Electron Localization Function as Information Measure

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Received: June 13, 2005; In Final Form: September 4, 2005

The conditional two-electron probability function, which defines the electron localization function (ELF) of Becke and Edgecombe in the Kohn−Sham theory, is interpreted as the nonadditive (interorbital) Fisher information contained in the electron distribution. The probability normalization considerations suggest a use of the related information measure defined in terms of the unity-normalized probability distributions (shape factors of the electron densities), as the key ingredient of the modified information-theoretic ELF. This modified Fisher information density is validated by a comparison with the original two-electron probability function. Illustrative applications to typical molecular systems demonstrate the adequacy of the modified information-theoretic ELF in extracting the key features of the electron distributions in molecules. The overall Fisher information itself and the associated information-distance quantities are also proposed as complementary localization functions.

1. Introduction

Some years ago, the electron localization function (ELF) for atomic and molecular systems was proposed by Becke and Edgecombe.[1] It has been successfully applied to visualize both the atomic shell structure and the distribution of the bonding and lone electron pairs in molecules, to classify and distinguish between single and multiple chemical bonds, and to monitor changes in the electron distribution in the bond-forming−bond-breaking processes.[2,3] An extension of the ELF to time-dependent systems has also been reported.[4]

It is the main purpose of this paper to provide the information-theoretic interpretation to the key ingredient of ELF, in terms of the Fisher (locality) measure of information.[5,6] It has been used in the past to investigate the kinetic energy functionals,[7,8] to derive the Kohn−Sham equations[9] of the density functional theory (DFT)[10] from the extreme physical information principle of Frieden,[6] and to formulate the local thermodynamic-like description of the molecular electronic structure.[11] It will be demonstrated that this analysis leads to alternative information measures of the electron localization in molecular systems, which will be tested against the original ELF. The proposed information-theoretic ELF (IT-ELF) will be validated by applying it to interpret the electronic structure in selected representative atomic and molecular systems.

2. Information-Theoretic Interpretation

The key ingredient of the electron localization function (ELF)[1] is the leading term of the Taylor expansion of the Hartree−Fock spherically averaged conditional (c) pair probability $P_c^{\sigma\sigma}(\mathbf{r}, s)$. This quantity measures the probability of finding in the distance s from a given (reference) electron at $\mathbf{r}$ the other (dependent) electron of like spin σ

$$P_c^{\sigma\sigma}(\mathbf{r}, s) = {}^1\!/_3 D_\sigma(\mathbf{r}) s^2 + ... \tag{1}$$

$$D_\sigma(\mathbf{r}) \equiv D_\sigma[\rho_\sigma; \mathbf{r}] = \sum_i^\sigma |\nabla\varphi_{i\sigma}(\mathbf{r})^2 - {}^1\!/_4 \nabla\rho_\sigma(\mathbf{r})^2/\rho_\sigma(\mathbf{r})$$
$$\equiv \sum_i^\sigma \tau_{i\sigma}(\mathbf{r}) - {}^1\!/_4 \nabla\rho_\sigma(\mathbf{r})^2/\rho_\sigma(\mathbf{r}) \geq 0 \tag{2}$$

where both the kinetic energy density $\tau_\sigma(\mathbf{r}) = \sum_i^\sigma \tau_{i\sigma}(\mathbf{r})$ and the spin density

$$\rho_\sigma(\mathbf{r}) = \sum_i^\sigma [\varphi_{i\sigma}(\mathbf{r})]^2 \equiv \sum_i^\sigma \rho_{i\sigma}(\mathbf{r}) \tag{3}$$

are the sums of additive contributions due to the molecular orbitals (MO) $\boldsymbol{\varphi}_\sigma = \{\varphi_{i\sigma}\}$, representing the spatial parts of the σ-type spin−orbitals. In the related one-determinant Kohn−Sham (KS) approximation of DFT,[10] the orbital densities $\boldsymbol{\rho}_\sigma = \{\rho_{i\sigma}\}$ are the (mutually closed) pieces of the overall spin density ρ_σ^s of the separable (s) noninteracting system, which by hypothesis equals that of the real interacting system of electrons in a molecule: $\rho_\sigma = \rho_\sigma^s$.

The probability function $D_\sigma(\mathbf{r})$ provides a measure of the localization of the reference electron, reaching the smallest values for the highly localized distribution of the reference electron. Indeed, it vanishes in the limiting case of the one-electron system and in the regions of the multielectron systems dominated by a single, localized σ spin−orbital of the reference electron, which effectively excludes by the Pauli principle another spinlike electron from its vicinity.

