A connection between domain-averaged Fermi hole orbitals and electron number distribution functions in real space

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We show in this article how for single-determinant wave functions the one-electron functions derived from the diagonalization of the Fermi hole, averaged over an arbitrary domain $\Omega$ of real space, and expressed in terms of the occupied canonical orbitals, describe coarse-grained statistically independent electrons. With these domain-averaged Fermi hole (DAFH) orbitals, the full electron number distribution function (EDF) is given by a simple product of one-electron events. This useful property follows from the simultaneous orthogonality of the DAFH orbitals in $\Omega$, $\Omega' = R^3 - \Omega$, and $R^3$. We also show how the interfragment (shared electron) delocalization index, $\delta^{m,\Omega}$, transforms into a sum of one-electron DAFH contributions. Description of chemical bonding in terms of DAFH orbitals provides a vivid picture relating bonding and delocalization in real space. DAFH and EDF analyses are performed on several test systems to illustrate the close relationship between both concepts. Finally, these analyses clearly prove how DAFH orbitals well localized in $\Omega$ or $\Omega'$ can be simply ignored in computing the EDFs and/or $\delta^{m,\Omega}$, and thus do not contribute to the chemical bonding between the two fragments. © 2009 American Institute of Physics.


I. INTRODUCTION

Extracting chemically meaningful information from the everyday more accurate electronic structures provided by modern computational chemistry methods is far from an established procedure. Among the plethora of techniques developed over the years to perform this task, the domain-averaged Fermi hole (DAFH) analysis formulated by Ponec\textsuperscript{1,2} has shown that reducing the two-particle complexity of the Fermi (or, in general, the full exchange-correlation) hole by averaging the reference electron over a 3D region of the real space is a very useful tool to understand and interpret different aspects of the nature of the chemical bond. At the moment, it has been applied to shed light in several interesting problems, such as the chemical bonding in hypervalent,\textsuperscript{3–5} electron-rich,\textsuperscript{6} or newly synthesized molecules,\textsuperscript{7} the structure of $\text{MOX}_4$ ($M = \text{Os,Ru}; \ X = \text{F,Cl,Br,I}$) species,\textsuperscript{8} the metal-metal bond in $\text{Re}_2\text{Cl}_8$,\textsuperscript{9} the localization of electron pairs in electron localization function domains,\textsuperscript{10} or the anatomy of bond formation.\textsuperscript{11,12} The technique has recently been generalized to open-shell systems,\textsuperscript{13} formulated using a one-electron approximation,\textsuperscript{14} and explained as an analytic model\textsuperscript{15} that expands its interpretative capability. For this contribution, it is particularly interesting that integrating a DAFH over its complementary real space region provides a measure of the degree of electron sharing between the regions.

On a different front, relatively recent work has revitalized old concepts initially put forward by Daudel,\textsuperscript{16} regarding the probability distribution of electrons in real space regions. Summarizing, if an arbitrary and exhaustive partition of the physical space into $m$ disjoint fragments or domains $\Omega_1, \Omega_2, \ldots, \Omega_m$ is introduced in a $N$ electron system, we define the electron number distribution function (EDF) for this partition as the probability distribution obtained by dividing the $N$ electrons into the $m$ basins in all possible ways, e.g., such that exactly $n_1$ electrons lie within $\Omega_1$, $n_2$ within $\Omega_2$, etc.\textsuperscript{16,17} A simple procedure to obtain the EDF when a system is described by a single Slater determinant and partitioned into only two complementary domains has been proposed by Savin et al.\textsuperscript{18} Efficient methods to deal with multideterminant wave functions and any number of fragments, including also the possibility to consider spin $\alpha$ and spin $\beta$ electrons separately, have been recently developed in our group.\textsuperscript{19–21}

