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Scaling Properties of Information-Theoretic Quantities in Density Functional Reactivity Theory

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Density functional reactivity theory (DFRT) employs the electron density and its related quantities to describe reactivity properties of a molecular system. Quantities from information theory such as Shannon entropy, Fisher information, and Ghosh-Berkowitz-Parr entropy are natural descriptors within the DFRT framework. They have been previously employed to quantify electrophilicity, nucleophilicity and the steric effect. In this work, we examine their scaling properties with respect to the total number of electrons. To that end, we considered their representations in terms of both the electron density and the shape function for isolated atoms and neutral molecules. We also investigated their atomic behaviors in different molecules with three distinct partitioning schemes: Bader's zero-flux, Becke's fuzzy atom, and Hirshfeld's stockholder partitioning. Strong linear relationships of these quantities as a function of the total electron population are reported for atoms, molecules, and atoms in molecules. These relationships reveal how these information-theoretic quantities depend on the molecular environment and the electron population. These trends also indicate how these quantities can be used to explore chemical reactivity for real chemical processes.

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I. INTRODUCTION

According to density functional theory (DFT),[1] the electron density determines everything in the ground state, including reactivity properties. Density functional reactivity theory (DFRT, often called conceptual DFT) [1-7] employs the electron density of a molecular system and related quantities such as the gradient and Laplacian of the density to describe the structure, stability, and reactivity properties of a molecular system. Quantities from information theory,[8,9] like the Shannon entropy,[10] Fisher information,[11] Kullback−Leibler divergence,[12] and Ghosh-Berkowitz-Parr (GBP) entropy,[13-15] are functions of the electron density, density gradient, and related quantities, so, from the perspective of DFRT, they are natural descriptors of chemical reactivity and other properties. Earlier, we have investigated some of these quantities from various viewpoints. For example, we have shown that the Kullback−Leibler divergence,[16-21] also called information gain, can be a quantitative measure of both electrophilicity and nucleophilicity, and it determines regioselectivity simultaneously.[22-24] In addition, we showed that the Fisher information can be employed to quantify the steric effect in atoms and molecules.[25-31] This new approach of quantification has been applied to numerous chemical processes including conformational stability and chemical reactions. The Fisher information is also closely related to several popular measures of electron localization and pairing[32-40]. In this contribution, we continue our study by showing the intrinsic scaling properties of Shannon entropy, Fisher information, and GBP entropy from the viewpoint of both theoretical analysis and numerical illustrations. We study these properties at the levels of atoms, molecules, and atoms in molecules with three different ways to partition atoms: Bader's zero-flux,[41-43] Becke's fuzzy atom,[44] and Hirshfeld's stockholder [45] approaches.

II. THEORETICAL FRAMEWORK

Central quantities in the information-theoretic approach are Shannon entropy S_S and Fisher information I_F, where the former is defined as[10,14,46,47]

$$S_S = -\int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\mathbf{r} \tag{1}$$

with ρ(**r**) as the ground state electron density of an N-electron system, which satisfies the normalization condition,

$$\int \rho(\mathbf{r}) d\mathbf{r} = N. \tag{2}$$

The Fisher information is defined by

$$I_F = \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} \tag{3}$$

with ∇ρ(**r**) being the density gradient. Earlier,[48] we have proved that for atoms and molecules Eq. (3) has an equivalent expression in terms of the Laplacian of the electron density, $\nabla^2\rho$,

$$I'_F = -\int [\nabla^2 \rho(\mathbf{r})] \ln \rho(\mathbf{r}) d\mathbf{r}\,. \tag{4}$$

Shannon entropy is a measure of the spatial delocalization of the electron density, and Fisher information measures the sharpness or localization of the same. These two quantities are complementary to each other but they are not independent, as we have proved earlier[25-28]. This interdependence can be well understood by the fact that the ground-state electron density determines everything, so its functionals, like the Shannon entropy and Fisher information, should be related.

Related to these quantities is the Ghosh-Berkowitz-Parr (GBP) entropy,[13,14]

$$S_{GBP} = \int \frac{3}{2} k \rho(\mathbf{r}) \left[c + \ln \frac{t(\mathbf{r};\rho)}{t_{TF}(\mathbf{r};\rho)}\right] d\mathbf{r} \tag{5}$$

where $t(\mathbf{r},\rho)$ is the kinetic energy density, which is related to the total kinetic energy T_S via

$$\int t(\mathbf{r};\rho) d\mathbf{r} = T_S, \tag{6}$$

and $t_{TF}(\mathbf{r};\rho)$ *is* the Thomas-Fermi kinetic energy density given by,

$$t_{TF}(\mathbf{r};\rho) = c_K \rho^{5/3}(\mathbf{r}) \tag{7}$$

with k as the Boltzmann constant (set to be unity for convenience in this work), $c = \frac{5}{3} + \ln\frac{4\pi c_K}{3}$, and $c_K = \frac{3}{10}(3\pi^2)^{2/3}$. The GBP entropy originates from the transcription of the ground-state density functional theory into a local thermodynamics, which can adequately be described by a phase-space distribution function f(**r**,**p**), using the electron position **r** and momentum **p** as its two basic variables, with the conditions that it is associated with the ground state electron density $\rho(\mathbf{r})$ and kinetic energy density $t(\mathbf{r};\rho)$ through the following relationships [13,14,49-53]

$$\rho(\mathbf{r}) = \int f(\mathbf{r},\mathbf{p})d\mathbf{p}, \tag{8}$$

$$t(\mathbf{r};\rho) = \frac{1}{2}\int f(\mathbf{r},\mathbf{p})p^2 d\mathbf{p}. \tag{9}$$

This GBP entropy was found to be efficient in describing chemical bond formation, and its correlation with Shannon entropy and Fisher information was recently disclosed by our numerical results.[11] The specific form of the local kinetic energy $t(\mathbf{r};\rho)$ we used in our previous work is [14]

$$t(\mathbf{r};\rho) = \sum_i \frac{1}{8}\frac{\nabla\rho_i\cdot\nabla\rho_i}{\rho_i}, \tag{10}$$

where ρ_i are the orbital densities. As has been recently shown, the results one obtains can differ significantly depending on the choice of local kinetic energy[54,55]. Therefore, in this work, we consider the choice employed in the original work of Ghosh, Berkowitz, and Parr, which has a better asymptotic behavior,[54]

$$t(\mathbf{r};\rho) = \sum_i \frac{1}{8}\frac{\nabla\rho_i\cdot\nabla\rho_i}{\rho_i} - \frac{1}{8}\nabla^2\rho \tag{11}$$

The GBP entropy obtained from this alternative local kinetic energy is denoted by S'_{GBP}. We notice that the asymptotically correct form, with $\frac{1}{4}\nabla^2\rho$, cannot be used due to negative values of the local kinetic energy entering into the logarithm.

Scaling properties of energy density functionals in DFT have been well studied in the literature[56-62]. There are two distinct categories of scaling, one via scaling the coordinate variable and the other through scaling the electron density. One can also scale both coordinate and density variables at the same time, leading to the so-called hybrid scaling. Here, we only consider the density scaling, which is related to a quantity's extensive/intensive nature. A density functional $Q[\rho]$ is homogeneous of degree n with respect to density scaling if the functional satisfies the following condition, [56,57]

$$Q[\zeta\rho]=\zeta^n Q[\rho]. \tag{12}$$

For example, Fisher information is homogeneous of degree one in density scaling because if one scales density by ζ times, I_F is amplified by ζ times as well, that is, $I_F[\zeta\rho] = \zeta I_F[\rho]$. However, Shannon entropy is not a homogeneous functional in density scaling, because no such condition is satisfied when the density is scaled by ζ times. This is also true for the GBP entropy functional, which is not known to satisfy any scaling relations.

