# A Chemically Meaningful Measure of Electron Localization

Martin Rahm*

Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853, United States

S *Supporting Information*

ABSTRACT: Electron localization and delocalization are commonly invoked in the day-to-day rationalization of chemistry. This work addresses the challenges of quantifying this elusive concept in a chemically useful manner. A general principle, requiring the simultaneous quantification of (1) a limited physical volume (classical criterion) and (2) same-spin loneliness (quantum criterion), is introduced. It is demonstrated how, by beginning with the Electron Localization Function (ELF) scalar field, one can choose to discard all points in space where the same-spin loneliness is lower than a certain value. Such a partitioning approach ensures that both criteria for quantifying localization (1 and 2) are simultaneously met. The most chemically instructive results arise when the dividing boundary condition is set by the local behavior of a homogeneous electron gas. The High Electron Localization domain Population (HELP) is introduced and applied for quantifying the localization of individual domains within molecules, as well as a measure of total electron localization in atoms and molecules. Several striking agreements with chemical intuition, experimental measurable quantities, and quantum chemical constructs are demonstrated along with understandable differences. Studies of diatomic molecules agree with current ideas on chemical bonding. The size-dependence and magnitude of localization in linear hydrocarbons is studied and compared to cyclic systems, such as benzene. The proposed methodology offers a straightforward measure for direct and quantitative comparisons between atoms, molecules, and extended condensed matter.
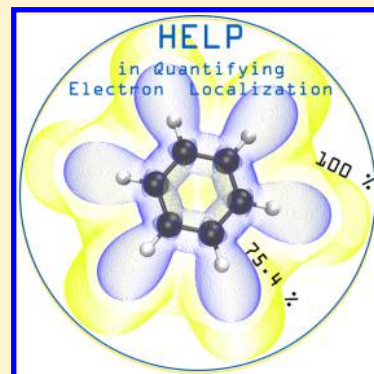
1. INTRODUCTION

The concept of electron localization, and delocalization, is commonly invoked in the day-to-day rationalization of chemistry. This work addresses the general challenge of quantifying electron localization. The validation of one method for achieving this in a *chemically relevant manner*, both for individual domains within a molecule and for entire molecular systems, will be demonstrated. This approach is in part based on an earlier study, which aimed at quantifying the activity of formal lone pair domains.[1]

Interestingly, there exists no clear definition for the degree of localization of electrons in atoms, molecules, or condensed matter. Instead, there exists quite some controversy on the matter.[2−10] One reason for this controversy is the invariance of the electron density with respect to unitary transformations of occupied molecular orbitals. This allows for canonical molecular orbitals to be the subject of various fundamentally different localization schemes. Prominent and useful examples include, but are not limited to, those developed by Edmiston and Ruedenberg,[11] Pipek and Mezey,[12] Boys,[13] and more recently by Knizia.[14] One alternative and complementary approach to the orbital analysis of chemistry lies with quantum chemical topology (QCT). Within QCT various property fields (densities) are routinely investigated in three dimensions, and examples of these will be given.

For chemists it can be relevant to ask questions such as

"By *how much* are the electrons in a given molecule, e.g. acetylene, C_2H_2, localized compared to those in that other molecule, e.g. benzene, C_6H_6?"

and

"Does a particular chemical reaction result in an overall net delocalization, or localization, and how significant is the change?".

Before we can try to answer such questions one first need a general expression for quantifying localization as a function of what is localized and delocalized, respectively. By assuming knowledge of localization, by whichever method or definition available to us, a simple formalism for its quantification can be defined as follows

$$\text{Localization} = \frac{n_{\text{loc}}}{n_{\text{tot}}} = \frac{n_{\text{loc}}}{n_{\text{loc}} + n_{\text{deloc}}} = \frac{1}{1 + \left(\frac{n_{\text{deloc}}}{n_{\text{loc}}}\right)} \quad (1)$$

where n_{tot} is the total number of electrons in the system, and n_{loc} and n_{deloc} are the number of localized and delocalized electrons, respectively. This expression is independent of the precise definition of localization itself. It implies the following:

A. Localization is inversely proportional to the number of delocalized electrons.

B. Localization in a hypothetical completely delocalized system of known dimensions can be expressed knowing only its volume and number of electrons or by its electron density in any point in space.

C. A real system will have some amount of inherent localization, which is independent of size. Therefore, for large

systems, we expect n_{loc}/n_{tot} to converge on a material-specific value.

In order to quantify electron localization, one needs to look at two sides of the same coin. Localization will here imply that two criteria are fulfilled:

1. A localized electron needs to be alone with respect to its same-spin counterparts (quantum criterion).

2. The volume of the lone electron (or lone pair of opposite-spin electrons) needs to be smaller than what can be considered delocalized (classical criterion).

The first criterion can in practice only truly be met for a system with two or fewer electrons (H, H_2, He^+, etc.). If we were only concerned with this criterion, then indeed all one- or two-electron systems would be completely localized in every point in space. In addition, the localization of the electron pair in H_2 and in, for instance, U^{90+} would be considered equal. The absurdity of considering this criterion alone is clear. That said, it is only one side of the coin, as it allows for *local* measures of same-spin loneliness in many electron systems, for example by analysis of the pair-probability function.[4,15−17] This is a topic we will return to.

The second criterion begs the question of how does one decide on a volume when, in principle, the molecular wave function extends into all space? Should one limit the system by a surface at which the electron density has a certain value? Or, alternatively, should maybe a volume, which on average contains a certain percentage of all electrons, be used? To exemplify the problem we take molecular hydrogen and implement the molecular boundary suggested by Boyd, $\rho(\mathbf{r})$ = 0.001 e/a_0^3.[18] This results in a molecular volume of 18 Å^3, which includes ∼96% of the two electrons. If we instead set the boundary condition to a density of 0.0001 e/a_0^3, then we end up with the chemically speaking quite large volume of 44 Å^3, which includes ∼99% of the two electrons. Density "cropping" options, such as this, are problematic not only because they are arbitrary but also because the outer regions of any >2-electron-system is prone to be the part most delocalized. This is primarily due to a lower electron density (increased volume), as well as an effectively increased Pauli (= same-spin, or exchange) repulsion in these regions. Aside from several technical matters, such as basis set deficiencies, disk space use, integration time, and the likely chemical utter uselessness of the diffuse outer regions, no matter what low number one chooses there will always be one that is lower.

Another crux, arguably relevant to chemistry, is intermolecular boundaries. At what point (in space) can electrons in formally localized chemical bonds or lone pair domains be considered localized, and when are they delocalized? From a molecular orbital perspective electron loneliness decreases where occupied molecular orbitals overlap, i.e. where multiple electron pairs contribute to the local electron density. This can naturally occur both in high-density regions, in and around the formal locations of chemical bonds, as well as in low-density outer regions.

One way to simultaneously deal with both suggested criteria for electron localization (1 and 2) is to turn them into one and the same criterion and let the volume, or boundary, be limited by a set value for the loneliness of the electrons. Before going on to describing one way to pursue this, some more background is needed.

Electrons are known quantum mechanically to be indistinguishable. Therefore, an attractive way for studying them is

to estimate their average behavior. One means to this end is the Electron Localization Function or ELF.[19]

1.1. The Electron Localization Function (ELF). As a well-known measure of electron loneliness, ELF enables analysis of the six-dimensional pair-probability function by relating it onto positional space through the use of a reference formalism[19] (eq 2). In the case of a single-determinant Kohn−Sham DFT wave function the close shell formulation[20] of ELF reads as

$$\text{ELF} = \eta(\mathbf{r}) = \frac{1}{1 + \left(\frac{D}{D_h}\right)^2} \tag{2}$$

where

$$D = \frac{1}{2}\sum_i |\nabla\varphi_i(\mathbf{r})|^2 - \frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \tag{3}$$

$$D_h = \frac{3}{10}(3\pi^2)^{2/3}\rho(\mathbf{r})^{5/3} \tag{4}$$

$$\rho(r) = \sum_i |\nabla\varphi_i(\mathbf{r})|^2 \tag{5}$$

there φ_i is the Kohn−Sham orbital of electron i, D is the excess kinetic energy density required to satisfy the Pauli exclusion principle, and D_h is the reference kinetic energy density set to equal that of a homogeneous electron gas[21] of identical electron density. With this formalism, ELF ranges from 0.0 to 1.0, where 1.0 is a situation void of Pauli repulsion, in which electrons are completely *alone* with respect to their same spin counterparts (thus upholding criterion 1). The relative measure gaged by D/D_h will throughout this work be referred to as *same-spin loneliness*. Lower degrees of loneliness will at times be referred to as situations of *same-spin crowding*. These choices of words are meant to paint a physical picture and ease understanding and are equivalent to formulations invoking high and low Pauli or exchange repulsion.