Since a deep, not fully explored link exists between the joint fluctuation in the electron population of two (or more) domains, and the strength of their electron sharing indices\textsuperscript{22–28} (or multicenter delocalization measures\textsuperscript{29–33}), access to EDFs may be useful in a wide number of problems. In our group we have used them to understand the origin of the additivity of the properties of functional groups,\textsuperscript{34} to provide extra information from general energy partitions,\textsuperscript{34–37} to define resonant structures and coarse-grained density matrices in real space,\textsuperscript{38,39} to classify chemical bonds,\textsuperscript{40} and to provide a new view of the bond paths of the quantum theory of atoms in molecules\textsuperscript{41} as privileged quantum-mechanical exchange channels.\textsuperscript{32}

Although DAFH and EDF analyses seem to be unrelated at first, and their results have been presented in an independent manner up to now, the three previous paragraphs point toward a possible link between them. The aim of this article is to uncover it. We are going to show how, for single-
determinant wave functions and a two-domain partitioning of space ($\Omega$ and $\Omega'$), the molecular orbitals that diagonalize the DAFH (the so-called DAFH molecular orbitals), $\phi_i$, and their occupation numbers, $n_i$, fully determine the EDF.

We will also show how the EDF, when expressed in terms of DAFH orbitals, is given by a simple product of individual effective electron probabilities, immediately related to the occupation numbers, $n_i$, of the DAFH orbitals originally defined by Ponec. These effective coarse-grained electrons are thus statistically independent, and provide a novel, in our opinion physically clear, interpretation of the $\bar{n}_i$, originally defined by Ponec. These effective coarse-grained electrons distinguishability of electrons. For a given $\bar{m}$, the DAFH, introduced by Ponec, and later applied to analyze chemical bonding in molecules, is defined as a physically meaningful way to coarse-grain the dependence of the hole on the reference electron at $r_1$. This is done by averaging its position over a given spatial domain $\Omega$,

$$p_\Omega(r_2) = \rho(r_2) - \frac{\rho_1(r_1,r_2)}{\rho(r_1)},$$

is the difference between the full electron density at point $r_2$, $\rho(r_2)$, and the conditional density that an electron lies at $r_2$ when another electron is at $r_1$, $\rho_1(r_1,r_2)/\rho(r_1)$, and neatly summarizes the effects of electron correlation. Notice that we are using the following normalization for the spinless second order density matrix, $\rho_2(r_1,r_2)$:

$$\rho_2(r_1,r_2) = 2 \left( \frac{N}{2} \right) \int |\psi|^2 dr_1 dr_2 dx_3 \cdots dx_N,$$

and that, for single-determinant descriptions, the hole only does contain correlation effects coming from antisymmetry, being then known as the Fermi hole.

Upon this, the DAFH, introduced by Ponec, and later applied to analyze chemical bonding in molecules, is defined as a physically meaningful way to coarse-grain the dependence of the hole on the reference electron at $r_1$. This is done by averaging its position over a given spatial domain $\Omega$,

$$p_\Omega(r_2) = \rho(r_2) - \frac{\rho_1(r_1,r_2)}{\rho(r_1)} dr_1.$$

Irrespective of the definition of $\Omega$, the integration of $p_\Omega(r_2)$ over $\mathbb{R}^3$ gives +1 electron. Since it is best for our present purposes to work with a quantity that integrates to the average number of electrons contained in $\Omega$, $N_\Omega = \int_\Omega \rho(r) dr$, a charge weighted DAFH (simply DAFH in what follows) is generally introduced: $G_\Omega(r_2) = N_\Omega p_\Omega(r_2)$. Separating the Coulombic and exchange-correlation parts of the second order density matrix, $\rho_2(r_1,r_2) = \rho(r_1) \rho(r_2) - \rho_{\Sigma}(r_1,r_2)$, $G_\Omega(r_2)$ can be recast in the following simple form:

$$G_\Omega(r_2) = \rho_{\Sigma}(r_1,r_2) dr_1.$$

$G_\Omega$ displays a large number of interesting properties. First, from its definition, $\int G_\Omega(r) dr = N_\Omega$, and for an exhaustive partition of space into disjoint domains, $\Sigma G_\Omega(r) = \rho(r)$, so the set of all DAFHs provides a partition of the density at each point in space into domain contributions. Let us now