A similar scaling related to the system size is through the shape function σ(**r**),[1,63-66] which is related to the electron density ρ(**r**) and the total number of electrons N through the following definition,

$$\rho(\boldsymbol{r}) = N\,\sigma(\boldsymbol{r}) \tag{13}$$

with the normalization condition

$$\int \sigma(\boldsymbol{r})d\boldsymbol{r} = 1. \tag{14}$$

With this, we can define the corresponding Shannon entropy, Fisher information, and GBP entropy in terms of the shape function, viz., S_σ, I_σ, and S_{GBP}^{σ}, respectively,[67-69]

$$S_\sigma = -\int \sigma(\mathbf{r})\ln\sigma(\mathbf{r})d\mathbf{r} \tag{15}$$

$$I_\sigma = \int \frac{|\nabla\sigma(\mathbf{r})|^2}{\sigma(\mathbf{r})}d\mathbf{r}\,, \tag{16}$$

$$I'_\sigma = -\int [\nabla^2\sigma(\mathbf{r})]\ln\sigma(\mathbf{r})d\mathbf{r} \tag{17}$$

and

$$S_{GBP}^{\sigma} = \int \frac{3}{2}k\sigma(\mathbf{r})\left[c + \ln\frac{t(\mathbf{r};\sigma)}{t_{TF}(\mathbf{r};\sigma)}\right]d\mathbf{r} \tag{18}$$

We can readily prove that S_S and S_σ, and I_F and I_σ are inter-related by the following analytical formulas,

$$S_\sigma = \frac{S_S}{N} - N\ln N \tag{19}$$

$$I_\sigma = \frac{I_F}{N} \tag{20}$$

and

$$I'_\sigma = \frac{I'_F}{N} \tag{21}$$

For the GBP entropy, since the density-scaling and *N*-scaling properties for the kinetic energy density $t(\mathbf{r},\rho)$ are unknown, it is unclear whether there exists any explicit relationship between the two quantities, S^{σ}_{GBP} and S_{GBP}. However, since the first term on the right-hand side of Eq. (5) is linear in $\rho(\mathbf{r})$ and we know that $t_{TF}(\mathbf{r};\rho)$ is the leading-order term in the local kinetic energy $t(\mathbf{r};\rho)$, especially in the conjointness conjecture,[70-72] we hypothesize that S_{GBP} is approximately homogeneous of degree one in *N*. That is,

$$S_{GBP} \;\approx\; N\; S^{\sigma}_{GBP}\,. \tag{22}$$

An analogous result should hold for S'_{GBP}. In this work we will examine the scaling properties of these information-theoretic quantities and verify their relationships for a set of atomic and molecular systems. We will also investigate these properties at the atoms-in-molecules level by using Bader's zero-flux, Becke's fuzzy atom, and Hirshfeld's stockholder approaches to partition molecules into atoms. In particular, we are interested in the scaling behavior of these information-theoretic quantities with respect to the change of the total number of electrons. For example, we would like to know whether S_σ and I_σ still depend on *N*. Another question is whether Eq. (22) is valid. We are also interested in demonstrating the equivalence between Eqs. (3) and (4), and Eqs. (20) and (21), at the whole-molecule and atom-in-molecule level. These scaling properties will reveal general changing patterns of these information-theoretic quantities in different molecular environments as a function of the electron population. These patterns not only provide insight into the meaning of these quantities, but also suggest how these quantities can be used to elucidate real chemical processes.

III. COMPUTATIONAL DETAILS

All electronic wave functions were obtained from the Gaussian 09 package, version D01.[73] For all atoms and molecules investigated in this work, the B3LYP hybrid functional and Pople's 6-311++G(d,p) basis set were employed.[74-78] For atoms, we considered neutral species from H to Kr. For molecules, a total of 42 neutral systems were considered, for which total molecular values of the Shannon entropy, two forms of Fisher information, and two forms of GBP entropy were calculated. These same molecules were systematically investigated in our previous work.[14] All molecules were fully optimized. The tight self-consistent field convergence criterion and ultrafine integration grids were employed. The information-theoretical quantities were obtained from the Multiwfn 3.2 package [79] developed by one of us, whose reliability and applicability have extensively been tested before. Atomic units were used throughout.

Besides neutral atoms and molecules, we also examine the scaling properties of information-theoretic quantities for atoms in molecules. To that end, we employ three schemes to perform the atomic partition, Becke's fuzzy atom approach, Bader's zero-flux atoms-in-molecules (AIM) criterion, and Hirshfeld's stockholder approach. The total population N of the system is the summation of electron density in each atomic contribution, N_A,

$$N = \sum_A N_A = \sum_A \int_{\Omega_A} \rho(\mathbf{r}) d\mathbf{r} \tag{23}$$

and the quantities in Eqs. (1), (3)-(5) can be rewritten as

$$S_S = -\sum_A \int_{\Omega_A} \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\mathbf{r} \tag{24}$$

$$I_F = \sum_A \int_{\Omega_A} \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} \tag{25}$$

$$I'_F = -\sum_A \int_{\Omega_A} \nabla^2\rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\mathbf{r} \tag{26}$$

$$S_{GBP} = -\sum_A \int_{\Omega_A} \frac{3}{2} k\rho(\mathbf{r}) \left[c + \ln \frac{t(\mathbf{r};\rho)}{t_{TF}(\mathbf{r};\rho)} \right] d\mathbf{r} \tag{27}$$

where Ω_A is the atomic basin of atom A in a molecule. The counterpart in terms of the shape function can be derived similarly. Alternatively, they can be directly derived from Eqs. (19)-(21). Notice that there are two choices of the local kinetic energy density, Eq. (10) and (11), yielding two GBP entropies, S_{GBP} and

S'_{GBP}. These formalisms have been implemented in the Multiwfn program as well. The basin integration employs an improved near-grid algorithm, which is simpler and more efficient to integrate atomic basins than the uniform integration grid. A detailed description of the implementation and quality control procedures is available elsewhere. It is worth noting that the construction of Becke's fuzzy atoms depends on two factors, the sharpness parameter and atomic radii. In present work, the sharpness parameter was selected to be 3 and modified CSD radii were employed; these choices have been found to be optimal for Becke's fuzzy atom partitioning.[80]

IV. RESULTS AND DISCUSSION

Table 1 shows the numerical results of information-theoretic quantities for 36 neutral atoms from hydrogen to krypton. The values of Shannon entropy and two forms of the Fisher information using the shape function $\sigma(\mathbf{r})$ were obtained from Eqs. (19) - (21), respectively. As can be seen from the Table, I_F, I_σ, I'_F, I'_σ, S_{GBP} and S'_{GBP} are positive quantities, but the Shannon entropies, S_S and S_σ, can be either positive or negative. S'_{GBP} is always a little smaller in magnitude than S_{GBP}. These two forms of GBP entropies are very much correlated with a correlation coefficient better than 0.999. It is also observed that I_F and I'_F values are identical to each other, confirming the equivalence that was previously mathematically proved. I_σ and I_σ' are also identical. As the total number of electrons increases, I_F, I_σ, I'_F, I'_σ, S_{GBP} and S'_{GBP} monotonically increase, but S_S and S_σ decrease (with a few exceptions for light atoms). This pattern suggests that some correlation with N might be possible. Figure 1 shows the quality of the correlation between S_σ, I_σ, and S_{GBP}, and the total number of electrons N. All of these regressions have correlation coefficient, R^2, larger than 0.99. We find from Figs. 1a and 1b that the Shannon entropy and Fisher information with the shape function $\sigma(\mathbf{r})$ are nearly linearly proportional to N,

$$S_\sigma = c_1 N + b_1, \tag{28}$$

$$I_\sigma = c_2 N + b_2. \tag{29}$$

This result shows that, at least for the atomic systems considered here, we have $S_S \approx c_1 N^2 + N^2 \ln N$, and $I_F \approx c_2 N^2$. That is, S_S and I_F are quadratic functions of N. This is indeed what we found. If we fit I_F and ($S_S - N^2 \ln N$) with respect to N in a quadratic form, their correlation coefficients are better than 0.99. Figure 1c indicates that the GBP entropy is approximately homogeneous of degree one in N. That was what we had anticipated from Eq. (22). Because the GBP entropy S_{GBP} (also S'_{GBP}), and Shannon entropy S_σ and Fisher information I_σ are all strongly correlated to N, it is unsurprising that we observed that they are also strongly correlated with each other.