Critics of ELF have brought up several well-justified concerns.[22] One relates to the physical interpretation of ELF, which in part varies with its definitions. These include Becke and Edgecombe's original Hartree−Fock formulation,[19] the DFT formulation by Savin et al. (eq 1),[20] the approximate density-based formulation of Tsirelson and Stash,[23] and the Virial theorem-based formulation by Fuentealba.[24]

Another cause of unease is the seemingly arbitrary definition of using the homogeneous electron gas as a reference for the Pauli kinetic energy density (D_h). In efforts to circumvent this, various other QCT localization methods have been devised. A nonexhaustive list includes the Localized Orbital Locator (LOL) method,[25] where the D_h term is removed, the Spin-Pair Composition Function,[26] and the Electron Localization Indicator (ELI),[27] of which the latter two provide virtually identical results as the original ELF[19] formulation. Other densities are the Fermi Hole Mobility Function[28] and Single Electron Densities.[29] Various indexes for quantifying delocalization by using ELF have been proposed.[30] One such approach is to analyze the relative fluctuations of basin populations, another to construct so-called bifurcation trees.[31,32] The ELF Delocalization Index (EDI), which is the ELF value at a critical bond point, is one instructive measure of how ELF behaves during the formation of covalent bonds.[33] The use of ELF in studies of molecules and materials is extensive,[34−40] and the development of the QCT field is rapid.[41−47]

For any density (or function) considered, local "basins" within it can be constructed using zero gradient surfaces, arising around local maxima in the density.[48] Such basins can then, for certain functions like ELF, be formally attributed to chemical concepts such as atoms, bonds, and lone pairs (Figure 1). In
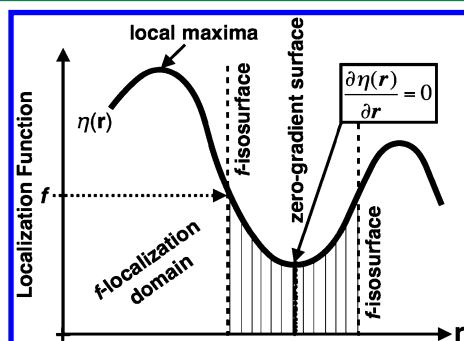

Figure 1. 3D-basins around local maxima in a localization function, $\eta(\mathbf{r})$, are defined by zero-gradient surfaces. The introduction of isosurfaces creates f-localization domains, in which the local value of $\eta(\mathbf{r})$ always exceeds f.

this work we will frequently refer to "domains". These arise when basins are limited by a boundary value f in the localization function. Specifically ELF f-localization domains can span a space in which $f < \eta(\mathbf{r}) < 1$, and where f is between 0 and 1. Choosing different values of f is commonly used for illustrative purposes, in making isosurface representations of ELF and similar functions. Figure 1 gives a brief crash course in how f-localization domains are constructed.

Figure 2 illustrates the ELF scalar field over the molecule ethanol for $f = 0.15$, 0.50, and 0.85. Note that it is only for high
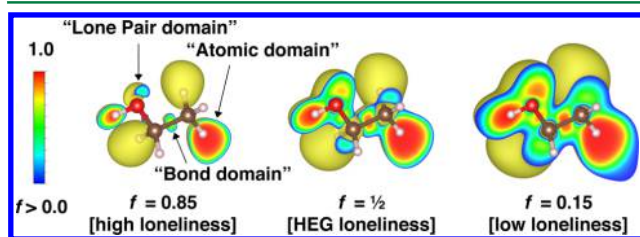

Figure 2. ELF f-isosurface representations of ethanol. $f = 0$ is the native ELF value, which includes all electrons (not shown). The mid range value of $f = 1/2$ represents $\eta(\mathbf{r}) = D = D_h$, where the local same-spin loneliness equals that of a homogeneous electron gas (HEG) of equal density. Only higher values of f allow for spatial separation into domains that can be *formally* equated to chemical bonds and lone pairs.

values of f, which implies domains of relative high same-spin loneliness, that domains resembling localized bonds and lone pairs appear as spatially separate.

Above which value of f should we look, to find the most chemically indicative measure of electron loneliness? If the native ELF value of $f = 0$ is chosen, then *all* electrons, including those most delocalized will be included. In the discussion and results that follow, a case will be made for $f \sim 1/2$, as the more chemically relevant value. Before moving to examples illustrating this, we will first briefly discuss the conceptual appeal of the homogeneous electron gas as the delocalized reference state.

1.2. The Homogenous Electron Gas. First, the physical picture: the homogeneous electron gas corresponds to the

hypothetical case of an even distribution of electrons in all points in space, half of which have the opposite spin to the other half, and all existing over a background of homogeneous positive charge that maintains charge neutrality. One advantage of this reference, which is popular in simpler solid-state models, and used for the construction of the local density approximation (LDA) density functional theory (DFT) approximation, is that the effect of the nuclear environment is averaged out. Thus, for a given density, and in a hypothetical situation devoid of quantum effects, these electrons *would be perfectly delocalized*. However, due to the Pauli exclusion principle the system possesses additional kinetic energy, the exchange energy.

In a real heterogeneous chemical system, we can investigate a given subset of the molecular space and find that *locally* the kinetic energy density due to the Pauli exclusion principle (eq 3) *exceeds* that of the reference state (eq 4). This is a consequence of the local electron density arising from more electrons than would be the case if that same density would represent the Pauli repulsion of all electrons (i.e., the total density), in a truly homogeneous electron gas representation of the entire molecule. Given a system, *any* local property needs to sum to its corresponding average property for the entire system. This is to say, local electron densities and local Pauli repulsion energy densities sum to the total number of electrons and total exchange energy of the system, respectively. Local measures of the homogeneous electron gas reference always sum to the total number of electrons. Obviously, local measures of Pauli repulsion in a supposed homogeneous electron gas reference *only* sum to the total exchange energy when the total system *is* a homogeneous electron gas, i.e. the hypothetical case near total delocalization. As such, the division D/D_h (in eq 2) couples the Pauli exclusion principle to the local electron density, which, if the molecule *had been* completely delocalized would represent the entire molecule. Since molecules look different, the homogeneous electron gas molecule is the only universal reference that any and all heterogeneous electronic systems can be *averaged* to.

1.3. The High Electron Localization domain Population (HELP). As mentioned, one way of simultaneously upholding both suggested criteria for electron localization (1 and 2) is to let the volume of a system be limited by a set value for the loneliness of the electrons. Following this reasoning, Rahm and Christe demonstrated empirical evidence for the relevance of the $D = D_h$ boundary (cf. eqs 3 and 4), when applied for intrabasin partitioning of lone pair domains.[1] *The High Electron Localization domain Population (HELP) was defined as the average number of electrons contained within an ELF domain limited to values where $\eta(\mathbf{r}) \geq 1/2$.* For practicality in integrating the number of electrons, Boyd's arbitrary boundary condition of 0.001 e/bohr[3] was implemented as the molecule's outer edge. For this low value, the density is decaying exponentially for most atoms,[18] and its exact value has negligible effects on the HELP population (one exception is the alkali metals, which require lower cutoff values). By this definition HELP provides a number of electrons that on average exhibit kinetic energies, due to the Pauli exclusion principle, equal to or lower than that of a local homogeneous electron gas of identical electron density. It can be calculated for any region of a molecule.

HELP is related to the original "loge theory" put forth by Daudel and co-workers, in which loges partition the whole space, and where a loge is a domain in which a certain number

of electrons are found.[16,49] The concept was developed by Bader, who developed the now well-known Quantum Theory of Atoms in Molecules (QTAIM),[48] in which the molecular space is partitioned using the gradient of the electron density (like in Figure 1). The fundamental difference between HELP and previous QCT approaches is that a part of the molecular space, where electrons are "less alone", is ignored.

When HELP was calculated for a large number of formal lone pair domains, situated on main group elements, it showed promising correlation with a range of physical properties and quantum mechanical constructs. These include the electrostatic surface potential (ESP), electron and proton affinity, ionization potential, HOMO and LUMO energies, atomic charge, and NBO lone pair orbitals, as well as characteristics of the molecular geometry.[1]

Although HELP appears to be a useful descriptor of chemistry when applied to lone pair domains, it was not sufficiently demonstrated whether the $D = D_h$ boundary condition (where $\eta(\mathbf{r})$ or $f = 1/2$) is the most instructive choice in separating localized from delocalized and relevant from less relevant. Therefore, this work is in part focused on investigating the entire ELF f-localization domain range, $f < \eta(\mathbf{r}) < 1$, where $f = 0 \rightarrow 1$.