II. METHODOLOGY

A. EDFs

Given a $N$-electron system described by a wave function $\Psi$ and a disjoint and exhaustive partition of the real space into $m$ domains $\Omega_m$ ($\bigcup_{m=1}^m \Omega_m = \mathbb{R}^3$), the probability that exactly $n_1$ electrons lie inside $\Omega_1$, $n_2$ electrons in $\Omega_2$, ..., and $n_m$ electrons in $\Omega_m$ ($0 \leq n_i \leq N$, $n_1 + n_2 + \cdots + n_m = N$) is given by

$$p(S) = \int_D |\Psi|^2 dr_1 \cdots dr_N,$$

where $S = \{n_1, n_2, \cdots \}$ defines a real space resonance structure (RSRS), the summation over the spin variables $\sigma_i$ ($i=1,N$) has been implicitly assumed, $D$ is a multidimensional domain in which the first $n_1$ electrons are integrated over $\Omega_1$, the second $n_2$ electrons over $\Omega_2$, etc., and $N = N_1!/(n_1!1!\cdots n_m!)$ is a factor that accounts for the indistinguishability of electrons. For a given $(N,m)$ pair, there are $N_\Omega = (N+m-1)!/[(N-1)!]$ RSRSs, and the set of all the $p(S)$ values defines the EDF of the system.

We have recently developed a method to obtain the EDF for multideterminant wave functions and an arbitrary number of spatial domains. A further extension has also been worked out that allows us to obtain the spin-resolved EDFs, i.e., to separately compute the probabilities that the $N^\alpha$ $\alpha$ electrons and $N^\beta$ $\beta$ electrons are distributed according to the structure $S = \{n_1^\alpha, \ldots, n_m^\alpha, n_1^\beta, \ldots, n_m^\beta\}$, where $n_i^\alpha + n_i^\beta = n_i$, $\sigma = \alpha, \beta$.

For our present purposes, however, only single-determinant wave functions of the form $\Psi(1,N) = \det[\psi_1(1) \psi_2(2) \cdots \psi_N(N)]$, and two-domain space partitions, $\Omega_1 = \Omega$ and $\Omega_2 = \Omega' = \mathbb{R}^3 - \Omega$ will be needed. Assuming that the $\psi_i$’s set is orthonormal, the probability that $n$ electrons lie in $\Omega$ and $N-n$ electrons in $\Omega'$ can be shown to be

$$p_{\Omega}(n) = \Lambda^{-1} \sum_{q \in S_n} \det[\tilde{S}_{ij}(q)],$$

where $\Lambda = n!(N-n)!$, $S_n$ is the set of $N!$ permutations of $(1,2,\ldots,N)$, and $q = (q_1,\cdots,q_n)$ one of these permutations. Each element $\tilde{S}_{ij}(q)$ is given by $S_{ij}(\psi)$ or $1-S_{ij}(\psi)$ depending on whether $(q_1 \leq q_n)$ or $(n < q_n \leq N)$, respectively, and $S_{ij}(\psi) = \langle \psi | \psi \rangle_{\Omega_i}$ is the domain overlap integral between spin-orbitals $\psi_i$ and $\psi_j$ (the integration over the spin variable is also implicitly assumed). Efficient recursive formulas for computing all the $p_{\Omega}(n)$’s have been given by Savin et al.
recall that when the exchange-correlation hole for a reference electron lying in \( \Omega \) is fully contained in \( \Omega \) itself, this domain contains a set of strictly localized electrons. With this, the maximum value of \( f_1 \mathcal{G}^\Omega(r)dr \), equal to \( N_\Omega \), is only attained in the case of strict localization. We may thus consider that the \( N_\Omega \) average electrons in the \( \Omega \) domain may be divided into localized, \( F(\Omega,\Omega) \), and delocalized, \( F(\Omega,\Omega^\prime) \) contributions, with \( F(\Omega,A) = \int_A \mathcal{G}^\Omega(r)dr \)

\[
N_\Omega = F(\Omega,\Omega) + F(\Omega,\Omega^\prime).
\] (7)