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10.1021/jp053184i CCC: $30.25

The two terms of eq 2 have a precise information-theoretic interpretation in terms of the density of the Fisher information measure for locality,[5,6] $I(\mathbf{r})$, of the one-electron probability density $p(\mathbf{r}) = q^2(\mathbf{r})$, $\int p(\mathbf{r})\, d\mathbf{r} = 1$, where $q(\mathbf{r})$ stands for the distribution amplitude

$$I[p] = \int p(\mathbf{r})\, [\nabla \ln p(\mathbf{r})]^2\, d\mathbf{r} = \int |\nabla p(\mathbf{r})|^2/p(\mathbf{r})\, d\mathbf{r} \equiv \int f[p; \mathbf{r}]\, d\mathbf{r}$$
$$= I[q] = 4 \int |\nabla q(\mathbf{r})|^2\, d\mathbf{r} \equiv \int f[q; \mathbf{r}]\, d\mathbf{r} \tag{4}$$

This information measure characterizes the distribution sharpness (localization), thus providing a complementary description of the probability distribution to the familiar Shannon entropy[12]

$$S[p] = -\int p(\mathbf{r}) \log p(\mathbf{r})\, d\mathbf{r} \tag{5}$$

with the latter reflecting the distribution smoothness (spread), thus indexing the uncertainty contained in p.

The kinetic energy term in eq 2 is seen to represent the sum of the orbital Fisher information densities[9]

$$\tau_\sigma(\mathbf{r}) = \sum_i^\sigma \tau_{i\sigma}(\mathbf{r}) = {}^1/_4 \sum_i^\sigma f\,[\rho_{i\sigma}; \mathbf{r}] \equiv {}^1/_4 \sum_i^\sigma f_{i\sigma}[\rho_{i\sigma}; \mathbf{r}] \equiv {}^1/_4 f_\sigma^{\,a}[\rho_\sigma\,; \mathbf{r}] \tag{6}$$

As such, it represents a quarter of the additive (a) Fisher information density $f_\sigma^{\,a}[\rho_\sigma; \mathbf{r}]$ contained in the orbital components $\boldsymbol{\rho}_\sigma = \{\rho_{i\sigma}\}$ of the overall spin density ρ_σ. A reference to eq 4 also shows that the second term in eq 2 can be similarly identified as providing a quarter of the total (t) Fisher information density in ρ_σ, $f_\sigma^{\,t}(\mathbf{r}) \equiv f_\sigma\, [\rho_\sigma; \mathbf{r}] \equiv f_\sigma^{\,t}[\rho_\sigma; \mathbf{r}]$

$$ {}^1/_4 f_\sigma^{\,t}(\mathbf{r}) = {}^1/_4 |\nabla \rho_\sigma(\mathbf{r})|^2/\rho_\sigma(\mathbf{r}) = {}^1/_4 f_\sigma^{\,t}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}\,; \mathbf{r}] = {}^1/_4 \{f_\sigma^{\,a}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}\,; \mathbf{r}] + f_\sigma^{\,n}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}\,; \mathbf{r}]\} \tag{7}$$

combining the additive (a) and nonadditive (n) parts.

Therefore, the $D_\sigma(\mathbf{r})$ function of eq 2 is proportional to the negative nonadditive contribution to $f_\sigma^{\,t}(\mathbf{r})$, defined in terms of the electron densities

$$D_\sigma(\mathbf{r}) = -{}^1/_4 f_\sigma^{\,n}[\rho_\sigma\,; \mathbf{r}] \tag{8}$$

This key ingredient of the ELF thus has a direct information-theoretic interpretation in addition to the conditional probability interpretation given in the original derivation.

As we have already remarked above, in the KS theory the MO densities $\boldsymbol{\rho}_{\boldsymbol{\sigma}}$, or their probability amplitudes (KS orbitals[10]) $\boldsymbol{\varphi}_{\boldsymbol{\sigma}}$, refer to the hypothetical noninteracting system, while the overall density ρ_σ corresponds to the interacting system. Hence, the source of the nonadditivity of eq 8 is the electron interaction in the real system. Therefore, the KS MO partitioning nonadditivity $f_\sigma^{\,n}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}]$ in the total Fisher information density $f_\sigma^{\,t}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}]$ in fact represents the electron interaction nonadditivity present in the real molecular system. Moreover, since the additive Fisher information density $f_\sigma^{\,a}(\mathbf{r})$ combines all the *intra*orbital contributions, $f_\sigma^{\,a}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}] = f_\sigma^{\,\mathrm{intra}}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}]$, the nonadditive part can be alternatively interpreted as measuring the *inter*orbital Fisher information density: $f_\sigma^{\,n}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}] = f_\sigma^{\,\mathrm{inter}}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}]$.

The nonadditive Fisher information is related to the nonadditive and correlation kinetic energies.[8] Therefore, the densities of the latter can be also considered alternative energetic measures of the electron localization.

We have thus demonstrated that the key ingredient of the ELF measures the nonadditive component of the Fisher information measure for locality (intrinsic accuracy) in the MO orbital resolution. This link between the molecular orbital localization concept and the Fisher information should not come as a surprise, since the latter itself characterizes the "narrowness" of the electron distribution (see eq 4). It is proportional to the squared gradient of the MO in question, thus reflecting the orbital localization (sharpness). Indeed, in the familiar normal distribution case, it represents the inverse of the distribution variance, called the invariance.