Table 2 exhibits the numerical values of the eight information-theoretic quantities, S_S, S_σ, I_F, I_σ, I'_F, I'_σ, S_{GBP}, and S'_{GBP}, for 42 molecular systems. The data in the Table were sorted according to the number of electrons in the molecules. As can be seen from the Table, S_S, I_F, I_σ, I'_σ, I'_F, S_{GBP}, and S'_{GBP} are always positive for these molecules, while S_σ is always negative. As N increases, we found that S_σ decreases and S_{GBP} increases, both monotonically. For example, the smallest value of S_S is for $F_2C{=}CF_2$ (1,1,2,2-tetrafluoroethene) with N=48, whereas for I_σ it is the largest for the same molecule. Again, we find that S'_{GBP} is always a little smaller than S_{GBP} in magnitude, and these two GBP quantities are strongly correlated, with R^2 better than 0.999. For molecular systems with the same number of electrons, for example, $FHC{=}CH_2$ and $MeHC{=}CH_2$, the former has a larger S_{GBP} (164.23 a.u. vs. 164.16 a.u.), but the latter possesses a larger S'_{GBP} (156.77 a.u. vs. 156.66. a.u.). These small but subtle differences might reflect the intrinsic difference between these two quantities for describing chemical reactivity and molecular properties. The reason that for isoelectronic systems, GBP entropy is similar but Fisher information is very different is because Fisher information includes electron gradient information and is sensitive to changes near the nuclei.

To illustrate the correlations for molecules, Fig. 2 displays three strong correlations of these quantities with respect to the total number of electrons in molecules, N. Just as for neutral atoms, S_σ and S_{GBP} are strong linear functions of N, with the correlation coefficient equal to 0.998 and 1.000, respectively. (Cf. Figs. 2a and 2c.) These strong correlations confirm the validity of Eqs. (22) and (28).

Unlike Fig. 1, no statistically significant correlation between I_σ and N was observed. Instead, as shown in Fig. 2b, a strong linear correlation between the Fisher information, I_F, and N was disclosed, with R^2=0.872. Recall that Fisher information has been proposed to serve as a quantitative measure of the steric effect, the different behavior of this quantity in atoms and molecules will enable us to discern different roles of the steric effect in different environment during the process of chemical reactions.

Now, let us examine the behavior of these information-theoretic quantities from the viewpoint of atoms in molecules by using Bader's AIM, Becke's fuzzy atom, and Hirshfeld's stockholder partition schemes, respectively. Shown in Fig. 3 are AIM results for these quantities for carbon atoms, where three scaling properties with respect to the total electron population on carbon atoms, N_C, obtained from 192 carbon atoms in 42 molecules studied in this work are exhibited. From the x-axis of the Figure, we can see that the total population obtained from the AIM approach for the carbon element of these systems ranges from 4.5 to 6.2, suggesting that its AIM charge varies from +1.5 to -0.2, a rather large span of charge variations. The three strong linear correlations in Figs. 3a-3c are for S_σ, I_σ, and S_{GBP}, respectively. Figures 3a and 3c are similar to Figs. 1 and 2, showing that even at the atoms-in-molecules level, S_σ and S_{GBP} are still linear functions of the electron population, same as neutral atomic and whole molecular levels. This result supports, once again, the validity of Eqs. (22) and (28). Figure 3b reveals the strong linear correlation between Fisher information with the shape function, I_σ, and the AIM atomic population on carbon atoms, N_{C}. It is similar to the result obtained from neutral atoms, shown in Fig. 1b. However, the slopes of these two lines have opposite signs, indicating that even though both are for atoms, neutral atoms and atoms in molecules have different behaviors for the scaling property of the I_σ function. In addition, we observed strong correlation between I_{F} and I'_{F}, and between I_σ and I'_σ for carbon atoms in molecules (plots not shown). For example, the correlation coefficient between I_{F} and I'_{F}, R^2 is equal to 1.000, indicating again that the two forms of the Fisher information are equivalent.

Figure 4 displays the scaling result for hydrogen atoms partitioned with the AIM approach for the 42 molecules studied in this work. Instead of a strong correlation between S_σ vs. N_{H} with a negative slope

(Fig. 3a), shown in Fig. 4a is the strong linear relationship between S_S and N_H with a positive slope. This result substantially differs from that of the carbon atoms. On the other hand, Figs. 4b and 4c show the two correlations, one between I_σ with N_H, and the other between S_{GBP} and N_H, which are similar to Figs. 3b and 3c for carbon atoms. This result shows that for different atoms, both I_σ and S_{GBP} scale linearly with respect to the total number of electrons. Since Fisher information was proposed to serve as a quantitative descriptor of the steric effect,[25-31,86-94] these linear strong correlations from Fisher information with respect to the electron population could provide insights for the source of the steric effect as well as its changing patterns in molecules.

Do the above scaling results for atoms in molecules depend on the partition scheme? To answer this question, besides the Bader's zero-flux AIM partition results shown above, we also calculated the atomic values of molecules for above information-theoretic quantities using both Becke's fuzzy atom and Hirshfeld's stockholder partitions. Figure 5 shows their scaling results for both carbon (Figs. 5a-5c) and hydrogen (Figs. 5d-5f) atoms from the Becke's partition approach. As can be seen from the six plots in Fig. 5, these linear correlations are closely related to those in Figs. 3 and 4 from the AIM approach. That is, for carbon atoms in molecules, using Becke's scheme, following three linear scaling relationships, i.e., S_σ, I_σ, and S_{GBP}, with respect to the electron populations on the carbon atom, N_C, are still valid, and for hydrogen atoms, they are S_S, I_σ, and S_{GBP}, which are the same as the AIM results. These results demonstrate that scaling properties for atoms in molecules do not significantly depend on the partition method employed.

In Fig. 6, we plot the same relationships for carbon and hydrogen atoms in molecules partitioned with Hirshfeld's stockholder partition approach. The only difference is Fig. 6c, where we plotted S'_{GBP} instead of $S_{GBP.}$ As can be seen from the Figure, the results are similar in most cases to those obtained using AIM and Becke's methods. The only exception is S'_{GBP} (Fig. 6c) for carbon atoms. Using the Hirshfeld partition, the strong linear correlation between S_{GBP} and N_C that we have seen previously from AIM and Becke's partition methods is no longer valid. However, if we employ the local kinetic energy density with a better asymptotic behavior, the strong correlation with the total electron population is then preserved. This different behavior of S_{GBP} and S'_{GBP} suggests that using the latter is a more reasonable and better choice. The poor scaling behavior of S_{GBP} with the Hirshfeld partition approach might be because the weighting function from the Hirshfeld partition is always much more diffuse than other two methods due to the long tails of the free-state reference density, making the asymptotic dependence of the local kinetic energy relatively important. We have employed a large number of mesh points for the integration (500 radial and 5810 angular points), so any poor correlations for atom-in-molecule quantities are probably not numerical artifacts.