HELP is based on ELF primarily because it is a well-known function for topological analysis. ELF is widely implemented in computational codes and allows access to the desired $D = D_h$ boundary. The quadratic formula of ELF does not affect the HELP partitioning, or the HELP values, and the exact same values can just as well be obtained from a topological gradient analysis of the following simpler function

$$\vartheta(\mathbf{r}) = \frac{D}{D_h} \qquad (6)$$

It should be mentioned, maybe ironically, that the HELP approach is not applicable to the no-same-spin electron systems where we started out (H, H_2, He, etc.), for which the electrons are perfectly alone with respect to same-spin counterparts (i.e., where there is no Pauli repulsion).

2. RESULTS AND DISCUSSION

2.1. Validating the HELP Boundary Condition in Practice. We first look at the pnictogen trihydrides − NH_3, PH_3, AsH_3, SbH_3, and BiH_3. How does the average electron population of the f-localization domain, formally equated to the Lewis-lone pair, vary as f goes from zero to one? At which value of f, if any, does correlation with chemistry arise?

Note that the integrated number of electrons in a given domain should *not* be interpreted representative of a single electron nor a pair of electrons. Rather, it is the average number of electrons in a domain arising due to multiple electrons. If one wishes to calculate the probability of finding individual electrons in individual domains, a different approach is needed. For example, the one developed by Francisco et al.[50]

Figure 3 reveals that it is only in the range $1/2 < f < 0.8$, where the ordering of HELP mirrors that of the elements in the Periodic Table. Outside the HELP boundary, including the native ELF values at $f = 0$, a random picture arises - the domain of bismuth has the highest population, whereas phosphorus get the lowest, and nitrogen takes an intermediate value.

Next, we investigate how the same series of lone pair domains correlate with atomic charge of the center atom, the activation barrier to pyramidal inversion, the electrostatic
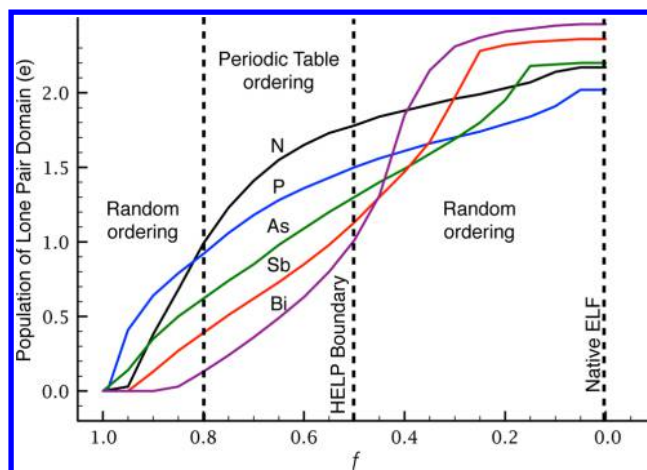

Figure 3. Average electron populations of f-localization domains, as a function of f, for XH_3 (X = N, P, As, Sn, and Bi), each in its calculated optimized geometry. $f = 1/2$ is the HELP boundary. The region between 0.5 and 0.8 is the only one in which the overall ordering is in agreement with chemical intuition (and the Periodic Table).

surface potential above the formal lone pair, and the energy of the highest occupied molecular orbital, HOMO (Figure 4).
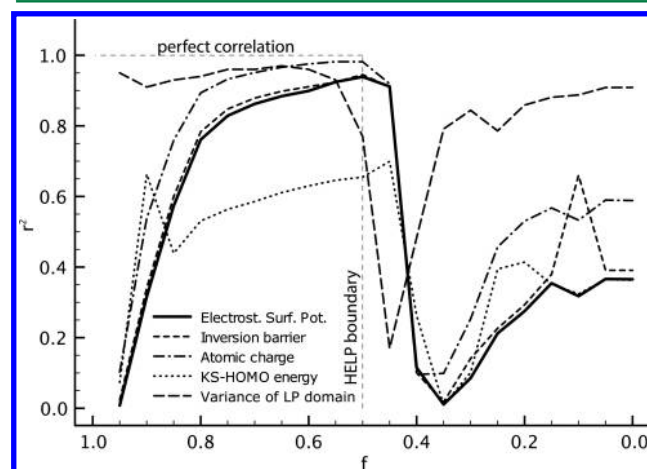

Figure 4. Physical relevance, measured as r^2, of f-localization domain populations, $f < \mu(\mathbf{r}) < 1$, where $0 < f < 1$, above and below the HELP boundary in XH_3 (X = N, P, As, Sn, and Bi).

The results are striking - gradual increase of several linear correlations, measured as the coefficient of determination (r^2), peaks near the HELP boundary, and then falls sharply. The sharp drop signifies a high degree of randomness outside the HELP boundary. Whereas the native ELF values (at $f = 0$) recapture some of the correlation, it is far from the r^2-values at $f = 1/2$.

Overall HOMO energy correlates with the lone pair f-localization domain populations to a lower degree. This is expected and can be explained by spatial delocalization of this orbital. Larger substituent groups, such as F or CH_3, which have more delocalized HOMO orbitals, decrease the correlation between the HOMO energy and HELP for the lone pair domain further (see the Supporting Information of ref 1).

The HELP methodology is based on integrating the one-electron density. One complementary way of investigating HELP's connection to localization is a "pair-density analysis", in which the two-electron pair density is considered.[51] The same-

spin pair populations of the lone pair f-localization domains in the $NH_3 - BiH_3$ series correlate well with the corresponding one-electron populations at all f-values (r^2 fluctuates between 0.80−0.93 for all values of f). The pair population enables the calculation of the population covariance matrix, in which the diagonal elements, the variances, σ^2, are a statistical measure of the quantum mechanical uncertainty of a domain's population (see ref 51 for details). The variances correlate with the f-localization domain populations in a similar fashion to the other examples illustrated in Figure 4. Close to $f = 1/2$, correlation between σ^2 and the f-localization domain population largely disappears.

Delving deeper into the example of activation barriers for pyramidal inversion around tricoordinated pnictogens, Figure 5
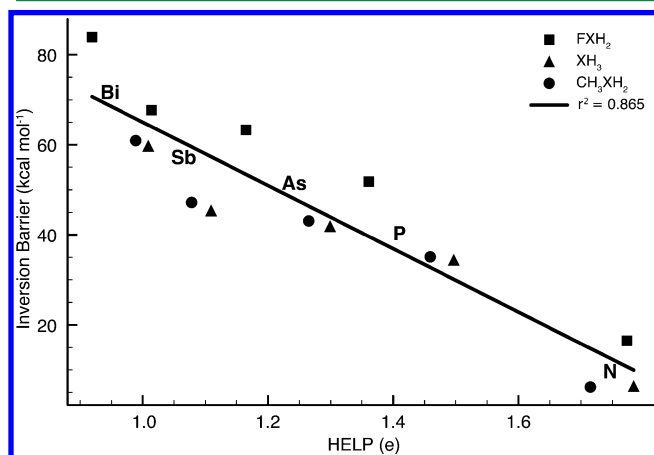

Figure 5. Activation energy for pyramidal inversion of XH_3, FXH_2, and CH_3XH_2 molecules (X = N, P, As, Sn, and Bi) as a function of HELP calculated for the corresponding lone pair domains.

exemplifies how the HELP methodology can be used to rationalize important aspects of chemistry. The size of the barrier to pyramidal inversion is crucial for asymmetric catalysis. In amines the barrier to inversion can be as low as 5−10 kcal/mol, which is too small to allow for isolation of individual stereoisomers under ambient conditions. In contrast, inversion barriers are typically in excess of 30 kcal/mol for phosphines. Many factors have been invoked to rationalize such differences in barrier heights.[52,53] Figure 5 shows a strong correlation between activation barriers and HELP, for various small molecules. The interpretation appears clear - *activation barriers to pyramidal inversion increase with delocalization of the lone pair domains, and de*localization *of said domains increase down the periodic* table. This interpretation is in agreement with chemical intuition, and various ways for analyzing chemistry, as we will now show.

2.2. HELP's Relation to VSEPR Thinking. Often, the "steric expression", or "activity", of the formal lone pair concept is invoked within semiclassical Valence Shell Electron Pair Repulsion (VSEPR)-thinking.[54,55] HELP and VSEPR-thinking are in agreement in the following sense: A high value of HELP, i.e. a large number of electrons contained within the f-localization domain defined by $f = 1/2$, implies *small* amounts of Pauli-repulsion and *little* same-spin crowding. The "steric activity" of such a domain is in other words predicted to be small, precisely because it is more localized. In contrast, a low value of HELP implies a situation of same-spin crowding, where the electron density in a region, regardless of its absolute

magnitude, has contributions from many different electron pairs, which repel each other due to quantum mechanical exchange interactions. A low value of HELP implies a heavily delocalized lone pair domain, which, in a VSEPR-sense, exerts significant "steric activity".