Hence, for the fixed electron density, and thus the fixed overall Fisher information $f_\sigma[\rho_\sigma; \mathbf{r}] = f_\sigma^{\,t}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}]$ (eq 7) of the system as a whole, the higher the additive Fisher information in the MO resolution, $f_\sigma^{\,a}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}]$ (eq 6), the lower the associated magnitude of the associated nonadditive part $f_\sigma^{\,n}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}]$ (eq 8), and thus the higher the degree of the electron localization. One can therefore conclude that the additive Fisher information itself can be regarded as a basis for an alternative, direct measure of the electron localization

$$\mathrm{elf}_\sigma^{\mathrm{F}}(\mathbf{r}) \equiv f_\sigma^{\,a}[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}] = \sum_i^\sigma |\nabla \rho_{i\sigma}(\mathbf{r})|^2/\rho_{i\sigma}(\mathbf{r}) = 4 \sum_i^\sigma |\nabla \varphi_{i\sigma}(\mathbf{r})|^2 \tag{9}$$

Finally, it should be observed that the above development applies only to the real probability amplitudes (orbitals) of eq 4. Therefore, it does not hold for the complex Macke-type orbitals, which yield the specified electron density,[13] e.g., the Harriman equi-orbitals. The latter exhibit the identical spatial distribution of electrons, $\rho_{i\sigma}(\mathbf{r}) = \rho_\sigma(\mathbf{r})/N_\sigma$, and include the density-dependent phase factor, which ensures their mutual orthogonality. Indeed, for these orbital densities, the Fisher information nonadditivity identically vanishes, as indeed expected of the uncorrelated electrons described by the equi-orbitals wrongly interpreted as the real (nonorthogonal) one-electron functions.

3. Normalization Considerations

As indicated in eq 4, the Fisher information functional, reminiscent of von Weizsäcker's nonhomogeneity correction[14] to the density functional for the electronic kinetic energy, is properly defined in terms of the unity normalized probability distributions, i.e., the shape factors of the corresponding electron densities, e.g.,

$$p_\sigma(\mathbf{r}) = \rho_\sigma(\mathbf{r})/N_\sigma \qquad \int p_\sigma(\mathbf{r})\, d\mathbf{r} = 1 \tag{10}$$

where $N_\sigma = \int \rho_\sigma(\mathbf{r})\, d\mathbf{r}$ is the total number of electrons of the spin variety σ, i.e., the number of the (singly occupied) KS spin−orbitals $\{\varphi_{i\sigma}\}$. Enforcing the proper normalization of the electron probability distribution gives rise to the total Fisher information density of the electron shape-function

$$f_\sigma[p_\sigma; \mathbf{r}] = f_\sigma[\rho_\sigma; \mathbf{r}]/N_\sigma \tag{11}$$

It should be realized that each orbital density represents the unity normalized conditional probability distribution, $\pi_{i\sigma}(\mathbf{r}) \equiv \pi_\sigma(\mathbf{r}|i)$, of finding an electron with spin σ at a given location in space, when it is known beforehand that this electron occupies the specified *i*th MO (a parameter)

$$\rho_{i\sigma}(\mathbf{r}) = p_{i\sigma}(\mathbf{r})/P_{i\sigma} \equiv \pi_{i\sigma}(\mathbf{r})$$

$$P_{i\sigma} = \int \mathrm{p}_{i\sigma}(\mathbf{r})\,\mathrm{d}\mathbf{r} = 1/N_\sigma \equiv P_\sigma$$

$$\sum_i^\sigma p_{i\sigma}(\mathbf{r}) = p_\sigma(\mathbf{r})$$

$$\sum_i^\sigma \int p_{i\sigma}(\mathbf{r})\,\mathrm{d}\mathbf{r} = \int \pi_{i\sigma}(\mathbf{r})\,\mathrm{d}\mathbf{r} = \sum_i^\sigma P_{i\sigma} = 1 \tag{12}$$

Here, $p_{i\sigma}(\mathbf{r})$ is the joint probability of simultaneous events in which an electron is found at $\mathbf{r}$ and it originates from spin−orbital $\varphi_{i\sigma}$, while the orbital probability vector $\mathbf{P}_\sigma = \{P_{i\sigma} = 1/N_\sigma\}$ groups for the condensed probabilities of finding an electron of spin σ on a specified MO.

It should be emphasized that the molecular spin probability distribution $p_\sigma(\mathbf{r})$ should be compared in terms of the Fisher information descriptors only with the molecularly normalized MO joint distributions $\{p_{i\sigma}(\mathbf{r})\}$ (eq 12), since only these orbital probability densities characterize the orbital distributions of electrons as subsystems-in-the-molecule. This is in contrast to the conditional probabilities $\boldsymbol{\pi_\sigma}(\mathbf{r}) = \{\pi_\sigma(\mathbf{r}|i)\} = \boldsymbol{\rho_\sigma}(\mathbf{r})$, equal to the orbital electron densities, which describe the separate probability distributions, as indeed reflected by the unity normalization of each of them.

