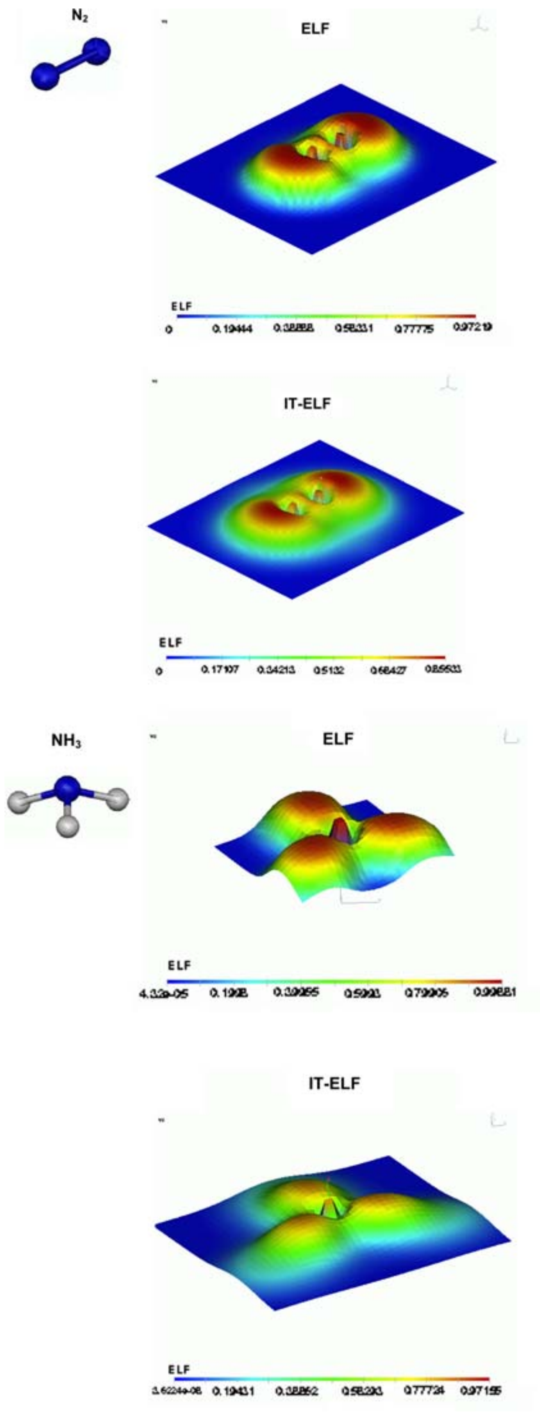
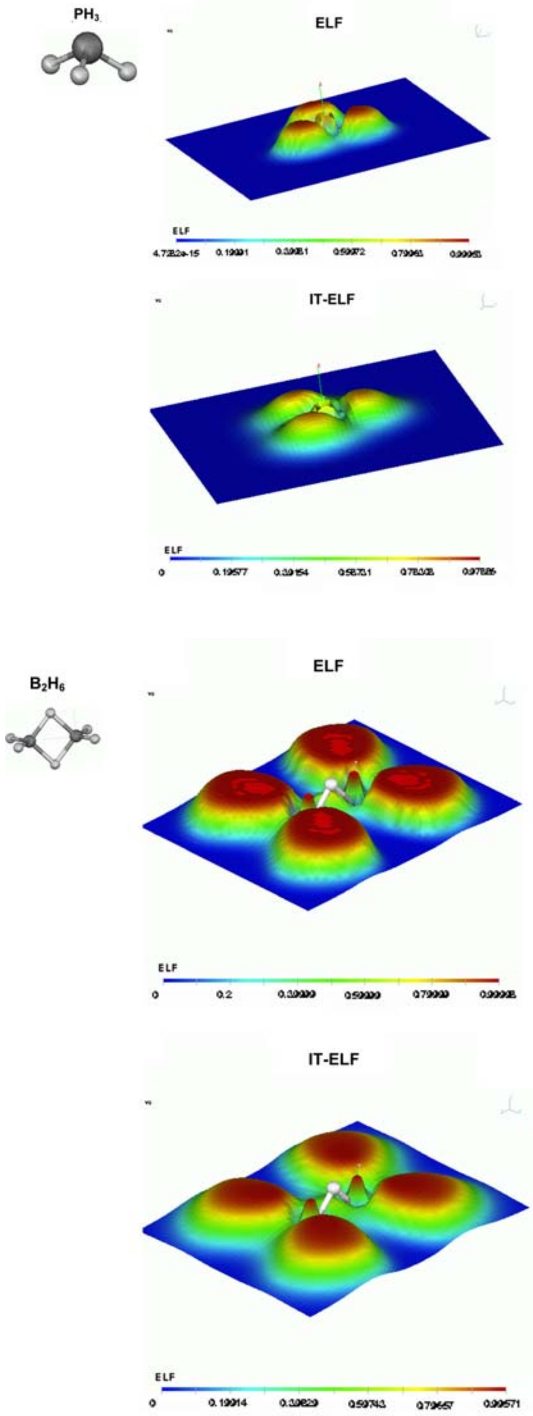