These two terms are equal to the localization, and half the delocalization indices introduced by Bader and Stephens, respectively. Despite their usefulness, DAFHs have been scarcely used up to now, mainly in single-determinant closed-shell molecules. An extension to open-shell systems has recently been formulated, but their spread to multiconfiguration descriptions is severely compromised by the limited computational availability of \( p^\Omega \). In these cases, an approximate DAFH that uses the domain overlap integrals between the natural molecular orbitals and their electron populations has also been recently proposed.14

C. DAFHs for single-determinant wave functions

Since, as we are going to show, the algebraic link between EDFs and DAFHs is only exact in the case of single-determinant descriptions, we will now work out the particular form that the DAFH acquires when \( \Psi(1,N) \) is given as

\[
\Psi(1,N) = \det[\varphi_1(1)\varphi_2(2) \ldots \varphi_N(N)].
\] (8)

Here, \( \varphi_i(x) \) is a spin orbital with spin \( \alpha \) for \( 1 \leq i \leq N^\alpha \) and spin \( \beta \) for \( N^\alpha + 1 \leq i \leq N^\alpha + N^\beta = N \), where \( N^\alpha \) and \( N^\beta \) are the number of \( \alpha \) and \( \beta \) electrons, respectively. We should notice that our treatment holds for an arbitrary Slater determinant and not only for restricted closed- or open-shell cases. In other words, we do not enforce \( N_\alpha \) to be necessarily equal to \( N_\beta \) and, even when \( N^\alpha = N^\beta = N/2 \), \( \varphi_i \) and \( \varphi_{i+N/2} \) are not forced to share the same spatial function.

It is now straightforward to obtain an expression \( \mathcal{G}^\Omega(r) \) in terms of these orbitals

\[
\mathcal{G}^\Omega(r) = \sum_{i,j} \varphi_i(r)S_{ij}(\varphi)\varphi_j^\alpha(r),
\] (9)

where \( S(\varphi)=\langle \varphi|\varphi \rangle_\Omega \) is the domain overlap matrix between the \( \varphi_i \)'s, which turns out to be diagonally blocked into \( \alpha \) and \( \beta \) submatrices, \( S^\alpha(\varphi) \) and \( S^\beta(\varphi) \), as a result of spin orthogonality, and \( \varphi_i \) and \( \varphi_j \) represent from now on the spatial parts of the corresponding spin orbitals \( \varphi_i^\alpha \) and \( \varphi_j^\beta \) in Eq. (8).

The above expression is bilinear in the occupied orbitals, and may be further simplified if the \( S(\varphi) \) matrix is diagonalized through an unitary transformation, \( U^\dagger U = \mathbf{1} \), such that \( S(\varphi)U = \mathbf{U} \). The eigenvectors define a new occupied orbital basis \( \varphi \), the DAFH orbitals, \( \mathbf{U} = \check{\varphi} \mathbf{U} \). In this basis \( \mathcal{G}^\Omega(r) \) becomes

\[
\mathcal{G}^\Omega(r) = \sum_{i=1}^N n_i|\varphi_i(r)|^2.
\] (10)

Since \( \mathcal{G}^\Omega \) may be seen as a domain restricted first order density, and the \( n_i \) eigenvalues satisfy \( 0 \leq n_i \leq 1 \) and add to the domain electron population, \( \Sigma n_i = N_\Omega \), each \( n_i \) was called by Ponec the DAFH orbital occupation number.