Since the gradient of the logarithm of the joint probability distributions $\mathbf{p}_\sigma(\mathbf{r}) = \{p_{i\sigma}(\mathbf{r})\}$ (see eq 4) is solely determined by the local, conditional probability factor $\pi_{i\sigma}(\mathbf{r})$

$$\nabla \ln p_{i\sigma}(\mathbf{r}) = \nabla \ln[P_{i\sigma}\,\pi_\sigma(\mathbf{r}|i)] = \nabla \ln \pi_\sigma(\mathbf{r}|i) \tag{13}$$

the additive Fisher information density of the joint probability distribution satisfies the following grouping rule for combining the intraorbital contributions into the molecular information content

$$f_\sigma^{\mathrm{a}}[\mathbf{p}_\sigma; \mathbf{r}] = \sum_i^\sigma P_{i\sigma}\, f_{i\sigma}[\pi_{i\sigma}; \mathbf{r}] = P_\sigma\, f_\sigma^{\mathrm{a}}[\boldsymbol{\pi_\sigma}; \mathbf{r}] \tag{14a}$$

and hence

$$I^{\mathrm{a}}[\mathbf{p}_\sigma] = \int f_\sigma^{\mathrm{a}}[\mathbf{p}_\sigma; \mathbf{r}]\,\mathrm{d}\mathbf{r} = \sum_i^\sigma P_{i\sigma} \int f_{i\sigma}[\pi_{i\sigma}; \mathbf{r}]\,\mathrm{d}\mathbf{r} = \sum_i^\sigma P_{i\sigma}\, I[\pi_{i\sigma}] \tag{14b}$$

In other words, the additive Fisher information in the joint MO probabilities $\mathbf{p}_\sigma(\mathbf{r}) = \{p_{i\sigma}(\mathbf{r})\}$ is the mean value of the Fisher information contained in the orbital densities $\boldsymbol{\rho_\sigma}$, i.e., the conditional electron probabilities $\boldsymbol{\pi_\sigma}$, with the unbiased weighting factors for each orbital, $P_{i\sigma} = P_\sigma = 1/N_\sigma$, determining the relevant weighting factor for each orbital "group" of events.

This grouping principle for the Fisher information can be compared with the corresponding formula[12,15] for the additive Shannon entropy in the MO resolution (see eq 5)

$$\begin{aligned} S^{\mathrm{a}}[\mathbf{p}_\sigma] &= -\sum_i^\sigma \int p_{i\sigma}(\mathbf{r}) \log p_{i\sigma}(\mathbf{r})\,\mathrm{d}\mathbf{r} = -\sum_i^\sigma \int P_{i\sigma}\, \pi_\sigma(\mathbf{r}|i) \log\,[P_{i\sigma}\pi_\sigma(\mathbf{r}|i)]\,\mathrm{d}\mathbf{r} \\ &= -\sum_i^\sigma P_{i\sigma} \log P_{i\sigma} - \sum_i^\sigma P_{i\sigma} \int \pi_\sigma(\mathbf{r}|i) \log \pi_\sigma(\mathbf{r}|i)\,\mathrm{d}\mathbf{r} \equiv S(\mathbf{P}_\sigma) + \sum_i^\sigma P_{i\sigma} S(\pi_{i\sigma}) \\ &= \log N_\sigma + N_\sigma^{-1} \sum_i^\sigma S(\pi_{i\sigma}) \end{aligned} \tag{15}$$

where we have used the normalization condition for the conditional orbital densities (see eq 12), $\int \pi_\sigma(\mathbf{r}|i)\,\mathrm{d}\mathbf{r} = 1$, involving the integration over the spatial event variable $\mathbf{r}$ for the fixed parameter *i*. This entropy combination rule reflects the fact that the overall uncertainty in the MO distributions $\mathbf{p}_\sigma$ does not depend on specific stages of acquiring knowledge about the distributions in question, here involving the intraorbital (conditional) probability stage and that of the (identical) probabilities of the MO in the molecule as a whole. The above combinational formula expresses the overall Shannon entropy in the MO joint probabilities $\mathbf{p}_\sigma(\mathbf{r})$ as the sum of the entropy in the equalized group probabilities $\mathbf{P}_\sigma = \{1/N_\sigma\}$ and the $\mathbf{P}_\sigma$-weighted average of the intragroup entropies, reflecting the uncertainties in the conditional probabilities $\boldsymbol{\pi_\sigma}(\mathbf{r}) = \{\pi_\sigma(\mathbf{r}|i)\}$. This comparison shows that, due to the local character of the Fisher information, the analogue of the global group uncertainty term of eq 15 is missing in the grouping formula (eq 14b).