Fig. 1 Comparison between the ELF and IT-ELF functions for N_2, NH_3, PH_3 and B_2H_6 on selected planes of section: along the bond axis (N_2), including three hydrogen atoms (NH_3 and PH_3), and passing through both terminal BH_2 groups (B_2H_6)

Fig. 1 continued



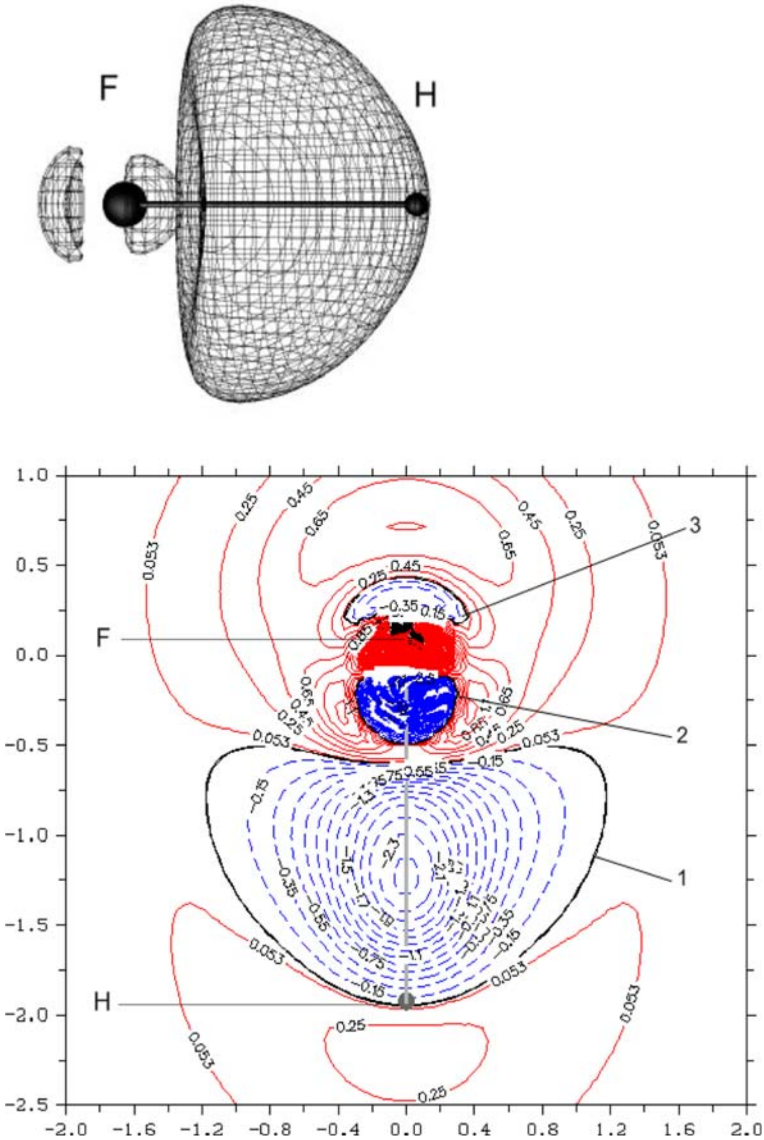


Fig. 2 The perspective view of the $\bar{f}^{\mathrm{nadd.}}(\boldsymbol{r}) < 0$ basins (*upper panel*) and the contour map of $\bar{f}^{\mathrm{nadd.}}(\boldsymbol{r})$ in the molecular plane (*lower panel*) of HF; the positive/negative contours are represented by the *solid/broken* lines, respectively. The same contour convention is observed in Figs. 3, 4

to illustrative diatomic and polyatomic systems, have validated the adequacy of this novel concept in the chemical interpretation of the computed electronic structure of molecular systems. In Figs. 2, 3, 4 we present representative results of such an analysis for HF, H_2O and butadiene.