The \( \varphi \) basis is simultaneously orthonormal in \( \mathbb{R}^3 \) and orthogonal in \( \Omega \). Moreover, in this case where \( \mathbb{R}^3 \) has been partitioned in only two disjoint domains \( (\Omega \cup \Omega^\prime = \mathbb{R}^3) \) we have \( \check{S}(\varphi) = \langle \varphi|\varphi \rangle_\Omega = \mathbf{1} - \check{S}(\varphi) \), so that \( \mathbf{U} \) also diagonalizes \( \check{S}(\varphi) \), with \( \mathbf{1} - \mathbf{n} \) as its eigenvalue matrix. The DAFH orbital basis \( \varphi \) is thus common for both the \( \Omega \) and \( \Omega^\prime \) domains, and \( \mathcal{G}^\Omega(r) = \sum (1-n_i)|\varphi_i(r)|^2 \).

In summary, any \((i,j)\) pair of equal-spin DAFH orbitals satisfy

\[
\langle \varphi_i|\varphi_j \rangle_{\mathbb{R}^3} = \delta_{ij},
\] (11)

\[
\langle \varphi_i|\varphi_j \rangle_{\Omega} = \delta_{ij} n_i,
\] (12)

\[
\langle \varphi_i|\varphi_j \rangle_{\Omega^\prime} = \delta_{ij}(1-n_i).
\] (13)

Since the \( \varphi \) orthonormal basis expands the same Slater determinant as the \( \varphi \) basis does, \( \rho(r) = \sum_n |\varphi_i(r)|^2 \), and each \( \varphi_i \) contributes exactly with one full electron to \( \rho \). Together with Eq. (12), this fact shows that the \( n_i \) eigenvalues admit another clear interpretation: the fraction of the effective electron described by \( \varphi_i \) that lies within \( \Omega \).

For single-determinant open-shell wave functions, \( \mathcal{G}^\Omega(r) \) may straightforwardly be rewritten as \( \mathcal{G}^\Omega(r) = \mathcal{G}_\alpha^\Omega(r) + \mathcal{G}_\beta^\Omega(r) \), where

\[
\mathcal{G}_\alpha^\Omega(r) = \sum_{i,j \in \alpha} \varphi_i(r)S_{ij}(\varphi)\varphi_j^\alpha(r),
\] (14)

and \( i \) and \( j \) run only over orbitals with \( \alpha \) or \( \beta \) spins. The DAFH orbitals may thus be generated for \( \alpha \) and \( \beta \) electrons independently.13

D. Relationship between EDF and DAFH

To uncover the relationship between DAFHs and EDFs, we notice that Eq. (2), which defines the EDF probabilities, does only rely on the domain restricted overlaps obtained from the one-electron functions appearing in Eq. (8). The invariance of single-determinant wave functions under unitary transformations of the occupied spin orbitals allows us to use directly Eq. (2) with the DAFH basis, \( \varphi \). In this basis, and thanks to the orthogonality properties of the DAFH orbitals, the domain restricted \( S \) matrix is diagonal, both in \( \Omega \) and \( \Omega^\prime \), with diagonal values \( \lambda_i \) equal to \( n_i \) or \( 1-n_i \), respectively. The determinant of the matrix becomes, thus, trivial. The \( p^\Omega(\text{ni}) \) probability of Eq. (2), describing the event that exactly \( n \) electrons lie in \( \Omega \) and \( N-n \) electrons in \( \Omega^\prime = \mathbb{R}^3-\Omega \), is then a sum of \( N! \) products of \( N \) DAFH occupation numbers.
Taking into account the probabilistic interpretation of the DAFH occupation numbers introduced in the last subsection
\(N_i = \langle \phi_i | \phi_i \rangle \) is the probability that the effective electron described by \(\phi_i \) lies in \(\Omega \), the above expression admits a straightforward interpretation.