Therefore, the total and additive Fisher information densities of eqs 6 and 7, which determine the nonadditive component of eq 8, have the same linear scaling with the overall number of electrons, when expressed in terms of the molecularly normalized probabilities

$$f_\sigma[\rho_\sigma; \mathbf{r}] = N_\sigma\, f_\sigma[p_\sigma; \mathbf{r}]$$

and

$$f_\sigma^{\mathrm{a}}[\boldsymbol{\rho_\sigma}; \mathbf{r}] = f_\sigma^{\mathrm{a}}[\boldsymbol{\pi_\sigma}; \mathbf{r}] = N_\sigma\, f_\sigma^{\mathrm{a}}[\mathbf{p}_\sigma; \mathbf{r}] \tag{16}$$

and hence

$$D_\sigma(\mathbf{r}) = -{}^1\!/_4 N_\sigma(f_\sigma[p_\sigma; \mathbf{r}] - f_\sigma^{\mathrm{a}}[\mathbf{p}_\sigma; \mathbf{r}]) \equiv -{}^1\!/_4 N_\sigma f_\sigma^{\mathrm{n}}[\mathbf{p}_\sigma; \mathbf{r}] \equiv N_\sigma d_\sigma[\mathbf{p}_\sigma; \mathbf{r}] \tag{17}$$

The conditional probability densities $\boldsymbol{\pi_\sigma}(\mathbf{r}) = \{\pi_\sigma(\mathbf{r}|i)\} = \boldsymbol{\rho_\sigma}(\mathbf{r})$ of eq 12 provide the convenient framework for an explicit expression for the nonadditive Fisher information density in terms of these MO probability variables (see eqs 12 and 15)

$$\begin{aligned} f_\sigma^{\mathrm{n}}[\mathbf{p}_\sigma; \mathbf{r}] &= |\nabla p_\sigma(\mathbf{r})|^2/p_\sigma(\mathbf{r}) - \sum_i^\sigma |\nabla p_i\sigma(\mathbf{r})|^2/p_{i\sigma}(\mathbf{r}) = N_\sigma^{-1}\{f_\sigma[\rho_\sigma; \mathbf{r}] - f_\sigma^{\mathrm{a}}[\boldsymbol{\rho_\sigma}; \mathbf{r}]\} \\ &= N_\sigma^{-1} \sum_i^\sigma \sum_j^\sigma \nabla \pi_{i\sigma}(\mathbf{r}) \cdot \nabla \pi_{j\sigma}(\mathbf{r})\,[\rho_\sigma(\mathbf{r})^{-1} - \pi_{i\sigma}(\mathbf{r})^{-1}\delta_{ij}] \end{aligned} \tag{18}$$

4. Electron Localization Functions

It follows from the original, two-electron conditional probability meaning of $D_\sigma(\mathbf{r})$ that the smaller the probability of