To summarize all possible correlations of these information-theoretic quantities with the total population of electrons on atoms, molecules, and atoms in molecules, Table 3 reports the correlation coefficients R^2 and root-mean-square deviation (RMSD) values. It shows that there are many strong linear correlations of these quantities with respect to the number of electrons. As can also be seen from the Table, for molecular systems there are good correlations between the number of electrons and S_σ, I_{F}, I'_{F}, S_{GBP}, and S'_{GBP}. For other quantities, especially $\mathrm{S_S}$, I_σ, or I'_σ, no correlation is apparent. For atoms in molecules, there are many more successful correlations, perhaps because the range of atom-in-molecule populations is relatively small. Of the descriptors we consider, we found robust correlations for $\mathrm{S_S}$, I_σ, and $\mathrm{S'_{GBP}}$. The first two quantities, interestingly enough, were among the least useful quantities for examining molecules as a whole. Also notice that for S_{GBP}, and S'_{GBP}, the latter always has no worse, and sometimes much better, correlations than the former, indicating that employing the local kinetic energy expression with a better asymptotic behavior is essential to ensure better scaling behaviors of the GBP entropy.

In addition, to demonstrate the equivalence of the two Fisher information, Eqs. (3) and (4), we tabulate their molecular and atoms-in-molecules values using the three partition schemes for the aniline molecule in Table 4. We can see from the Table that their total molecular values are always the same, numerically confirming that these two quantities are identical. This equivalence at the molecular level does not depend on the choice of partition schemes. On the other hand, their atomic values are significantly different except when Bader's AIM partitioning is used because the two expressions differ by a term involving the Laplacian of the electron density. Different partition schemes give totally different atomic values as well, with greater variability at the atomic level than the molecular level.

Do these scaling properties help us understand physiochemical properties of molecular systems and chemical processes? Absolutely! These scaling properties of information-theoretic quantities reveal the general pattern of their changes in different molecular environments. The total electron population of atoms in molecules is simply the indication of their charge in the system. Also, recall that Hirshfeld charge can be used as a quantitative measurement of both electrophilicity and nucleophilicity, and it determines regioselectivity simultaneously [22,23,81]. In addition, the Fisher information has been shown to quantify the steric effect for atoms and molecules. The patterns unveiled in this work help us identify rules and principles in chemical processes from these quantities, which have direct physiochemical meanings and consequences. For example, we now know that Shannon entropy behaves differently for different atoms in molecules, and both Fisher information with shape function and Ghosh-Berkowitz-Parr entropy are linear functions of the atomic charge. Do these relationships play a role in real chemical processes? Are there any other patterns to be unveiled? Work on answering these questions and applying these ideas to real chemical processes is underway.

As a first step along these lines, let us make a link to conceptual density functional theory by taking the partial derivative of Eqs. (1) and (3) with respect to the total number of electrons N while holding the external potential $\upsilon(\mathbf{r})$ from the atomic nuclei fixed,

$$\left(\frac{\partial S_S}{\partial N}\right)_{\upsilon} = -\int \left(\ln \rho(\mathbf{r}) + 1\right) f(\mathbf{r}) d\mathbf{r} \tag{30}$$

and

$$\left(\frac{\partial I_F}{\partial N}\right)_{\upsilon} = \int \left\{ \frac{2\nabla\rho(r)\cdot\nabla f(r)}{\rho(\mathbf{r})} - \frac{f(\mathbf{r})\left|\nabla\rho(\mathbf{r})\right|^2}{\rho^2(\mathbf{r})} \right\} d\mathbf{r} \tag{31}$$

where $f(\mathbf{r})$ is the Fukui function defined as[82-85]

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\upsilon} . \qquad (32)$$

The integrands in both Eq. (30) and Eq. (31) tend to be small (even negative) where the Fukui function is large, suggesting that highly regioselective molecules (where the Fukui function is localized) will have small values for these quantities. Of course, the dominant trend for I_F (less so for S_S) is imposed by the strong correlation between I_F and the total number of electrons (so that Eq. (31) is nearly constant). At the atoms-in-molecules level, expressions like Eq. (30) should be small for reactive atoms. Information-theoretic quantities, then, especially when evaluated at the atoms-in-molecules level, are expected to provide interesting chemical information.

V. CONCLUSIONS

As a continuation of our efforts to better understand the properties of information-theoretic quantities such as Shannon entropy, Fisher information, and Ghosh-Berkowitz-Parr entropy, in this work, we have examined their scaling properties with respect to the total electron population. We considered the representation of these quantities with both electron density and shape function for 36 isolated atoms and 42 neutral molecules. We also investigated their atomic behavior in molecules using three popular partitioning schemes from the literature: Bader's zero-flux, Becke's fuzzy atom, and Hirshfeld's stockholder partitionings. Numerous strong linear relationships of these quantities as a function of the total electron population have been unveiled for atoms, molecules and atoms in molecules. We found that Shannon entropy and Fisher information in terms of the shape function strongly correlate with the total electron population for atoms in molecules. The Ghosh-Berkowitz-Parr entropy with the electron density is also linearly proportional to the total number of electrons in atoms and molecules as a whole and usually (but not always) for atoms in molecules. For different atoms in the same molecule, we observed that Shannon entropy behaves differently. We also found that results for atoms in molecules are usually (but not always) insensitive to the partitioning scheme. Finally, we confirmed the equivalence of the two forms of the Fisher information we previously proposed.

The scaling properties we reveal in this work disclose general changing patterns of these information-theoretic quantities in different molecular environments as a function of the electron charge. As important quantities in density functional reactivity theory, with links to other important quantities (like the Fukui function), information-based descriptors provide are a useful tool for understanding and predicting chemical reactivity and other molecular processes. We are in the process of applying these quantities and their properties to real chemical problems, whose results will be reported elsewhere.

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Table 1. Information-theoretic quantities for 36 neutral atoms. Atomic units.

Atom	N	S_S	S_σ	I_F	I_σ	I'_F	I'_σ	S_{GBP}	S'_{GBP}
H	1	4.21	4.21	3.97	3.97	3.97	3.97	7.80	7.41
He	2	4.10	0.66	22.90	11.45	22.90	11.45	14.42	13.42
Li	3	7.69	-0.73	57.39	19.13	57.36	19.12	22.19	21.06
Be	4	8.85	-3.33	109.10	27.28	109.10	27.27	28.82	27.49
B	5	8.83	-6.28	175.48	35.10	175.47	35.09	36.07	34.34
C	6	7.85	-9.44	255.96	42.66	255.96	42.66	43.08	40.91
N	7	6.14	-12.74	349.61	49.94	349.61	49.94	49.95	47.30
O	8	3.91	-16.15	460.35	57.54	460.35	57.54	56.37	53.35
F	9	1.11	-19.65	585.14	65.02	585.14	65.02	62.72	59.29
Ne	10	-2.18	-23.24	723.32	72.33	723.32	72.33	69.02	65.15
Na	11	-0.88	-26.46	881.74	80.16	881.70	80.15	76.85	72.54
Mg	12	-1.25	-29.92	1058.09	88.17	1058.07	88.17	83.64	78.92
Al	13	-1.84	-33.49	1251.46	96.27	1251.44	96.26	90.56	85.86
Si	14	-3.26	-37.18	1460.74	104.34	1460.74	104.34	97.33	92.50
P	15	-5.22	-40.97	1686.21	112.41	1686.21	112.41	104.01	98.94
S	16	-7.61	-44.84	1928.83	120.55	1928.83	120.55	110.22	105.02
Cl	17	-10.36	-48.77	2187.77	128.69	2187.77	128.69	116.41	111.01
Ar	18	-13.53	-52.78	2463.43	136.86	2463.43	136.86	122.47	116.90
K	19	-12.65	-56.61	2756.13	145.06	2756.01	145.05	130.41	124.36
Ca	20	-13.10	-60.57	3067.36	153.37	3067.29	153.36	137.48	131.02
Sc	21	-16.11	-64.70	3393.39	161.59	3393.34	161.59	144.65	138.05
Ti	22	-19.52	-68.89	3734.41	169.75	3734.38	169.74	151.52	144.72
V	23	-23.28	-73.13	4090.76	177.86	4090.73	177.86	158.30	151.26
Cr	24	-28.83	-77.47	4455.67	185.65	4455.64	185.65	165.35	158.29
Mn	25	-31.48	-81.73	4846.89	193.88	4846.87	193.87	171.79	164.13
Fe	26	-37.54	-86.15	5248.62	201.87	5248.61	201.87	178.24	170.80
Co	27	-42.16	-90.55	5668.61	209.95	5668.60	209.95	184.62	176.95
Ni	28	-46.92	-94.98	6102.6	217.95	6102.59	217.95	191.04	183.09
Cu	29	-51.90	-99.44	6551.43	225.91	6551.43	225.91	197.39	189.17
Zn	30	-55.22	-103.88	7024.07	234.14	7024.06	234.14	203.69	194.80
Ga	31	-57.72	-108.32	7510.26	242.27	7510.23	242.27	210.19	201.14
Ge	32	-60.77	-112.80	8015.02	250.47	8015.01	250.47	216.65	207.37
As	33	-64.14	-117.33	8536.55	258.68	8536.55	258.68	223.01	213.51
Se	34	-67.70	-121.89	9075.94	266.94	9075.93	266.94	229.05	219.36
Br	35	-71.54	-126.48	9629.24	275.12	9629.24	275.12	235.05	225.18
Kr	36	-75.59	-131.11	10205.00	283.47	10205.00	283.47	240.99	230.96