An Example. An instructive comparison can be made between NH_3 and BiH_3, for which the H−N−H and H−Bi−H bond angles are 106.6° and 91.3°, respectively. What is a good rationale for this difference in molecular geometry? There are of course many ways of rationalizing this. Within VSEPR specifically the difference is explained by invoking a more diffuse or "sterically active" lone pair on BiH_3. The HELP analysis is in agreement with this intuitive picture. The HELP value for the lone pair domain on isolated ammonia calculates as 1.78 electrons (high loneliness or little same-spin crowding), whereas for BiH_3 it calculates as only 1.01 electrons (low loneliness or more same-spin-crowding).

How well does HELP reflect *changes* to the notion of "crowding" or "activity" of a given domain? To illustrate this, two ammonia molecules were forced together head-on, $[H_3N−NH_3]$, to a N−N distance of 2 Å (Figure 6). In this situation
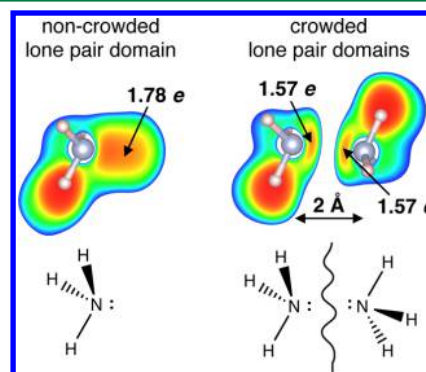

Figure 6. HELP offers one way of *quantifying* elusive chemical concepts such as "steric congestion" and "activity" of a given domain, which can be useful for rationalizing geometric preferences. A lowered HELP value implies increased same-spin crowding, a physical consequence of increased "sterics". The HELP range, (blue) $1/2 < \eta(\mathbf{r}) < 1.0$ (red), is here illustrated by a plane through the molecule ammonia. Population values are shown for the lone pair domains in the free molecule and in a head-on-squeezed conformation.

steric repulsion is by any measure expected to be large. HELP does capture the change, and the increased steric repulsion is evidenced by a lowering of the lone pair domain population from 1.78 electrons in free ammonia to 1.57 electrons in the congested complex (Figure 6). This value is close to that predicted for free phosphine ($\sim$1.50 e).[1] The ability to gage and illustrate the steric congestion of individual domains in this manner should prove instructive in the analysis of chemical structure in general.

2.3. On HELP's Relation to Molecular Orbital Thinking. The linear trend shown in Figure 5 describes how the barrier to pyramidal inversion, specifically for these simple XH_2R molecules, is related to HELP as

$$\text{Activation barrier (kcal/mol)} = -61 \times \text{HELP} + 120$$

This relation predicts the barrier to *vanish* when HELP equals 1.97 ($\sim$2.0) electrons. The ideal value of 2 electrons *is* expected and can be rationalized by example from orbital arguments as follows: In the planar transition state geometry of

ammonia, the N−H single bonds can, to a good degree of approximation, be described by atomic sp^2-hybrid orbitals on nitrogen interacting with $1s$ orbitals on the hydrogens. In both such a hybridized orbital picture, *and* in a molecular orbital picture, the lone pair, in contrast, is described by a doubly occupied atomic $2p$-orbital. As long as the two opposite-spin electrons, here represented by the $2p$-orbital, remain in this space, they will experience little Pauli repulsion. Therefore, when calculating ELF for this species, the resulting lone pair domain will be highly spatially related to the atomic $2p$-orbital, and the ELF value within the lone pair domain will be high (close to 1). When we consider the integrated number of HELP-electrons in the lone pair domain we disregard some amount of electrons that nevertheless experience spin crowding, and we are left with a value of 2.06 in the transition state geometry (up from 1.78 in ground state NH_3). The value of ∼2.0 is here slightly overestimated and will decrease if larger more diffuse basis sets are used. This is because of spatial overlap between diffuse tails of occupied orbitals, an effect that becomes increasingly important for heavier elements, and in larger molecules.

In contrast, the native ELF population ($f = 0$) of the investigated lone pair domains always exceeds two, irrespective of the lone pair-bearing element and irrespective of the geometry. This is a consequence of considering *all* parts of the electron density within the ELF basin, including those parts of the density that arise from multiple orbitals overlapping. As shown in Figure 4, the highest degree of correlation presents itself at the HELP boundary and not for any other value of f. For a more in-debt discussion on the relationship between orbital hybridization and HELP for lone pair domains, please see the previous work.[1]

We can conclude that the HELP-values of group 14 lone pair domains *approach* 2.0 electrons, as the p-character (and the same-spin loneliness) approach 100%. This situation requires a planar geometry for XL_3-type molecules. *These results are in complete agreement with the expectations of an orbital analysis* and are a testament to the great complementarity of QCT (real space) and orbital (Hilbert space) analyses. In general, a clear HELP-to-orbital connection requires a high degree of *spatial* correlation between a HELP-domain and an occupied orbital. This connection will diminish for more complicated situations. For instance, when the atomic p-orbital in question is affected by ligand charge transfer or is engaged in π-bonding.

2.4. HELP as a Global Measure of Electron Localization. Thus, far we have only considered individual domains, and specifically lone pair domains, within molecules. Strictly speaking, one underlying ambiguity associated with such domains lies with the definition of interdomain-boundaries using zero-gradient surfaces (Figure 1). We will now minimize this ambiguity, by proceeding to discuss the use of HELP to quantify electron localization in any given *total* system. Only one disparate global domain, limited by the f-boundary, will be considered.

Just as before, localization implies the fulfillment of two criteria: (1) a physically limited volume (the classical criterion) and (2) same-spin loneliness (the quantum criterion). As we shall see, HELP offers a balanced trade-off to both criteria. *The amount of localization will here be quantified using eq 1, where n_{loc} and n_{deloc} are taken to be the average number of electrons above and below the f-boundary, respectively.* Using this definition, localization will from here on out be discussed in percent. In what follows, note that whereas *absolute* localization percentages

typically vary slightly with the computational level of theory, e.g. the choice of density functional or size of basis set, relative trends remain (see the Supporting Information).

Before proceeding to discuss larger molecules we begin with individual ground state atoms.

Atoms. For individual atoms ($Z = 3−18$), the ordering of localization varies throughout the entire f-range, and several atoms cross close to $f = 1/2$ (Figure 7). In general the following observations can be made:
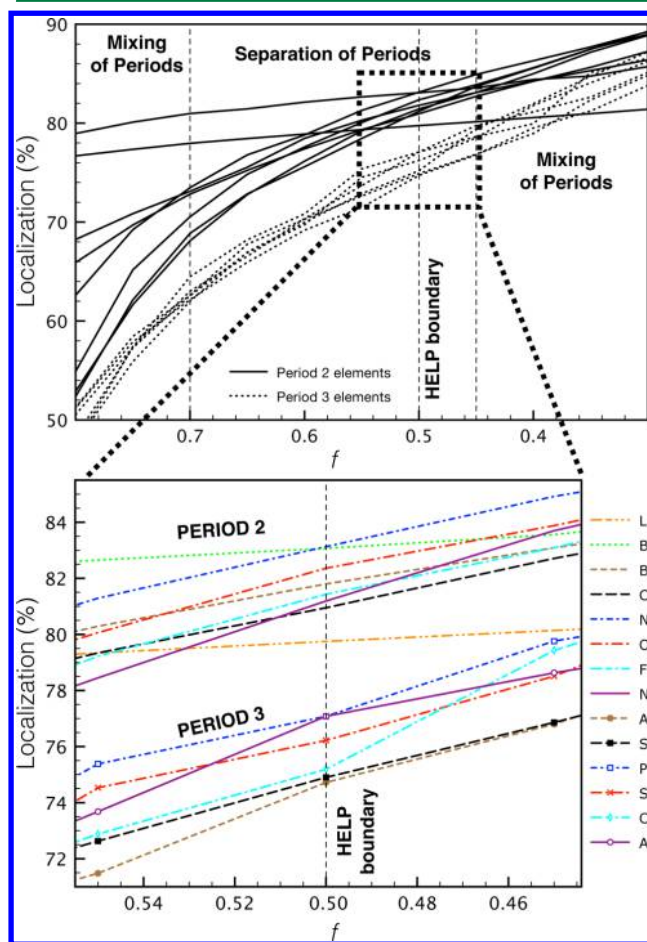

Figure 7. Quantification of electron localization in ground-state atoms, as a function of f. Periods 2 and 3 of the Periodic Table are clearly separated around the HELP boundary. Possible exceptions are Na and Mg, which have been omitted because of technical difficulties.

● Atoms of the second and third periods of the Periodic Table are clearly separated only in the range $0.45 < f < 0.70$, indicating a higher chemical relevance of this region. Note that the same range has been observed earlier, in Figure 3, where it arose from a completely different study.

● Lithium and beryllium have the flattest dependences on f. This is expected as Li and Be have the smallest number of same-spin electrons.