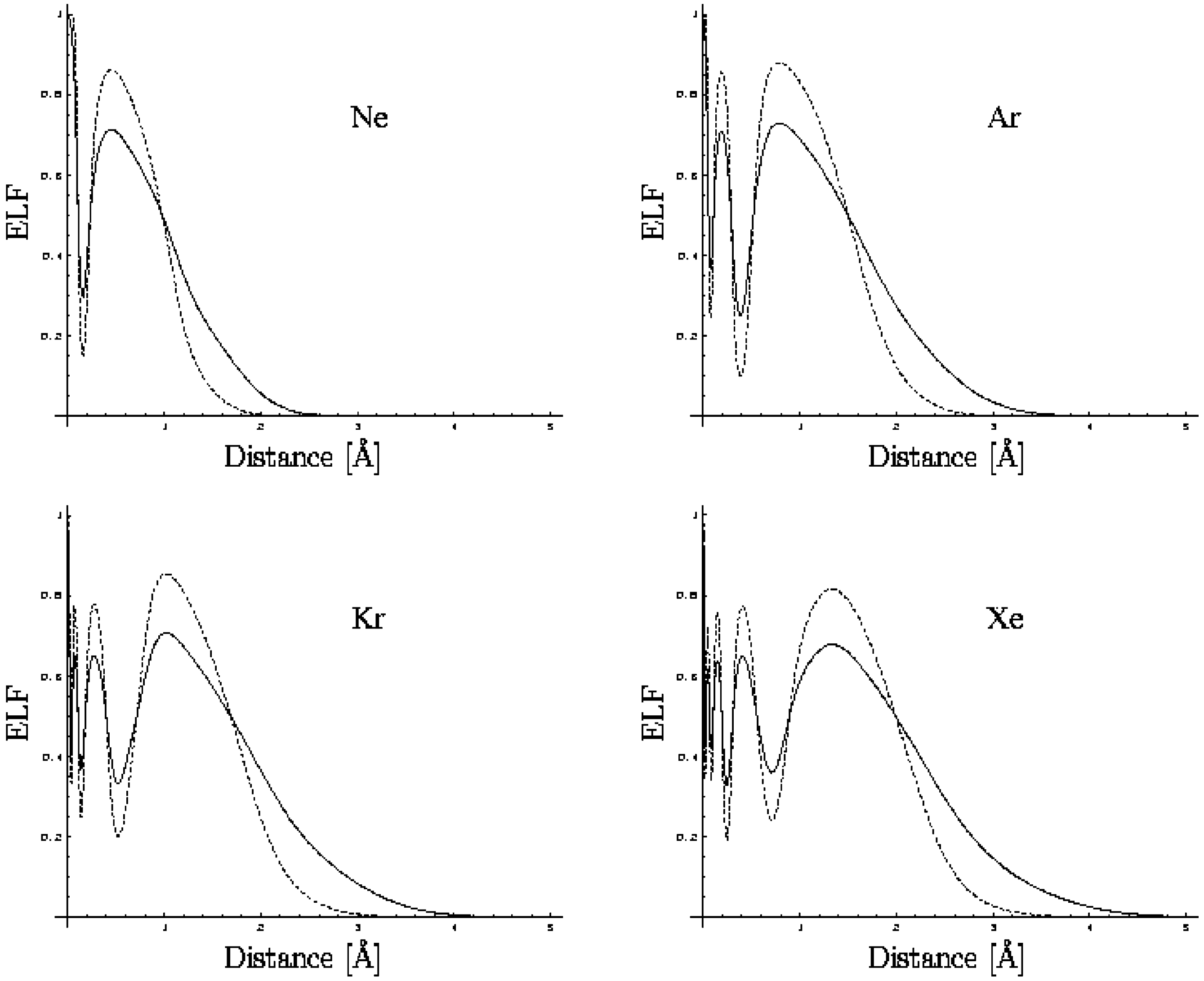

Figure 1. Plots of ELF (dashed line) and IT-ELF for Ne, Ar, Kr, and Xe.

finding a second spin-like electron near the reference point at **r** the more highly localized is the reference electron.[1] Therefore, there is an overall "inverse" relationship between this conditional probability, proportional to the negative nonadditive component of the Fisher information in MO resolution, and a realistic measure of the electron localization.

The original ELF[1] has been constructed using the following "squared" reciprocity relation

$$\mathrm{ELF}_\sigma(\mathbf{r}) = (1 + \chi_\sigma[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}]^2)^{-1} \quad \chi_\sigma[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}] = D_\sigma[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}]/D_\sigma^{\ 0}(\mathbf{r}) \tag{19}$$

with respect to the local density approximation (LDA) value

$$D_\sigma^{\ 0}(r) = D_\sigma^{\ 0}[\rho_\sigma; r] = [3(6\pi)^{2/3}/5]\rho_\sigma(r)^{5/3} \tag{20}$$

This definition, dimensionless and invariant with respect to the unitary transformations of orbitals, has been designed to directly reflect the electron localization relative to the above LDA reference. It assumes the values between 0 and 1 and exhibits the desirable features of reaching the upper limit ELF = 1 for the perfect localization and ELF = $^1/_2$ for a delocalized (homogeneous) electron gas. It should be realized, however, that this expression has been "tailored" somewhat arbitrarily by selecting the square of $\chi_\sigma = D_\sigma/D_\sigma^{\ 0}$ in the denominator and adopting the uniform density electron gas reference to give ELF = $^1/_2$. This particular version of ELF was shown to realistically reveal the location of atomic shells as well as the core and valence (binding and lone) electron pairs in molecules. Clearly, any alternative choice of ELF should also deliver all these features of the electron configuration with comparable accuracy and clarity of the graphical visualization.

As we have argued in the preceding section, the overall and MO information-theoretic quantities should be expressed in terms of the overall shape factor (eq 10) and probabilities of the orbital subsystems in molecules (eq 12). The LDA reference function expressed in terms of the molecular probability distribution becomes

$$d_\sigma^{\ 0}[p_\sigma(\mathbf{r})] = [3(6\pi)^{2/3}/5][\rho_\sigma(\mathbf{r})/N_\sigma]^{5/3} = D_\sigma^{\ 0}[\rho_\sigma; \mathbf{r}]/N_\sigma^{\ 5/3} \tag{21}$$

Hence, the modified ELF ratio (see eq 17)

$$\chi_\sigma[\mathbf{p}_\sigma; \mathbf{r}] = d_\sigma[\mathbf{p}_\sigma; \mathbf{r}]/d_\sigma^{\ 0}(p_\sigma(\mathbf{r})) = N_\sigma^{\ 2/3} D_\sigma(\mathbf{r})/D_\sigma^{\ 0}(\mathbf{r}) = N_\sigma^{\ 2/3}\chi_\sigma[\boldsymbol{\rho}_{\boldsymbol{\sigma}}; \mathbf{r}] \tag{22}$$

which can be used to construct the IT-ELF.