It follows from the first panel of Fig. 2 that there are some small core regions on the fluorine atom of the negative values of $\bar{f}^{\mathrm{nadd.}}(\boldsymbol{r})$, reflecting the nodal structure of

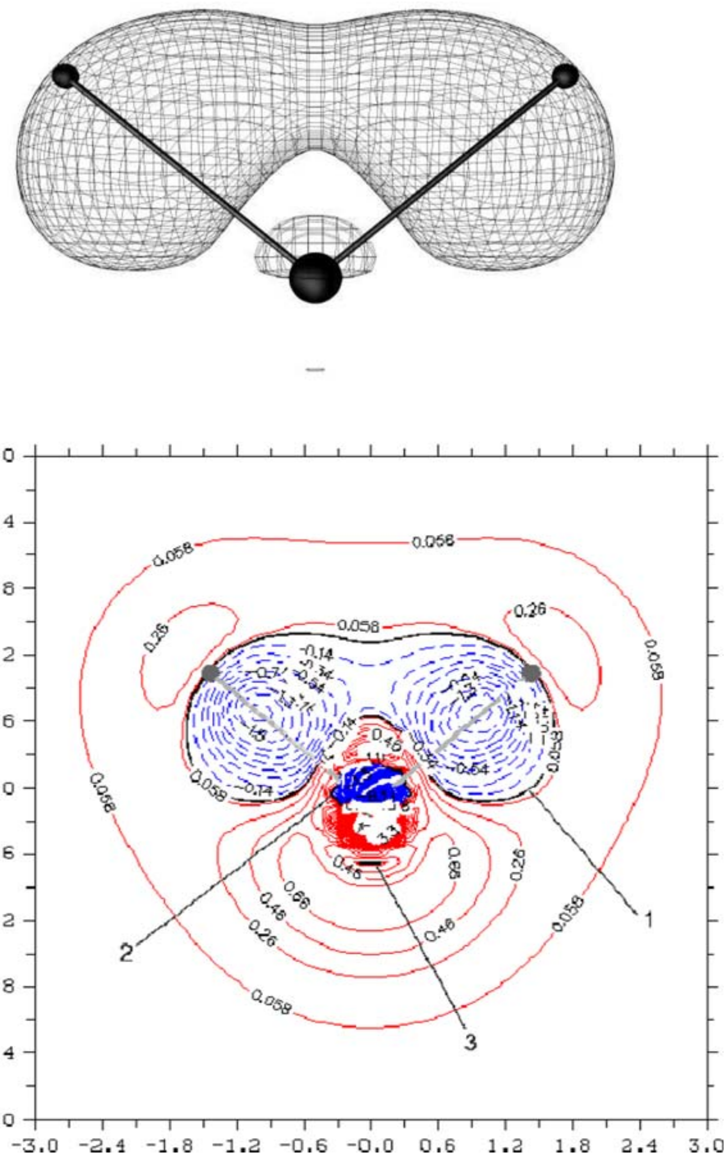


Fig. 3 The same as in Fig. 2 for H_2O

its 2*s* orbital, besides the largest basin extending over the bonding part of the valence shells of the two atoms, where the chemical bond is located. As also reflected by the contour map in the second panel of the figure, this dominating electron *inflow* region of the diminished Fisher information, which marks the accumulation of the valence electrons delocalized between the two atoms, are surrounded by the $\bar{f}^{\mathrm{nadd.}}(\boldsymbol{r}) > 0$ environment of the electron-*outflow* regions. The latter exhibit the cylindrical polarization/hybridization of the heavy atom, reflecting its promotion in the presence of