Table 2. Information-theoretic quantities for 42 molecular systems. Atomic units.

Molecule	N	S_S	S_σ	I_F	I_σ	I'_F	I'_σ	S_{GBP}	S'_{GBP}
$CH_2=CH_2$	16	21.86	-43.00	507.98	31.75	507.98	31.75	109.16	104.74
$FHC=CH_2$	24	18.50	-75.50	1082.22	45.09	1082.22	45.09	164.23	156.66
$MeHC=CH_2$	24	32.02	-74.94	759.74	31.66	759.74	31.66	163.16	156.77
$CH_2=CH(CN)$	28	27.95	-92.30	1092.74	39.03	1092.74	39.03	191.74	183.11
$CH_2=CH(CHO)$	30	28.48	-101.09	1205.85	40.19	1205.85	40.19	204.96	195.95
Butadiene	30	37.09	-100.80	1005.62	33.52	1005.62	33.52	204.22	195.92
$F_2C=CH_2$	32	15.08	-110.43	1655.77	51.74	1655.77	51.74	219.24	208.49
$FHC=CHF$	32	15.15	-110.43	1656.65	51.77	1656.65	51.77	219.29	208.62
trans-MeHC=CHMe	32	42.16	-109.59	1011.54	31.61	1011.54	31.61	217.16	208.81
cis-MeHC=CHMe	32	42.12	-109.59	1011.32	31.60	1011.32	31.60	217.12	208.77
$Me_2C=CH_2$	32	42.14	-109.59	1011.33	31.60	1011.33	31.60	217.11	208.74
$(CH_3O)CH=CH_2$	32	33.64	-109.85	1210.40	37.83	1210.40	37.83	217.99	208.83
Cyclopentadiene	36	40.99	-127.87	1247.88	34.66	1247.88	34.66	244.39	234.59
Pyrrole	36	36.63	-127.99	1336.36	37.12	1336.36	37.12	244.73	234.45
2-Methyl-butadiene	38	47.15	-136.99	1257.07	33.08	1257.07	33.08	258.12	247.86
1-Methyl-butadiene	38	47.22	-136.99	1257.29	33.09	1257.29	33.09	258.19	247.93
$CH_2CH=CHOBH_3$	38	43.07	-137.09	1383.89	36.42	1383.89	36.42	259.20	248.28
$CH_2=CH(NO_2)$	38	26.23	-137.54	1747.77	45.99	1747.77	45.99	259.88	247.91
$F_2C=CHF$	40	11.76	-147.26	2230.3	55.76	2230.29	55.76	274.32	260.48
$Me_2C=CHMe$	40	52.23	-146.25	1262.88	31.57	1262.88	31.57	271.06	260.73
$(Me)_2NCH=CH_2$	40	48.16	-146.35	1352.86	33.82	1352.86	33.82	271.44	260.74
$EtOCH=CH_2$	40	43.84	-146.46	1462.27	36.56	1462.27	36.56	271.98	260.84
$(CN)_2C=CH_2$	40	34.10	-146.70	1677.67	41.94	1677.67	41.94	274.35	261.51
Benzene	42	45.62	-155.90	1493.23	35.55	1493.22	35.55	285.21	273.59
$CH_3COOCH=CH_2$	46	40.02	-175.25	1907.55	41.47	1907.55	41.47	313.61	299.85
$CH_2=C(NO_2)(NH_2)$	46	32.03	-175.42	2088.19	45.40	2088.19	45.40	314.23	299.77
$F_2C=CF_2$	48	8.39	-185.64	2803.95	58.42	2803.94	58.42	329.35	312.36
$Me_2C=CMe_2$	48	62.26	-184.52	1514.31	31.55	1514.31	31.55	324.94	312.67
Maleic anhydride	50	30.29	-195.00	2344.33	46.89	2344.33	46.89	341.72	325.65
C_6H_5-Me	50	55.75	-194.49	1744.84	34.90	1744.84	34.90	339.17	325.58
C_6H_5-F	50	42.24	-194.76	2067.27	41.35	2067.27	41.35	340.28	325.50
C_6H_5-NH_2	50	51.52	-194.57	1834.36	36.69	1834.36	36.69	339.63	325.53
C_6H_5-OH	50	47.05	-194.66	1942.83	38.86	1942.83	38.86	340.04	325.54
C_6H_5-CN	54	51.70	-214.45	2077.92	38.48	2077.92	38.48	367.78	351.94
C_6H_5-HCO	56	52.18	-224.49	2190.81	39.12	2190.81	39.12	380.96	364.77
$(EtO)_2C=CH_2$	64	65.59	-265.14	2415.68	37.75	2415.68	37.74	434.62	416.76
$(CN)_2C=C(CN)_2$	64	46.42	-265.44	2847.48	44.49	2847.48	44.49	439.60	418.30
C_6H_5-NO_2	64	49.90	-265.39	2732.57	42.70	2732.57	42.70	435.86	416.70
C_6H_5-CF_3	74	45.74	-317.88	3468.00	46.86	3468.00	46.86	504.22	481.17
C_6H_5-$N(Me)_3$	74	80.98	-317.41	2594.49	35.06	2594.49	35.06	500.69	481.51
2,3-Diacetoxy-1,3-butadiene	90	73.28	-404.17	3804.01	42.27	3804.01	42.27	612.98	586.03
$(C_2H_5COO)_2C=CH_2$	92	78.58	-415.15	3810.73	41.42	3810.73	41.42	626.05	598.96

Table 3. Correlation coefficients and root-mean-square deviation (RMSD) values of all least square fitts with respect to the total number of electron populations for the information-theoretic quantities presented in this work at atomic, molecular and atoms-in-molecules levels with AIM, Becke, and Hirshfeld partitionings.