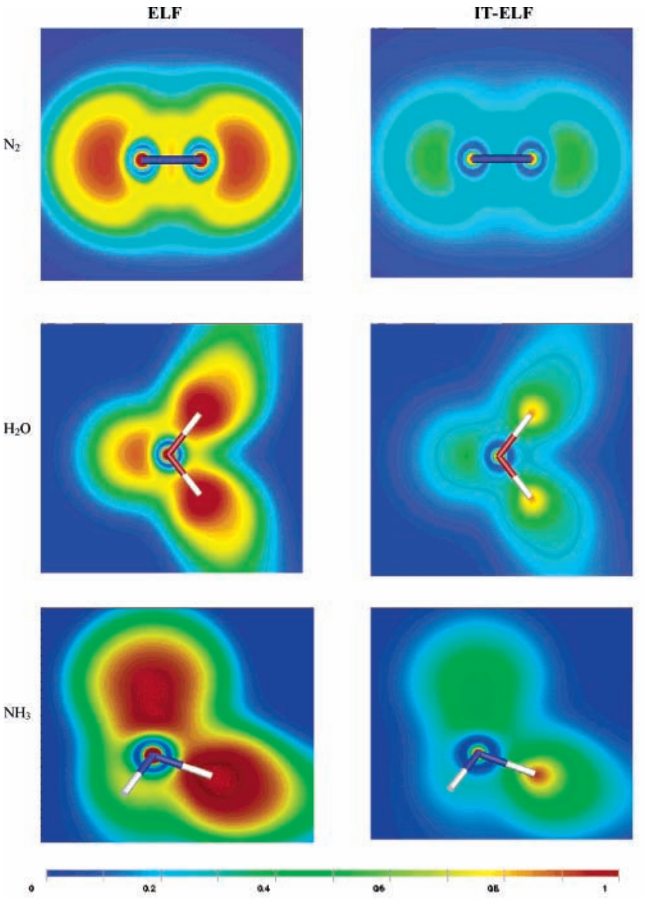

Figure 2. Plots of ELF and IT-ELF for N_2, H_2O, and NH_3 on selected planes. The color scale for the ELF values is given in the bottom of the figure.

The simplest option is to use the ordinary "inverse" relationship in the spirit of the original expression (eq 19)

$$\mathrm{elf}_\sigma(\mathbf{r}) = N_\sigma^{2/3}/(N_\sigma^{2/3} + \chi_\sigma[\mathbf{p}_\sigma; \mathbf{r}]) = (1 + \chi_\sigma[\boldsymbol{\rho}_\sigma; \mathbf{r}])^{-1} \qquad (23)$$

Above, we have modified the original construction to regain the assumed normalization of Becke and Edgecombe: $\mathrm{elf}_\sigma(\mathbf{r}) = {}^1/_2$ for the perfectly delocalized, homogeneous electron gas, when $\chi_\sigma[\boldsymbol{\rho}_\sigma; \mathbf{r}] = 1$, and $\mathrm{elf}_\sigma(\mathbf{r}) = 1$, for the perfectly localized case, when $\chi_\sigma(\boldsymbol{\rho}_\sigma; \mathbf{r}) = 0$.

It should also be observed that the original ELF of eq 19 is recovered through the corresponding squared inverse relationship

$$\mathrm{ELF}_\sigma(\mathbf{r}) = N_\sigma^{4/3}/(N_\sigma^{4/3} + \chi_\sigma[\mathbf{p}_\sigma; \mathbf{r}]^2) = (1 + \chi_\sigma[\boldsymbol{\rho}_\sigma; \mathbf{r}]^2)^{-1} \qquad (24)$$

In Figure 1, representative graphs of the IT-ELF function $\mathrm{elf}_\sigma(\mathbf{r})$ (eq 23) for the rare gas atoms Ne, Ar, Kr, and Xe are presented. For comparison, the dashed curves represent the original function $\mathrm{ELF}_\sigma(\mathbf{r})$ (eq 19). The qualitative behavior of the two curves is seen to be very similar. In general, the IT-ELF exhibits smaller outer amplitudes and thus a larger spatial extension than the original ELF. Figures 2 and 3 report illustrative comparisons of the molecular ELF and IT-ELF plots. Again, the topology of the two functions is qualitatively the same. The atomic shell structures as well as lone pairs are clearly displayed by both functions. As already discussed for the rare gas atoms, the main difference is the decay of the outer amplitudes, faster in the case of the squared inverse relationship of the original ELF. As a consequence, the IT-ELF generates a chemically "softer", i.e., more extended distribution of the localized electrons in comparison to the "harder" distribution resulting from the original ELF definition. A reference to the NH_3 and PH_3 plots in Figures 2 and 3 also reveals that the IT-ELF distinguishes lone pairs and hydrogen atoms somewhat more clearly than the original localization function. The comparison of ELF and IT-ELF of [1.1.1] and [2.2.2] propellanes in Figure 4 demonstrates the topological similarity of the two functions.