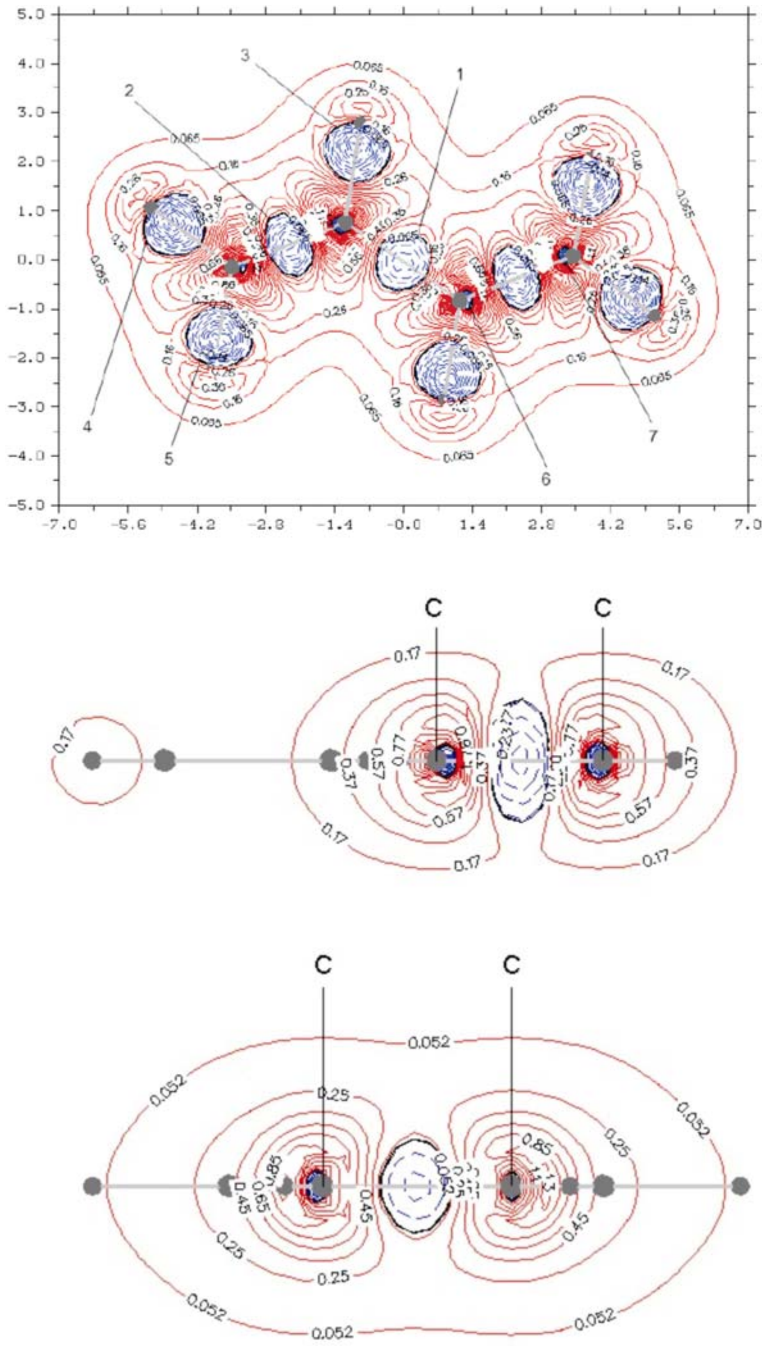


Fig. 4 The contour maps of $\bar{f}^{\text{nadd.}}(\boldsymbol{r})$ in butadiene: in the molecular plane (*upper panel*), and in perpendicular cuts passing through the two carbon atoms of the peripheral (*middle panel*) and central (*lowest panel*) C–C bonds, respectively

the hydrogen, and the H→F *charge transfer* (CT). The relatively large, and almost symmetrically placed bonding region, which excludes the 1s inner shell of F, testifies to a strong covalent component in H–F bond, as indeed expected for this interaction between the two electronically "hard" atoms.

In the water molecule (Fig. 3) one detects two overlapping, outer basins of the negative non-additive Fisher information in the O–H bonding regions, and two small inner shell-regions of the negative CG density. The bonding basins are located between the corresponding pairs of nuclei, which define these localized single bonds, and the lowering of the CG density in each bond is seen to be the strongest in the direction linking the two nuclear attractors. The overlapping character of these two regions of the negative non-additive kinetic-energy, reflected by the present non-additive Fisher-information probe, indicates delocalization of the bonding electrons of one O–H bond into the bonding region of the other chemical bond, as indeed implied by the delocalized character of the occupied canonical MO. The contour map for the cut in the molecular plane also reveals a strong buildup of this information/kinetic-energy quantity in the lone-pair region of oxygen, and—to a lesser degree—in the non-bonding regions of two hydrogens. This effect should indeed be expected for the nearly tetrahedral sp^3-hybridization promotion of the heavy atom.