R^2			C			H		
	atomic	molecular	AIM	Becke	Hirshfeld	AIM	Becke	Hirshfeld
S_S	0.9177	0.5118	0.9590	0.9255	0.7195	0.9938	0.9686	0.8905
S_σ	0.9953	0.9979	0.9979	0.9957	0.9800	0.9026	0.3132	0.0242
I_F	0.9367	0.8722	0.6349	0.0069	0.5690	0.8385	0.3022	0.2982
I_σ	0.9998	0.0425	0.9932	0.9885	0.9714	0.8869	0.7848	0.8011
I'_F	0.9367	0.8722	0.6361	0.1273	0.7051	0.8394	0.0008	0.5454
I'_σ	0.9998	0.0425	0.9932	0.9746	0.9397	0.8877	0.2328	0.6954
S_{GBP}	0.9998	0.9999	0.9957	0.9810	0.4428	0.9992	0.9628	0.9085
S'_{GBP}	0.9998	0.9999	0.9984	0.9937	0.8856	0.9997	0.9888	0.9758

RMSD			C			H		
	atomic	molecular	AIM	Becke	Hirshfeld	AIM	Becke	Hirshfeld
S_S	7.6075	11.4166	0.1959	0.1730	0.1518	0.0247	0.0222	0.0305
S_σ	2.8032	3.7214	0.0432	0.0315	0.0251	0.0257	0.0278	0.0307
I_F	785.6621	274.6937	0.4227	0.6350	0.6214	0.0867	0.0553	0.0640
I_σ	1.0539	6.5881	0.2742	0.1395	0.1088	0.0765	0.0693	0.0753
I'_F	785.6714	274.6938	0.4227	1.0929	1.2113	0.0865	0.2277	0.1901
I'_σ	1.0539	6.5882	0.2741	0.2228	0.2106	0.0760	0.3015	0.2227
S_{GBP}	1.0827	1.2215	0.1638	0.1559	0.2153	0.0171	0.0402	0.0383
S'_{GBP}	0.9872	0.3389	0.0960	0.0913	0.1183	0.0108	0.0211	0.0210

Table 4. The total and atom-in-molecule values of the two representation of the Fisher information under the three partitioning schemes, AIM, Becke, and Hirshfeld, for the aniline molecule. Atomic units.

	AIM Partition		Becke Partition		Hirshfeld Partition	
	I_F	I'_F	I_F	I'_F	I_F	I'_F
C1	243.493	243.492	244.643	246.189	244.636	245.524
C2	244.310	244.316	244.971	245.351	244.393	244.143
C3	244.540	244.545	245.240	245.762	244.631	244.425
C4	244.381	244.378	245.086	245.473	244.474	244.178
C5	244.540	244.545	245.240	245.762	244.631	244.425
C6	244.310	244.316	244.971	245.351	244.393	244.143
H1	4.274	4.271	3.560	2.970	4.207	4.456
H2	4.319	4.316	3.631	3.144	4.252	4.504
H3	4.306	4.303	3.628	3.167	4.249	4.507
H4	4.319	4.316	3.631	3.144	4.252	4.504
H5	4.274	4.271	3.560	2.970	4.207	4.456
N1	340.674	340.679	339.084	337.611	337.147	333.946
H6	3.309	3.305	3.556	3.733	4.444	5.574
H7	3.309	3.306	3.556	3.733	4.444	5.574
Total	1834.359	1834.359	1834.359	1834.358	1834.359	1834.357

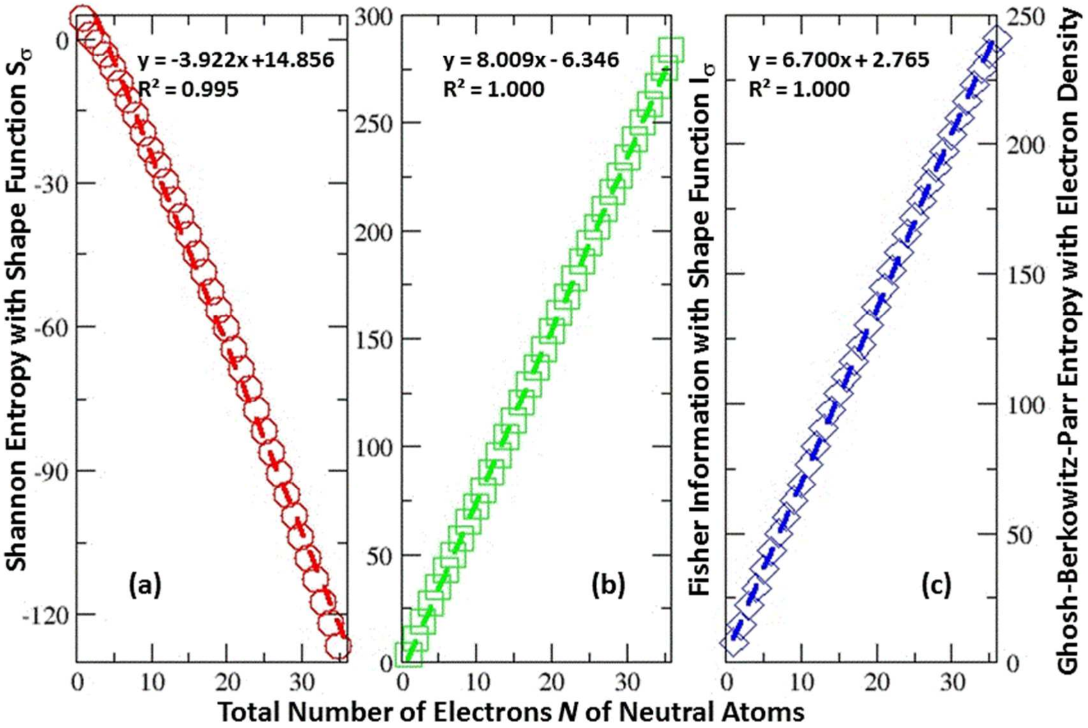


Figure 1. Scaling properties of (a) Shannon entropy S_σ, (b) Fisher information I_σ and (c) Ghosh-Berkowitz-Parr entropy S_{GBP} with respect to the total number of electrons N for 36 neutral atoms from H to Kr.

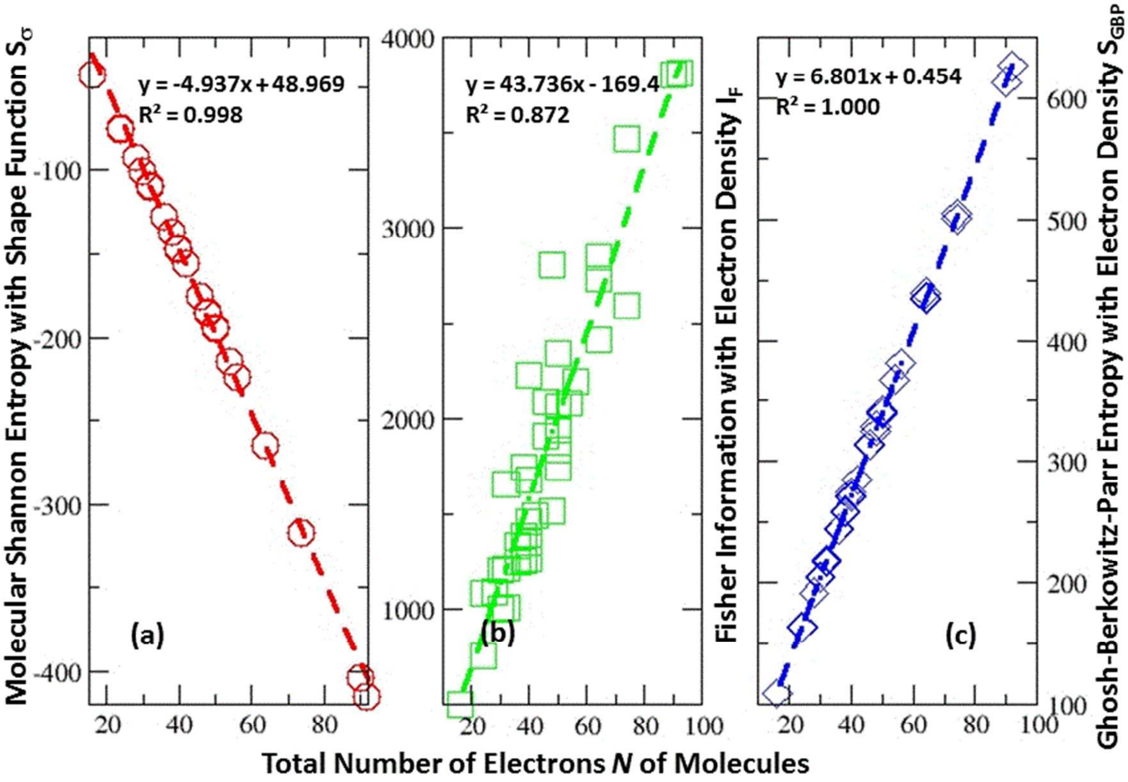


Figure 2. Scaling properties of (a) Shannon entropy S_σ, (b) Fisher information I_F, and (c) Ghosh-Berkowitz-Parr entropy S_{GBP} with respect to the total number of electrons N for a total of 42 molecular systems.