● Whereas sodium and magnesium appear similarly localized compared to elements in the second period, their precise f-dependencies could not be accurately estimated. This because of technical issues arising from these atoms nonclosed and diffuse outer shells, which render results sensitive to the choice of electron density cutoffs (see the Supporting Information).

● With the exception of Na and Mg, electrons are more localized in the second period elements, compared to the third
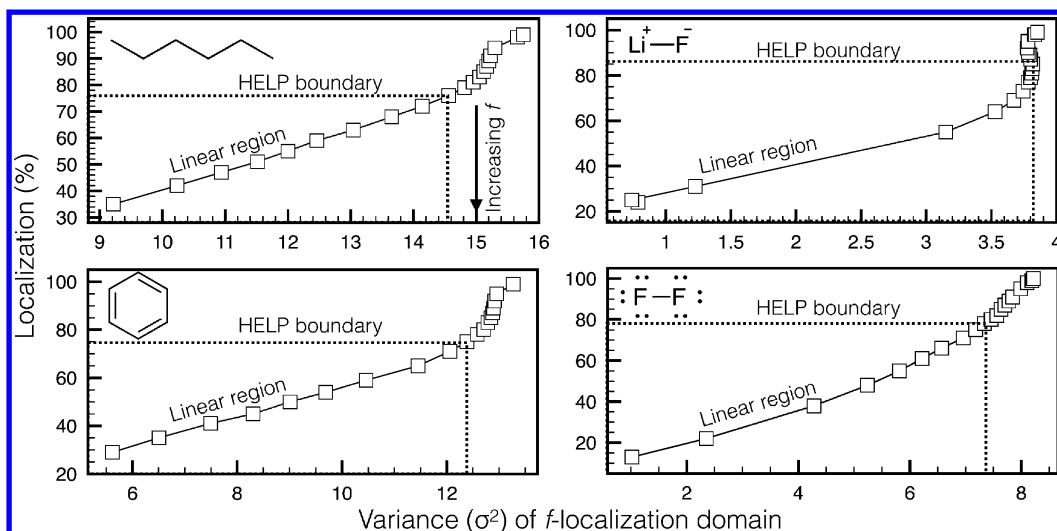
Figure 8. Statistical analysis of the two-electron pair density reveals that the variances (σ^2) of f-localization domains correlate linearly with the corresponding one-electron domain populations but only above the HELP boundary.

period elements. This is expected, as there are more electrons in the latter group of elements, a fact that both decrease same spin loneliness and increase volume. An increasing amount of "core electrons" do not contradict this trend, for inner regions also become increasingly spin-crowded due to spatial overlap between electrons in different shells.

● High-spin and electronegative atoms (N, O, P, and S) are comparably more localized than other atoms in the same period. This is expected, as Pauli repulsion will be maximized in high-spin systems.

● The investigated atoms of rows 13 and 14 (B, C, Al, and Si) are less localized, compared to other elements in their respective period. This is arguably in accord with their lower electronegativity, and larger size (by any definition), relative to other p-block elements.

As we see from Figure 7 the elements of the second period take localization values between 79 and 83%, at the HELP boundary. The third period, in contrast, range from 74 to 77%. We will return to the meaning and analytical use of these values as we next move to discuss the localization of molecules constructed by these atoms.

Molecules. We will now briefly return to the study of the two-electron pair density, in particular the variance, σ^2, which is a statistical measure of the quantum mechanical uncertainty of a domain's population.[51] σ^2 has been found to linearly correlate to localization percentages determined above the HELP boundary in a range of molecules. Examples are shown in Figure 8. At the HELP boundary a break in the linear trend occurs. The break is very distinct in LiF, clear in hydrocarbons, while subtler in F_2 (Figure 8). The persistence of this behavior in a range of molecules provides further validation for the HELP boundary in quantifying electron localization. f-localization domain populations obtained for $f > 1/2$ are linearly related to the factual fluctuations of the electron pairs.

Is chemically meaningful *quantification* of electron localization in molecules and extended systems possible? Figure 9 shows calculated localization percentages as a function of f in a series of fundamentally different chemical species. For now familiar reasons, results at the edges of the range are sporadic and largely random. However, toward the middle, close to the HELP boundary, chemical relevance emerges.
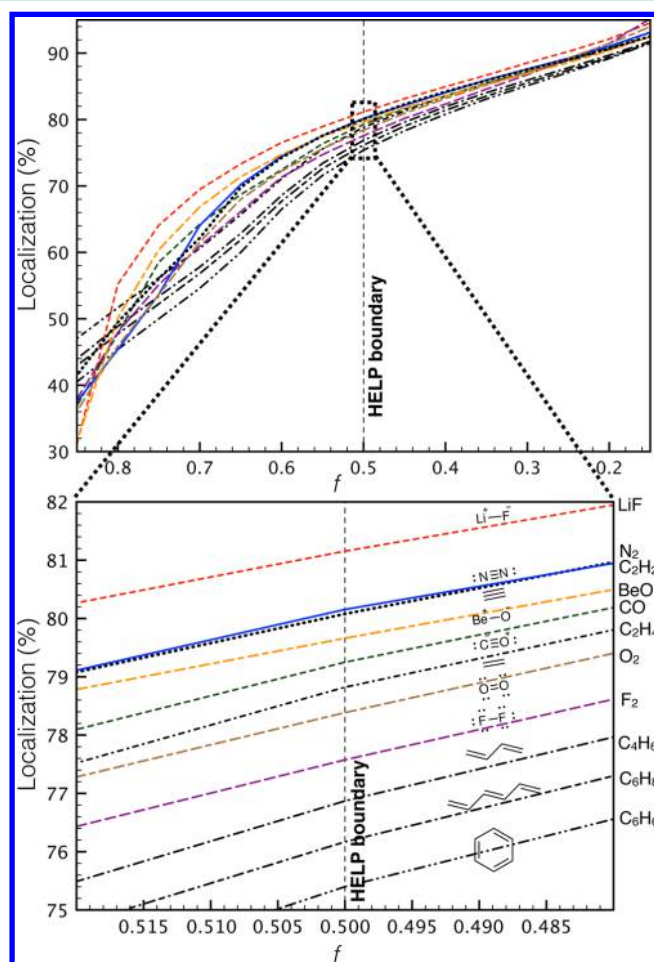

Figure 9. Quantification of electron localization in selected diatomics and larger molecules, as a function of f.

Diatomics. We look first at a selection of diatomics: LiF, BeO, N_2, CO, O_2, and F_2. In good agreement with chemical intuition, higher degrees of localization are predicted for strongly ionic species, such as LiF and BeO. The strong triple bond of molecular nitrogen is also identified as quite localized. In the weakly polar molecule CO (and also in ethylene)

localization is lessened. Finally O_2 and F_2 are predicted to be the most delocalized of the second-period diatomics investigated. This is in qualitative agreement with Shaik et al., who have pointed out in their analysis of charge-shift bonding that bonding with "excessive exchange repulsion is typical to electronegative and lone-pair-rich atoms".[56]

Larger Molecules. Figure 9 clearly demonstrates how localization in conjugated hydrocarbons varies with size: ethylene (C_2H_4) > butadiene (C_4H_6) > hexatriene (C_6H_8) > heptaene ($C_{14}H_{16}$), etc. This is in agreement with π-conjugation arguments. Interestingly, a lower degree of localization is predicted for benzene (C_6H_6). We will return to this and other cyclic systems. The electron localization in acetylene, C_2H_2, is predicted near identical to that in molecular nitrogen. This can be rationalized as a consequence of their isoelectronic relationship.

On HELP's Relation to Chemical Bonding. It is concluded that for intermediate values of f (and always at $f = 1/2$), all investigated molecules show *lower* degrees of localization than their constituent atoms, or molecular fractions, considered separately. For example, the localization in F_2 is lower than that in free F atoms (Figures 7 and 8). Similarly, the localization in acetylene is predicted to markedly decrease when three such monomers combine to form benzene. This means that the HELP analysis correctly captures how bond formation occurs through the sharing (and delocalization) of electrons. Subsequent papers will investigate the use of HELP in describing chemical bonding in greater detail.

It is apparent that differences in localization, predicted between systems of similar elemental constitution, e.g. alkenes, are small in absolute numbers. Differences between molecules that consist of the same elements are on the order of a few percent or less. This should not necessarily be interpreted as "they are all the same". The localization percentages differ increasingly when domain populations are derived using higher f-values. However, any advantage of analyzing such larger differences appears mostly esthetic, and we remind that it is at the HELP boundary that meaningful correlations to chemistry appear most consistently. Whereas localization values of isomers are predicted similar, the small differences between them are indicative of chemical change in a meaningful manner. This is apparent from a regular ordering within and between different classes of compounds, which will be discussed in more detail below. A more pronounced change in localization is seen upon element-substitution, especially when going down the Periodic Table.