Since electrons 1 to \(n \) reside in \(\Omega \), and electrons \(n + 1\) to \(N \) in \(\Omega'\), any restricted permutation of these two disjoint subsets will provide a common \(\prod_{i=1}^{N} S_n(q_i)\) value. The number of these permutations is \(\Lambda=n!(N-n)!\), canceling the overall \(\Lambda^{-1}\) factor in Eq. (15). \(p_\Omega(n)\) is thus the sum of \(\binom{N}{n}\) terms of the form \(\prod_{i=1}^{n} \lambda_i\). Each of them describes the probability of a joint event in which every electron, described by one of the \(N\) DAFH orbitals, is statistically independent of the others, and lies either in \(\Omega \) or in \(\Omega'\) with probability \(\lambda_i\). The overall \(p_\Omega(n)\) is thus obtained as the classical probability that a set of \(N\) independent objects (electrons), with probabilities \(n_i\) and \(1-n_i\) to lie in two domains \(\Omega \) and \(\Omega'\) is partitioned such that \(n\) of these objects are found in the first, and \(N-n\) in the second domain.

Thus, if we start with the one-particle EDF \(p_i(x)\), describing the probability that an electron associated to the \(i\)th DAFH orbital lies in \(\Omega \) or \(\Omega'\), the full \(N\) electron distribution function is simply obtained as the \(2^N\)-dimensional vector \(p_N = \sum_{i=1}^{N} p_i\), i.e., the direct product of the \(N\) independent \(p_i\)’s.

We may clarify these ideas with a simple fully developed example, in which we have three electrons. Then,
\[
p_\Omega(0) = (1-n_1)(1-n_2)(1-n_3),
\]
\[
p_\Omega(1) = n_1(1-n_2)(1-n_3) + (1-n_1)n_2(1-n_3)

+ (1-n_1)(1-n_2)n_3,
\]
\[
p_\Omega(2) = n_1n_2(1-n_3) + n_1(1-n_2)n_3 + (1-n_1)n_2n_3,
\]
\[
p_\Omega(3) = n_1n_2n_3.
\]

Notice how, for instance, \(p_\Omega(1)\) is the sum of the probabilities of the three events in which one electron lies in \(\Omega \) and the other two in \(\Omega'\).

In summary, we have shown that if \(S(1,2)\) is a single Slater determinant, the DAFH orbitals of an arbitrary domain \(\Omega\) may be understood as describing statistically independent coarse-grained effective electrons. It is also clear that, taking into account that \(S\) is blocked into \(\alpha\) and \(\beta\) diagonal terms, the same arguments apply to the \(\alpha\) and \(\beta\) sets on their own, and that the full \(N\)-electron EDF is a direct product of statistically independent \(\alpha\) and \(\beta\) components. Using a thermodynamic analogy, \(\alpha\) and \(\beta\) electrons do not sense each other at the single-determinant level, much in the same way as gases \(A\) and \(B\) in an ideal mixture.

Hence, the spin-resolved probability that exactly \(n^\alpha\) \(\alpha\) and \(n^\beta\) \(\beta\) electrons lie within \(\Omega\) (and, consequently, that \(N^\alpha-n^\alpha\) \(\alpha\) electrons and \(N^\beta-n^\beta\) \(\beta\) electrons are contained in \(\Omega'\)) is obtained as
\[
p_\Omega(n^\alpha; n^\beta) = \prod_{i=1}^{n^\alpha} p_i^\alpha \prod_{j=1}^{n^\beta} p_j^\beta,
\]
where \(p_i^\alpha(n^\alpha)\) and \(p_j^\beta(n^\beta)\) are given by equations analogous to Eq. (15),
\[
p_\alpha(n^\alpha) = \Lambda_{\alpha}^{-1} \sum q_{\alpha,i} \prod_{q_{\alpha,i}} \mu_\alpha(q_i), \quad 1 \leq i \leq N^\alpha,
\]
\[
p_\beta(n^\beta) = \Lambda_{\beta}^{-1} \sum q_{\beta,i} \prod_{q_{\beta,i}} \mu_\beta(q_i), \quad N^\alpha < i \leq N.
\]