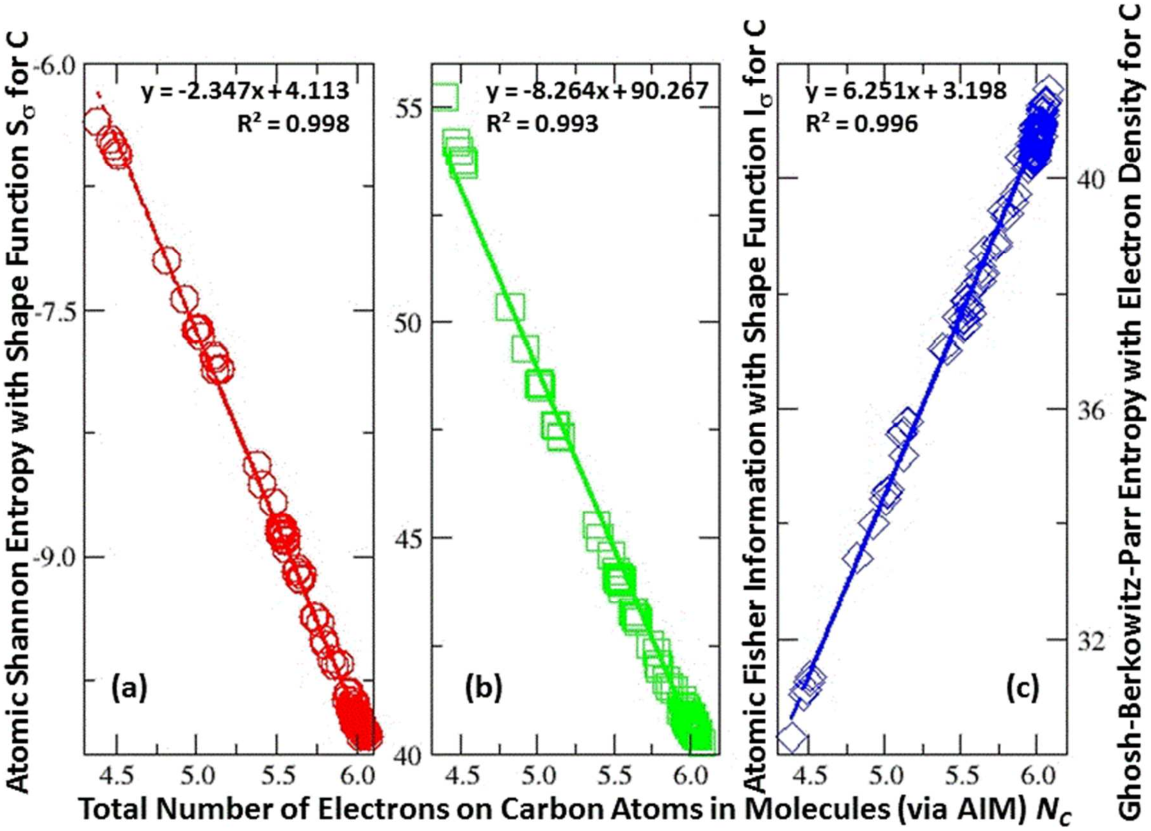


Figure 3. Scaling properties of (a) Shannon entropy S_σ, (b) Fisher information I_σ, and (c) Ghosh-Berkowitz-Parr entropy S_{GBP} with respect to the total number of electrons N_C from Bader's atoms-in-molecules (AIM) approach on 192 carbon atoms in 42 molecular systems studied in this work.

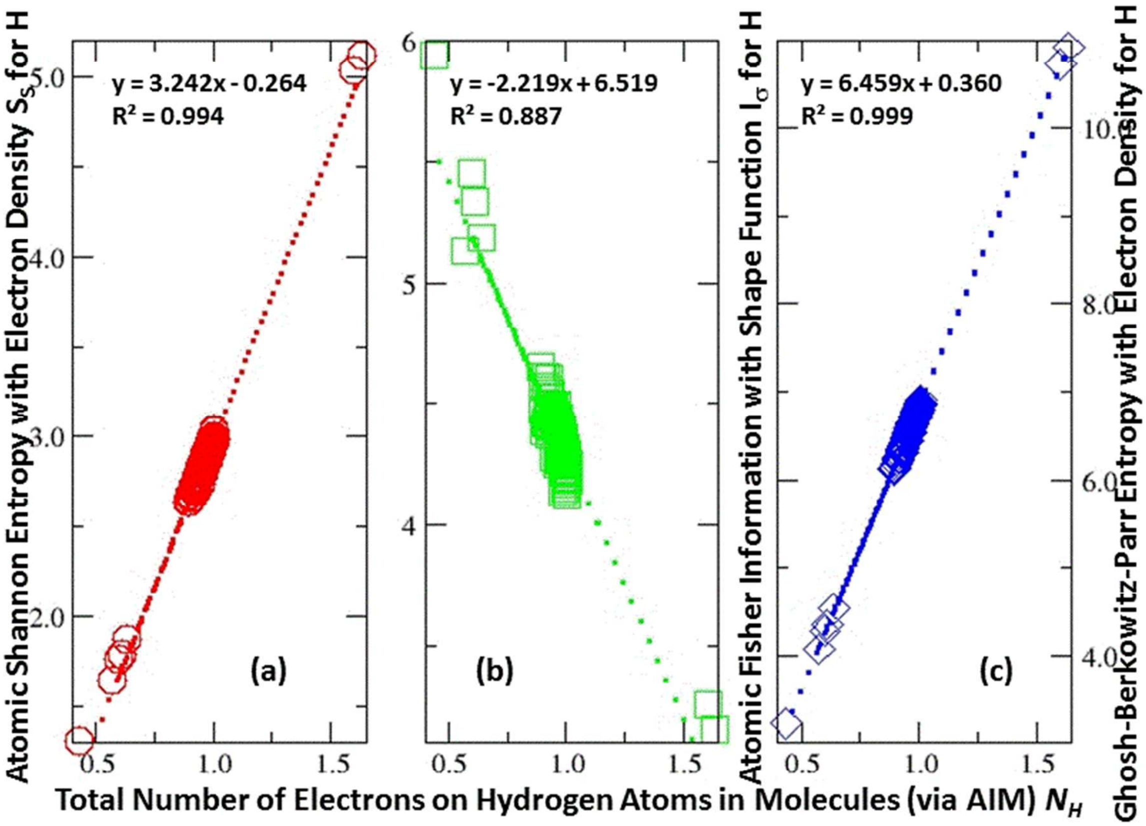


Figure 4. Scaling properties of (a) Shannon entropy S_S, (b) Fisher information I_σ, and (c) Ghosh-Berkowitz-Parr entropy S_{GBP} with respect to the total number of electrons N_H from Bader's atoms-in-molecules (AIM) approach for 252 hydrogen atoms in 42 molecular systems studied in this work.