As apparent from the examples shown in Figure 9, localization quantified in this manner does relate to physical size. We know to expect this from eq 1, which predicts localization to be inversely proportional to the size of the system, counted as the total number of electrons, n_{tot}. We now proceed to investigate this proportionality in more detail.

2.5. What Is the Size-Dependence of Delocalization? Delocalization is evident when treating electrons in the solid state. There electronic levels can be approximated by the superposition of infinite plane waves.[57] Molecular electrons are in principle no different; they are standing waves in oddly shaped boxes. Because of this we can expect, to some degree of approximation, that localization should scale inversely with molecular size (cf. eq 1 and its implications A-C). To test this notion, we first take three molecules, methane, ethylene, and acetylene, and gradually "grow their size", by expanding them into the alkane, alkene, and alkyne series, respectively. This *in*

silico experiment is designed to probe the effect of size while keeping the chemistry as constant as possible.

One thing that is relevant to compare is how the fraction of localized electrons (eq 1) *changes* as the chains grow. The zero-gradient condition (eq 7) should be expected for any system in which localization is independent of size, i.e. in a system where chemical bonds are completely additive entities. It should also hold true for any system that is very large, because then any measure of localization should have converged to a material specific value.

$$\frac{dn_{loc}}{dn_{tot}} = 0 \tag{7}$$

at $f = 0$, i.e. when all electrons are considered. This is the reason why such an approach cannot be used as a measure of total/global/molecular localization. At the other extreme, at $f = 1$, no electrons are considered and the system is not defined. Just as for lone pair domains, the real utility of a localization scalar field, such as ELF, emerges when a relevant subset of electrons are considered.

The linear alkane series (C_nH_{2n+2}) is here represented by $n = 1-8$ and 15, whereas the linear alkene series (C_nH_{n+2}) was calculated for $n = 2, 4, 6, 8, 10, 12,$ and 14, and the alkyne series (C_nH_2) for $n = 2, 4, 6, 8,$ and 10. What is striking is that each class of compounds forms separate and near-perfect ($r^2 > 0.9999$) linear functions of localization vs n_{tot}^{-1} (Figure 10).
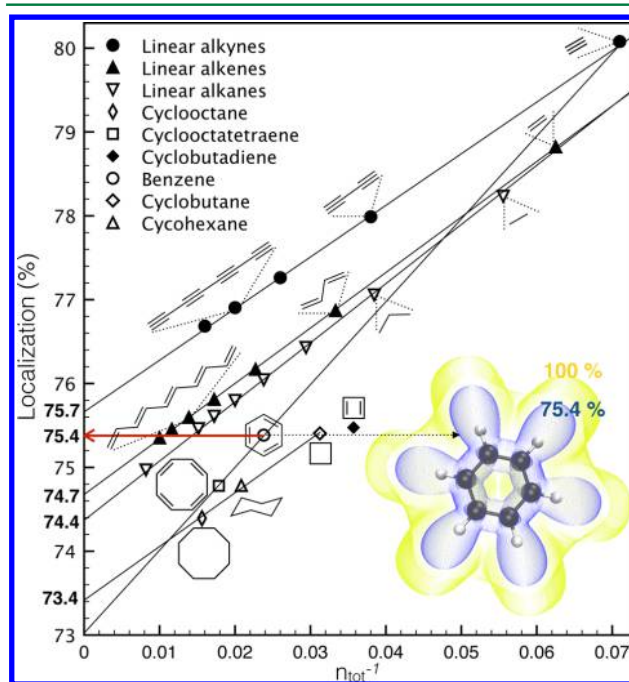

Figure 10. Localization quantified in various cyclic and linear hydrocarbon series shows explicit ($r^2 > 0.9999$) inverted dependences on size, measured as number of electrons (n_{tot}). Inset shows visualization of the total HELP-domain in benzene, calculated to include 75.4% of all electrons.

This is true for all intermediate, $0.3 < f < 0.8$, values of f and is in perfect agreement with the prediction of eq 1. Not only is localization shown inversely proportional to the size of these systems (measured here as the number of electrons, n_{tot}), but alkanes, alkenes, and alkynes are also shown to have different values for any given value of n_{tot}. It is by no means obvious that

CH_4 should fall on the same "localization-line" as C_2H_6 and $C_{15}H_{32}$, which is different from that of C_2H_4 and $C_{14}H_{16}$. The ratio of carbon–carbon to carbon–hydrogen bonds is different in all of them. The clean separation of alkanes, alkenes, and alkynes indicates that this analysis is sensitive enough to function as a QCT-based chemical classification tool, even for states of matter consisting of the same basic atomic building blocks.

How do the three series compare? Many chemists would expect alkynes and alkenes to be inherently more delocalized, due to the presence of π-conjugation. Alkanes are sometimes interpreted from a different perspective, as a string of localized sp^3-bonds. In other words, the interactions of atomic s- and p-levels forming carbon single (σ) bonds are commonly viewed as additive and local entities, whereas the interactions of bond-orthogonal p-levels producing (π) bonding is seen as inherently delocalized. We remind first that π-conjugation only refers to 2 out of the total number of 7 electrons in the repeating CH-group in alkenes and, second, that the volume of the system is not considered in such arguments.

In returning again to the criteria for electron localization, we must consider *two* measures - first the loneliness of electrons (quantum criterion) and, second, their volume (classical criterion). The volume criterion is important! For instance, by using the common molecular boundary of $\rho(\mathbf{r}) = 0.001$ e/a_0^3 the CH_2 repeating unit calculates as a full 20% larger than the CH-unit! The corresponding difference *per electron* is five percent. Therefore, even though the alkane, alkene, and alkyne series were specifically chosen to make the total electron count a good approximation to the size of the system, their inherent sizes are different. This has the consequence that as n_{tot} increases, molecular volume grows quicker in alkanes than in alkenes and alkynes. This is one reason why the HELP analysis predicts alkynes to be more localized than alkenes, which in turn are predicted more localized than alkanes. It is here pertinent to remind that *alkanes do experimentally have higher polarizability than comparable alkenes* and that the latters higher reactivity is of no consequence to this discussion. In other words, whereas the prediction of alkanes as being the least localized, i.e. more delocalized, makes little sense in the context of chemical *reactivity*, it does make sense in the context of polarizability.

More localized *f*-localization domains (i.e., where $f > 1/2$) capture only highly localized parts of the molecular space, which are less sensitive to changes in volume. Consequently, they predict the opposite of HELP, namely that alkenes are more delocalized overall.

2.6. What About Cyclic Systems? Benzene is special, for historical reasons. For one, it exemplifies the central chemical notion of "aromaticity", which predict a special stabilizing effect in cyclic systems with $4n + 2$ π-electrons. Interestingly, the localization value of 75.4%, predicted for benzene, is in between those estimated for infinite polyacetylene and polyyne chains (Figure 10). At first glance, this analysis therefore can seem to suggest a connection between the notion of aromaticity and localization. However, the "anti-aromatic" ($4n$ π-electron) cyclobutadiene, C_4H_4, is also, and despite its smaller size, predicted to have a very similar value of 75.5%. If cyclobutadiene and benzene had been of the "same class" of cyclic systems we would expect them to fall on the same sloped line, similar to the behavior of other related hydrocarbons. Since they do not, HELP seems capable of identifying benzene and

cyclobutadiene as being part of two fundamentally different chemical series.

Instead, it is the larger cyclooctatetraene, C_8H_8, a puckered antiaromatic yet fairly persistent structure, and acetylene, C_2H_2, who form a near-perfect ($r^2 > 0.9999$) localization-line with benzene. In other words, the monomer (acetylene), its cyclic trimer (benzene), and tetramer (cyclooctatriene) all share the exact same localization-size dependence, whereas the cyclic dimer (cyclobutadiene) is a clear outlier. This conclusion is in agreement with work by Wu, Schleyer, and co-workers, who have concluded that "instead of the conventional interpretation of cyclobutadiene as the antiaromatic paradigm, it should be regarded as a unique molecule".[58]

It is interesting to note that in contrast to methane, ethane, and ethylene, which all fall on their respective linear localization lines, these results imply that acetylene, somehow, is both a linear alkyne and "inherently cyclic". Note also that the benzene-series have the steepest slope in Figure 10. This means that localization *in this series* (not benzene per say) is inherently more responsive to changes in size. The expansion into the cyclic polyacetylene series (cyclobutadiene excluded) is more freely delocalizing and more akin to the ideally delocalized system implied by eq 1, compared to the other series. The prediction becomes that as cycles of the benzene-series grow larger ($n_{tot}^{-1} \rightarrow 0$), localization will converge on a system specific value for localization, which happens to be 73% when the HELP boundary and this basis set is used. The exact absolute value is not very important. What is, is that this value is markedly lower than most other systems considered, including the infinite polyethylene chain and benzene. It is given by the intercept with the y-axis in Figure 10.