The first of the contour maps in Fig. 4 testifies to the efficiency of the CG criterion in localizing all nine bonding regions in butadiene, a relatively more "spherical" basins for the six C-H bonds, and more "ellipsoidal" ones for the three C–C bonds. It should be realized at this point that the molecular cut of this panel reflects only the σ bonds between the neighboring carbon atoms and misses the effects due to their partial π components, which add to the resultant contour values shown in the remaining diagrams corresponding to the perpendicular cuts along the peripheral and central C–C bonds. The differences between these two additional plots and the molecular-plane map of the first panel in the figure thus reflect the extra contributions due to the partial π components of these three C–C bonds. It follows from these two maps in the bond-planes, perpendicular to the molecular plane passing through all nuclei, that the π bond between the neighboring peripheral carbons is much stronger than its central counterpart. This is in agreement with conjectures from the independent results obtained using alternative measures of the chemical bond multiplicity [6,29,42,78].

7 Conclusion

In this article we have stressed the role of the supplementary information-theoretic variational principles in determining the optimum distributions of the electron probabilities/densities in molecular fragments, generated for specific interpretation purposes in chemistry. The information and constraint parts of these extremum information rules influence the shape and physical properties of such subsystems, e.g., their in situ charge sensitivities. The complementary additive and non-additive components of alternative measures of the information content can be used as tools for exploring the electronic structure of molecules. We have illustrated the use of the complementary additive and non-additive components of both the global and local measures of the entropy-deficiency (missing-information), defined either in terms of the subsystem electron probabilities themselves or the associated conditional probability distributions, in the simplest scenario of the local partitioning of the molecular electron density. It was demonstrated that all these information principles generate the familiar stockholder partitioning scheme of Hirshfeld. Its generalization to the subsystem partitioning of the *two*-electron densities has also been reported [6,12].

The additivity of the energy contributions in the hypothetical KS (non-interacting) system in the MO resolution has been stressed, and the system non-additive kinetic energy (Fisher information) in the AO resolution has been defined. The corresponding non-additive information terms in both the MO and AO resolutions of the real (interacting) system have been then used as criteria for the localization of electrons and of the chemical bonds in molecules. The representative applications of these non-additive Fisher-information densities fully confirm their usefulness in extracting a useful chemical interpretation from the computed electron distributions in several illustrative molecular systems. The inverse of the MO-non-additive kinetic-energy (Fisher information) density was shown to give rise to the ELF concept, while the AO-non-additive kinetic-energy (Fisher information) generates the recently proposed CG indicator of the presence of chemical bonds. The numerical data reflecting the overall Fisher information decrease in the molecular bonding regions, which quantitatively describe the electron delocalization/covalency effects, can be also generated by numerical integration [55,79]. This analysis will be the subject of a separate report.

Most of existing theoretical interpretations of the origins of the covalent chemical bond at molecular equilibrium geometry emphasize, almost exclusively, the potential (interaction) aspect of this phenomenon, focusing on the mutual attraction between the accumulation of electrons between the two atoms (the negative "bond-charge") and the partially screened (positively charged) nuclei. The ELF and contragradience criteria, which reflect the non-additive kinetic-energy/Fisher-information terms, adopt the complementary view by stressing the importance of the kinetic-energy bond component. In accordance with the molecular virial theorem, however, the overall kinetic/Fisher-information data only blur the picture of the subtle information origins of chemical bonds. As we have emphasized in the present analysis, the overall kinetic energy change due to chemical bond formation, relative to the separated atoms, exhibits a net increase at the equilibrium positions of the nuclei, reflecting the overall contraction of the electronic density in the presence of the remaining nuclear attractors in the molecule. Let us again recall that the lowering of the kinetic energy component is observed only at an early approach of atoms when they form the chemical bond, at large internuclear separations. Only by focusing on the *non-additive* part of this component can one uncover the real information origins of chemical bonds, and define the useful local probes for their localization and eventually—the quantitative information descriptors based upon the kinetic energy/Fisher-information.

Acknowledgments I would like to thank Dr. Sigfrido Escalante and Mr. Piotr de Silva for preparing Fig. 1 and Figs. (2–4), respectively.

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