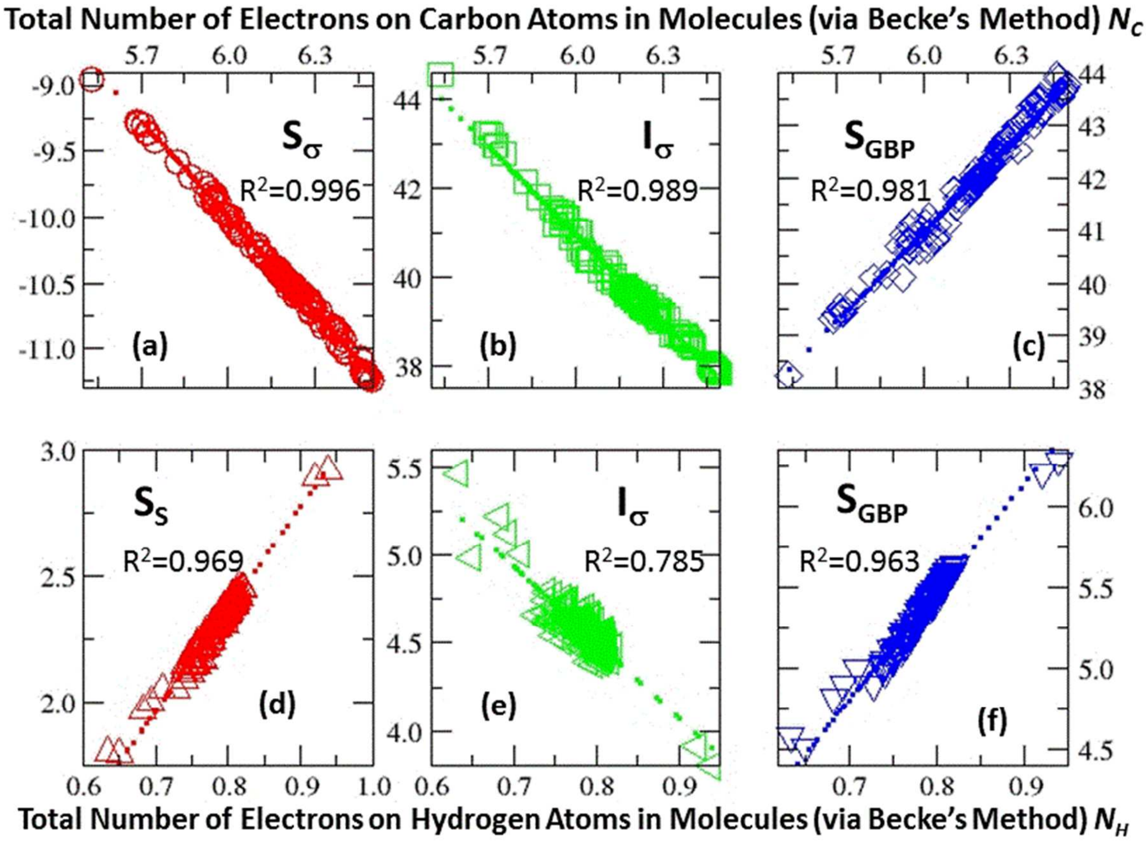


Figure 5. Scaling results for (a-c) carbon and (d-f) hydrogen atoms in molecules results with Becke's fuzzy partitioning approach for 192 carbon atoms and 252 hydrogen atoms in 42 molecular systems studied in this work.

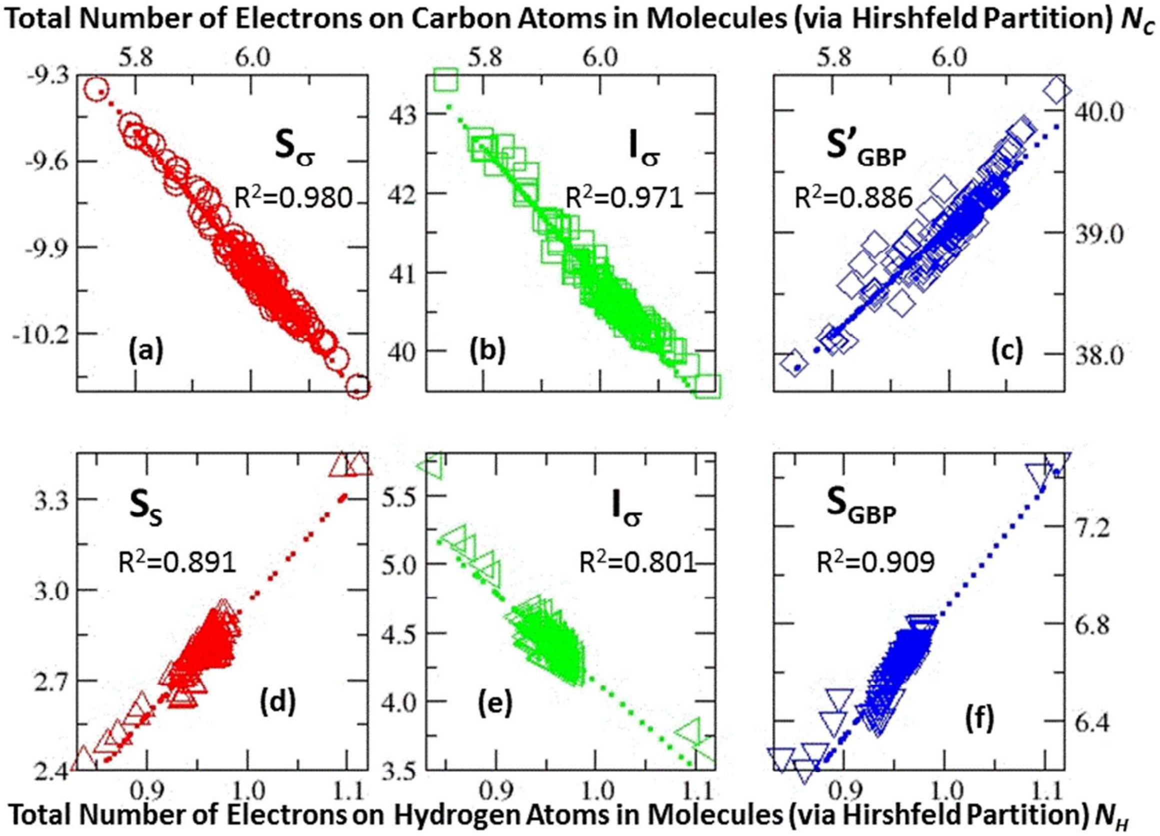
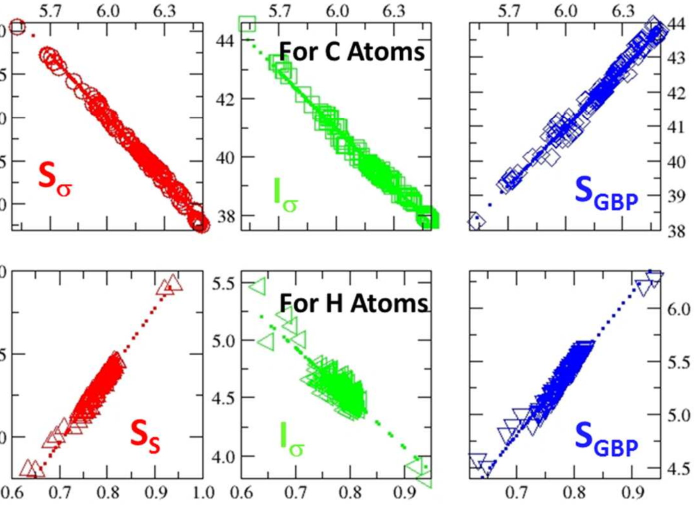


Figure 6. Scaling results for (a-c) carbon and (d-f) hydrogen atoms in molecules with Hirshfeld's stockholder partitioning approach for 192 carbon atoms and 252 hydrogen atoms in 42 molecular systems studied in this work.

TOC Graphic



A number of strong linear correlations between information-theoretic quantities and electron populations for atoms, molecules, and atoms-in-molecules have been disclosed.