The same trend is seen for the cyclic alkanes. Cyclobutane, cyclohexane, and cyclooctane fall on another perfect line, which intercepts the y-axis in Figure 10 at 73.4% localization. In general, cyclic systems are predicted more delocalized than the corresponding linear systems. One consequence of this is that the repeating CH and CH_2 units in large cyclic alkenes and alkanes cannot be rigorously equated to the same repeating unit in a linear polymer. Of course, chemically, they behave very similar. Nonetheless, this analysis has revalued a small and definite difference. The physical implications of these different degrees of localization are unclear, yet one can speculate that they are a reflection of localization being naturally favored by increasing spatial dimensions—one-dimensional materials (e.g., linear polymers) allowing for less delocalization than two-dimensional materials (e.g., cyclic systems or sheets).

One general conclusion of these results is independent of the exact *f*-boundary chosen (as long as *f* is not chosen close to 1 or 0): Even though chemical bonds in smaller alkanes, alkenes, and alkynes are undoubtedly similar, they cannot be claimed completely additive local entities. For any system where bonds are *truly* additive the equality of eq 7 must hold. This situation can occur when considering a system of noncovalently interacting species, such as van der Waals complexes, complexes of electrostatically bound "hard" ions, and possibly weaker hydrogen bonded systems. As demonstrated, this situation will also occur as a system grows in size, and $n_{tot}^{-1} \rightarrow 0$, for which a material specific value for localization will be reached.

When treating any extended systems theoretically, using periodic boundary conditions, eq 7 must hold with respect to expansion of the repeating unit cell. The calculation of localization percentage for two unit cells of different size, and

finding them equal, is thus one way of ensuring that no computational artifacts limits electron delocalization.

3. CONCLUDING REMARKS

A previous study[1] introduced a measure named the High Electron Localization domain Population (HELP). It demonstrated that if molecular space is separated into domains, using a limiting value for same-spin loneliness that equals that of a homogeneous electron gas, then a clear correlation could be seen between the average number of electrons found in "lone pair domains" and a multitude of chemical and physical measurable and quantum chemical constructs.

In this work, all possible dividing values, or boundaries, have been investigated. The results support the HELP approach as the best choice for dividing what is more chemically relevant in the molecular space from what is less so. For instance, quantification of lone pair domains using the HELP boundary results in the highest correlations with activation barriers to pyramidal inversion and atomic charges, as well as the electrostatic surface potential. Needless to say, the concept of lone pair domains is central in the chemical sciences. Meaningful quantification of their "activity" is highly desirable.

Next, moving beyond individual domains of molecules, overall quantification of electron localization has been investigated. Again, the HELP boundary comes out as a relevant choice. For single atoms, the different periods of the Periodic Table can be distinguished and discussed. Studies of selected diatomic molecules have demonstrated that chemical bonding can be addressed. The HELP approach correctly predicts that chemical bonding coincide with delocalization of shared electrons, a circumstance we know to expect from molecular orbital theory. The ability to gage the relative magnitude of this delocalization, within periods of the Periodic Table, suggests that ionic bonds are more localized, whereas molecules with high degrees of electron-correlation, such as O_2 and F_2, are more delocalized.

The effect of physical size on localization is demonstrated by investigating linear and cyclic alkanes, alkenes, and alkynes. As expected, larger hydrocarbons are predicted more delocalized than smaller ones. Benzene, the archetypical aromatic molecule, is predicted to take a value intermittent to the infinite polyacetylene and polyyne chains! The described approach is sensitive enough to distinguish subtle but distinct differences in localization between classes of hydrocarbons, which is not obvious considering that they are made up of the same elements. This is a capacity we expect should extend far beyond the molecules and series investigated herein. Absolute differences in localization are small but predictive for isomers and grow more substantial upon elemental substitution, especially down the Periodic Table. One implication of these results is that the concept of chemical bonds in expanding alkanes and alkenes are demonstrated as nonadditive entities. This can be seen a physical consequence of a growing "molecular box", which promotes increased electron delocalization. For large systems the degree of localization converges to a material-specific value.

The strong correlation of the HELP approach with experimental observables and numerous chemical descriptors and indeed with chemical intuition, with a few understandable differences, suggests many future utilities. For one, HELP does appear both a useful local and interesting global chemical descriptor. This work suggests it is capable of quantifying elusive chemical concepts such as "steric congestion" and "activity" of formal lone pair domains. Its boundary condition might aid the development of more accurate density functionals.

This work has demonstrated that the separation of the three-dimensional space of electronic systems, into more and less localized, does enable chemically relevant quantification of molecular electron localization. There can never be a singular defining fundamental measure of electron localization, for it is inherently a relative measure. The best we can hope for are understandable measures that give reasonable and useful results. The suggested methodology is by no means *the* but *a* quantification of localization. It offers a straightforward measure for quantitative comparisons between atoms, molecules, and extended condensed matter.

4. COMPUTATIONAL METHODS

With the exception of inversion barriers, which were estimated by single point CCSD(T)/aug-cc-pVTZ-PP calculations, all molecular geometries, HELP calculations, and other analyses were evaluated from M06-2X[59]/cc-pwCVTZ wave functions, obtained using Gaussian 09, revision A.02.[60] The hybrid meta exchange-correlation density functional M06-2X is a high accuracy general purpose DFT functional as demonstrated by extensive benchmarking.[61−64]

Generation and analyses of the electron density and the ELF scalar field were performed over 0.05 Bohr (0.026 Å) resolution grids using the open-source program Dgrid version 4.6.[65] Initial boxes were extended by 4−6 Bohr in all three dimensions, until all domains could be extended to their $\rho(\mathbf{r}) = 0.001$ e/Bohr^3 and $\eta(\mathbf{r}) = f$ limiting values. Scans over the f-localization range were performed in 0.05 increments. The spin-polarized definition of Kohout and Savin was used for the calculation of ELF.[66]

Whereas period 1−3 elements were described by the correlation consistent cc-pwCVTZ basis set,[67,68] the cc-pwCVTZ-PP[69] basis set was employed for the treatment of all period 4−6 elements. The latter includes a small-core relativistic Stuttgart pseudopotential that accurately recovers both scalar and spin−orbit relativistic effects of inner core electrons of the heavier elements. In the case of bismuth, which is one of the heaviest nuclei considered, its 23 outermost electrons were treated by a (23s23p15d3f1g)/[7s6p5d3f1g] Gaussian contraction. The large basis set ensures a highly flexible description of the valence and subvalence space and is necessary since neglecting d-subshells is known to produce artifacts in ELF.[70] The previous paper[1] includes comparison with all-electron relativistic calculations and showed that the usage of pseudopotentials does not affect results relating to valence shell lone pair domains. Note that calculations of total localization preclude the use of pseudopotentials. Core electrons cannot be assumed 100% localized, due to spatial overlaps.

ELF properties calculated with Hartree−Fock and B3LYP is known to compare well with CISD, CCSD-BB, and CASSCF multireference calculations in a range of cases.[71] Control electron density and ELF calculations on the $NH_3 \rightarrow BiH_3$ series has previously been performed using the BP86[72,73] functional and the B3LYP[74] hybrid functional, with close to identical results compared to M06-2X. To estimate the robustness of electron populations over the f-localization range we have in this work also calculated the entire alkane and alkene series with the ωB97X-D hybrid functional.[75] ωB97X-D is a reliable functional for general-purpose use.[62]

Deviations between the two were found to exceed 0.1% only for $f > 0.6$. Comparisons were also made with the LC-BLYP[76] functional, which provided slightly lower degrees of localization. In doing this work, it was found that very large and diffuse basis sets do lower the HELP values slightly. Validation studies with the aug-cc-pVQZ basis set did not affect relative trends or any of the general conclusions of this work. Please see the Supporting Information for details on the stability of the HELP approach with respect to the level of theory.