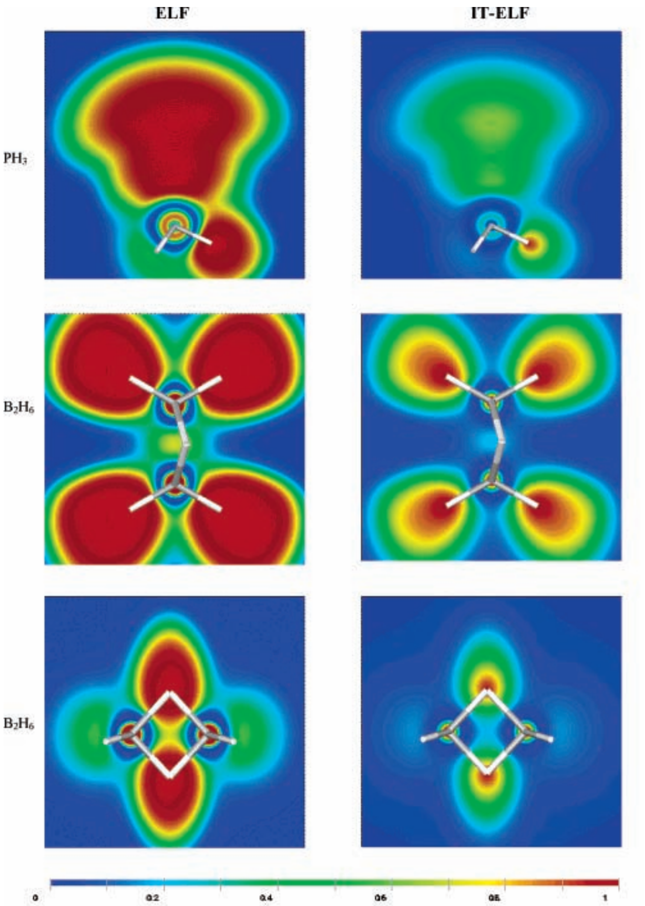

Figure 3. Plots of ELF and IT-ELF for PH_3 and B_2H_6 on selected planes. The color scale for the ELF values is given in the bottom of the figure.

All calculations have been performed with deMon2k[21] using the local VWN functional[22] in combination with the DZVP basis set.[23] The molecular structures were optimized at the respective level of theory.

5. Concluding Remarks

It has been shown that the conditional two-electron probability function, which defines the ELF,[1] in fact measures in the MO resolution the nonadditive part of the density of the Fisher information for locality (intrinsic accuracy). This interpretation gives rise to the modified IT-ELF, based upon the first-power inverse relationship, which compares favorably with the original ELF. Additional possibilities are offered by the Fisher information distance concept,[11,16] related to the Kullback−Leibler cross-entropy[17]

$$\Delta S[p|p^0] = \int p(\mathbf{r}) \ln [p(\mathbf{r})/p^0(\mathbf{r})]\, d\mathbf{r} \geq 0 \qquad (25)$$

between the (normalized) molecular (p) and promolecular (p^0)[18] probability distributions of electrons. The density of the above

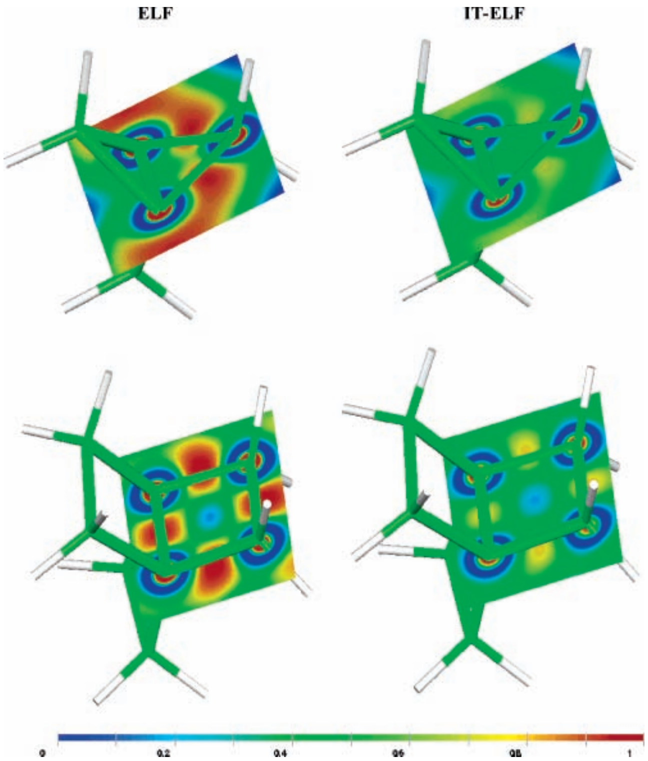

Figure 4. Plots of ELF and IT-ELF for [1.1.1] propellane (top) and [2.2.2] propellane (bottom). The color scale for the ELF values is given in the bottom of the figure.

entropy deficiency (missing information) was previously shown to also reveal all chemically important features of the molecular electronic structure,[19,20] including the localized bonding and lone electrons, orbital hybridization, and so on. Also, the density of the molecular displacement of the Shannon entropy (eq 5), relative to that of the promolecular (free-atom) distribution, $\Delta H = S[p] - S[p^0]$, has been found to provide a useful tool for diagnosing the molecular electron density in terms of chemical concepts (eq 20c). Indeed, these two information concepts are mutually related, since the Fisher information $I[p]$ is proportional to the cross-entropy (entropy deficiency) of Kullback and Leibler[17] between the probability distribution $p(x)$ and its infinitesimally shifted version $p(x + \Delta x)$.[6]

Acknowledgment. This work was financially supported by the CONACyT projects 40379-F and G34037-E.

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