Here, \(\Lambda_{\sigma} = [\sigma!(N^\sigma-n^\sigma)!]\) \((\sigma=\alpha, \beta)\), \(q_{\alpha,i}\) and \(q_{\beta,i}\) run over all the restricted permutations of the \(N^\alpha\) and \(N^\beta\) electrons, respectively, and the \(\mu_\sigma\) are given as follows: \(\mu_\sigma = n_i\) for \(q_i\) \(\leq n^\sigma\) and \(\mu_\sigma = 1-n_i\) for \(q_i > n^\sigma\) in Eq. (21), and \(\mu_\sigma = n_i\) for \(N^\sigma < q_i \leq N^\alpha + n^\beta\) and \(\mu_\sigma = 1-n_i\) for \(q_i > N^\alpha + n^\beta\) in Eq. (22).

Equation (20) shows the statistical independence of the \(\alpha\) and \(\beta\) subsets of electrons. Needless to say, the \(p_\alpha(n^\alpha)\) and \(p_\beta(n^\beta)\) EDFs are equal for closed-shell determinants, but different for open-shell ones.

The set of \(p_\Omega(n^\alpha; n^\beta)\)’s for all possible values of \(n^\alpha\) and \(n^\beta\) define the spin-resolved EDF of the system. From it, \(p_\Omega(n)\) is obtained by adding all the \(p_\Omega(n^\alpha; n^\beta)\)’s for which \(n^\alpha+n^\beta = n\).

### E. Chemical bonding indicators from DAFH orbitals

Let us now merge the ideas explained in the previous subsections to show how we may chemically interpret our results. As we have been showing in recent works, the use of EDFs introduces a very appealing statistical interpretation of chemical bonding.

First, let us examine the interfragment delocalization or shared-electron distribution index, which, as explained in Sec. II B, measures the amount of electronic charge (measured in pairs of electrons due to the symmetrization of the \(F\)'s) that is delocalized between domains \(\Omega \) and \(\Omega'\). Delocalization indices are the real space analogs of standard bond orders in orbital space. Recalling Eqs. (10)-(13), a direct consequence of the statistical independence of the effective electrons described by the \(\phi\) orbital basis is the exact partition of \(\delta_{\Omega,\Omega'}\) into orbital contributions
\[
\delta_{\Omega,\Omega'} = \sum_{i=1}^{N} \delta_i \delta_{\Omega,\Omega'} = 2 \sum_{i=1}^{N} n_i(1-n_i).
\]

The above expression provides appealing pictures of the origin of any sizeable contribution to the bond order between two real space domains. From Eq. (23), whenever a DAFH orbital is extremely localized either in \(\Omega\) \((n=1)\), or in \(\Omega'\) \((n=0)\), its contribution to \(\delta_{\Omega,\Omega'}\) will be negligible. This is the case for almost all core orbitals, and also for many of the valence ones. Only an orbital that delocalizes over the two \(\Omega, \Omega'\) regions will provide a sensible contribution to \(\delta\), its maximum being attained in the case of complete delocalization, \(n=1/2\), which (save by accident) will only occur for domains equivalent by symmetry. In this case, each fully delocalized electron will contribute 1/2 to the overall \(\delta\).

An important point does also follow. According to this view, covalency results from delocalization of single elec-
trons, thus covering two-center one-electron links. In H\textsubscript{2}\textsuperscript{+}, for instance, \( \delta^{\Omega} = 1/2 \), in agreement with naive interpretations. Moreover, since for restricted closed-shells every \( \alpha \phi_i \) has an equivalent \( \beta \) counterpart, the effective electrons contributing to \( \delta \) form bonding pairs. It is the Pauli principle that forces closed-shell electrons to go into \( \alpha \) - \( \beta \) pairs for single-determinant wave functions, and thus the responsible for the electron pair.