Graphical representations were generated using VMD 1.9.[77] and VESTA 3.1.[78] Simple run scripts, input files, and step-by-step instructions for performing the HELP analysis are given in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tests of the reliability with respect to the level of theory and step-by-step instructions for performing the HELP analysis. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00396.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: martinr@kth.se.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ ABBREVIATIONS

ELF, Electron Localization Function; HELP, High Electron Localization domain Population

■ REFERENCES

(1) Rahm, M.; Christe, K. O. *ChemPhysChem* **2013**, *14*, 3714−3725.
(2) Hoffmann, R.; Shaik, S.; Hiberty, P. C. *Acc. Chem. Res.* **2003**, *36*, 750−756.
(3) Shaik, S. *New J. Chem.* **2007**, *31*, 2015−2028.
(4) Bader, R. F. W.; Johnson, S.; Tang, T.-H.; Popelier, P. L. A. *J. Phys. Chem.* **1996**, *100*, 15398−15415.
(5) Grushow, A. *J. Chem. Educ.* **2011**, *88*, 860−862.
(6) Truhlar, D. G. *J. Chem. Educ.* **2012**, *89*, 573−574.
(7) Tro, N. J. *J. Chem. Educ.* **2012**, *89*, 567−568.
(8) Hiberty, P. C.; Volatron, F.; Shaik, S. *J. Chem. Educ.* **2012**, *89*, 575−577.
(9) Landis, C. R.; Weinhold, F. *J. Chem. Educ.* **2012**, *89*, 570−572.
(10) DeKock, R. L.; Strikwerda, J. R. *J. Chem. Educ.* **2012**, *89*, 569−569.
(11) Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457−465.
(12) Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916−4926.
(13) Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296−299.
(14) Knizia, G. *J. Chem. Theory Comput.* **2013**, *9*, 4834−4843.
(15) Lennard-Jones, J. *J. Chem. Phys.* **1952**, *20*, 1024−1091.
(16) Daudel, R.; Bader, R. F. W.; Stephens, M. E.; Borrett, D. S. *Can. J. Chem.* **1974**, *52*, 1310−1320.
(17) Bader, R. F. W.; Stephens, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 7391−7399.
(18) Boyd, R. J. *J. Phys. B: At. Mol. Phys.* **1977**, *10*, 2283−2291.
(19) Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397−5403.
(20) Savin, A.; Jepsen, O.; Flad, J.; Andersen, O. K.; Preuss, H.; von Schnering, H. G. *Angew. Chem.* **1992**, *104*, 186−188. (See also *Angew. Chem., Int. Ed. Engl.,* **1992**, *31*(2), 187.10.1002/anie.199201871
(21) Wigner, E.; Seitz, F. *Phys. Rev.* **1933**, *43*, 804−810.
(22) Kohout, M. *Faraday Discuss.* **2007**, *135*, 43−54.
(23) Tsirelson, V.; Stash, A. *Chem. Phys. Lett.* **2002**, *351*, 142−148.
(24) Fuentealba, P. *Int. J. Quantum Chem.* **1998**, *69*, 559−565.
(25) Schmider, H. L.; Becke, A. D. *J. Mol. Struct.: THEOCHEM* **2000**, *527*, 51−61.
(26) Silvi, B. *J. Phys. Chem. A* **2003**, *107*, 3081−3085.
(27) Kohout, M. *Int. J. Quantum Chem.* **2004**, *97*, 651−658.
(28) Luken, W. L.; Culberson, J. C. *Int. J. Quantum Chem.* **1982**, *22*, 265−276.
(29) Luechow, A.; Petz, R. *J. Comput. Chem.* **2011**, *32*, 2619−2626.
(30) Silvi, B.; Gatti, C. *J. Phys. Chem. A* **2000**, *104*, 947−953.
(31) Savin, A.; Silvi, B.; Colonna, F. *Can. J. Chem.* **1996**, *74*, 1088−1096.
(32) Calatayud, M.; Andres, J.; Beltran, A.; Silvi, B. *Theor. Chem. Acc.* **2001**, *105*, 299−308.
(33) Contreras-Garcia, J.; Recio, J. M. *Theor. Chem. Acc.* **2011**, *128*, 411−418.
(34) Grin, Y.; Savin, A.; Silvi, B. The ELF perspective of chemical bonding. In *The Chemical Bond: Fundamental Aspects of Chemical Bonding*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2014; pp 345−382.
(35) Hoffmann, A. V.; Hlukhyy, V.; Faessler, T. F. *Z. Anorg. Allg. Chem.* **2014**, *640*, 2882−2888.
(36) Hu, S.; Mace, A.; Johnsson, M.; Gnezdilov, V.; Lemmens, P.; Tapp, J.; Moeller, A. *Inorg. Chem.* **2014**, *53*, 7661−7667.
(37) Lepetit, C.; Poater, J.; Alikhani, M. E.; Silvi, B.; Canac, Y.; Contreras-Garcia, J.; Sola, M.; Chauvin, R. *Inorg. Chem.* **2015**, *54*, 2960−2969.
(38) Mancera, L. A.; Benoit, D. M. *J. Phys. Chem. A* **2015**, *119*, 3075−3088.
(39) Zins, E.-L.; Silvi, B.; Alikhani, M. E. *Phys. Chem. Chem. Phys.* **2015**, *17*, 9258−9281.
(40) Navas, J.; Sanchez-Coronilla, A.; Gallardo, J. J.; Cruz Hernandez, N.; Pinero, J. C.; Alcantara, R.; Fernandez-Lorenzo, C.; De los Santos, D. M.; Aguilar, T.; Martin-Calleja, J. *Nanoscale* **2015**, *7*, 6216−6229.
(41) Contreras-Garcia, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D. N.; Yang, W. *J. Chem. Theory Comput.* **2011**, *7*, 625−632.
(42) Causa, M.; D'Amore, M.; Garzillo, C.; Gentile, F.; Savin, A. *Struct. Bonding (Berlin, Ger.)* **2013**, *150*, 119−142.
(43) Andres, J.; Gonzalez-Navarrete, P.; Safont, V. S. *Int. J. Quantum Chem.* **2014**, *114*, 1239−1252.
(44) Bezugly, V.; Wielgus, P.; Kohout, M.; Wagner, F. R. *J. Comput. Chem.* **2010**, *31*, 2273−2285.
(45) Kumar, A.; Gadre, S. R.; Mohan, N.; Suresh, C. H. *J. Phys. Chem. A* **2014**, *118*, 526−532.
(46) Popelier, P. L. A. *Chem. Bond* **2014**, *1*, 271−308.
(47) Menendez, M.; Martin Pendas, A.; Braida, B.; Savin, A. *Comput. Theor. Chem.* **2015**, *1053*, 142−149.
(48) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1990.
(49) Daudel, R.; Brion, H.; Odiot, S. *J. Chem. Phys.* **1955**, *23*, 2080−2083.
(50) Francisco, E.; Pendas, A. M.; Blanco, M. A. *Comput. Phys. Commun.* **2008**, *178*, 621−634.
(51) Poater, J.; Duran, M.; Sola, M.; Silvi, B. *Chem. Rev. (Washington, DC, U. S.)* **2005**, *105*, 3911−3947.
(52) Rauk, A.; Allen, L. C.; Mislow, K. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 400−414.
(53) Montgomery, C. D. *J. Chem. Educ.* **2013**, *90*, 661−664.
(54) Gillespie, R. J.; Nyholm, R. S. *Q. Rev., Chem. Soc.* **1957**, *11*, 339−380.

(55) Gillespie, R. J.; Robinson, E. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 495−514.

(56) Shaik, S.; Danovich, D.; Wu, W.; Hiberty, P. C. *Nat. Chem.* **2009**, *1*, 443−449.

(57) Ashcroft, N. W.; Mermin, N. D. *Solid State Physics*; Harcourt: Orlando, 1976.

(58) Wu, J. I.-C.; Mo, Y.; Evangelista, F. A.; Schleyer, P. V. R. *Chem. Commun. (Cambridge, U. K.)* **2012**, *48*, 8437−8439.

(59) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215−241.

(60) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N. K. R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford, CT, 2009.

(61) Valero, R.; Gomes, J. R. B.; Truhlar, D. G.; Illas, F. *J. Chem. Phys.* **2008**, *129*, 124710/1−124710/7.

(62) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2011**, *7*, 669−676.

(63) Goerigk, L.; Grimme, S. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670−6688.

(64) Peverati, R.; Truhlar, D. G. *J. Phys. Chem. Lett.* **2011**, *2*, 2810−2817.

(65) Kohout, M. *Dgrid, version 4.6*; 2011.

(66) Kohout, M.; Savin, A. *Int. J. Quantum Chem.* **1996**, *60*, 875−882.

(67) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(68) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358−1371.

(69) Peterson, K. A.; Yousaf, K. E. *J. Chem. Phys.* **2010**, *133*, 174116/1−174116/8.

(70) Kohout, M.; Savin, A. *J. Comput. Chem.* **1997**, *18*, 1431−1439.

(71) Feixas, F.; Matito, E.; Duran, M.; Sola, M.; Silvi, B. *J. Chem. Theory Comput.* **2010**, *6*, 2736−2742.

(72) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098−3100.

(73) PERDEW, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822−8824.

(74) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372−1377.

(75) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615−6620.

(76) Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. *J. Chem. Phys.* **2001**, *115*, 3540−3544.

(77) Humphrey, W.; Dalke, A.; Schulten, K. *J. Mol. Graphics* **1996**, *14*, 33−38.

(78) Momma, K.; Izumi, F. *J. Appl. Crystallogr.* **2011**, *44*, 1272−1276.