A statistical connection to EDFs is also made evident when we notice that each \( n_i(1-n_i) \) term in Eq. (23) may be reinterpreted as the covariance of the one-electron distribution function \( p_i = (n_i,1-n_i) \) introduced above. Using \( p_i(1,0) \) and \( p_i(0,1) \) as the probabilities that electron \( i \) lies either in \( \Omega \) or in \( \Omega' \), respectively, \( \text{cov} (p_i) \) is

\[
\text{cov}(p_i) = -p_i(1,0) \times p_i(0,1) = -n_i(1-n_i),
\]

so \( \delta^{\Omega} \Omega' = -2 \sum_i \text{cov}(p_i) \), where \( \text{cov}(p_i) \) is the covariance of the electron described by \( \phi_i \). This shows that, as a result of the statistical independence of the effective DAFH electrons, the covariance of the full \( N \) electron DAFH, which is already known to be related to \( \delta \) through the relation \( \delta^{\Omega} \Omega' = -2 \text{cov}(p_i) \), may be divided into one-electron fluctuation contributions.

Bond orders are not the only indices that get an interpretation from DAFH analyses. They also serve the purpose of decomposing the interaction energy between the \( \Omega \) and \( \Omega' \) domains in our interacting quantum atoms approach.44,45,46 We have shown how the covalent-like contribution to that interaction energy is given by the exchange-correlation contribution

\[
\mathcal{V}^{\Omega \Omega'}_{xc} = \int_\Omega \int_{\Omega'} dr_1 dr_2 \rho_\upsilon^i(r_1, r_2),
\]

the quantum-mechanical glue that drives binding in the absence of charge-transfer. Writing our single-determinant wave functions again in the \( \phi \) basis (for a closed-shell determinant), \( \rho_\upsilon^i(r_1, r_2) \) may be recast as

\[
\rho_\upsilon^i(r_1, r_2) = 4 \sum_{\alpha \beta = j} \Phi_i(\alpha_1, \beta_1) \Phi_j(\alpha_1, \beta_1) \Phi_j(\alpha_2, \beta_2) \Phi_j(\alpha_2, \beta_2).
\]

Since the DAFH basis is orthogonal in both \( \Omega \) and \( \Omega' \), any nondiagonal component of \( \mathcal{V}^{\Omega \Omega'}_{xc} \) will be small, in general: contributions coming from regions with a positive value of the product \( \Phi_i(\alpha_1, \beta_1) \Phi_j(\alpha_1, \beta_1) \) in \( \Omega \) and/or \( \Omega' \) tend to compensate others coming from regions with a negative value of this product. Diagonal terms \( i = j \) will also contribute vanishingly to \( \mathcal{V}^{\Omega \Omega'}_{xc} \) when \( \phi_i \) is very localized in \( \Omega \) or \( \Omega' \), due to the negligible value of \( \Phi_i(\alpha_1, \beta_1) \Phi_j(\alpha_1, \beta_1) \) within \( \Omega' \) in the first case, and to the negligible value of \( \Phi_i(\alpha_1, \beta_1) \Phi_j(\alpha_1, \beta_1) \) in the second.

We are thus led to the conclusion that not only delocalized DAFH orbitals drive the final value of \( \delta^{\Omega \Omega'} \) (bond order), they also control the covalent interaction between the domains through the large \( \mathcal{V}^{\Omega \Omega'}_{xc}(ii) \) diagonal contributions. In most cases, the full \( \mathcal{V}^{\Omega \Omega'}_{xc} \) value will be very approximately equal to a sum of components running only over delocalized orbitals.

Notice also that \( \phi_i \)’s with large contributions to \( \delta \) will also provide large contributions to \( V_{xc} \), so a bond order-bond energy correlation will also exist.

Finally, we would like to add that due to our present modeling conditions (two-fragments, single-determinant descriptions), our expression for \( \delta^{\Omega \Omega'} \) coincides with the covalent bond order \( P^{\Omega \Omega'} \) defined by Cioslowski and Mixon [see Eq. 10 of Ref. 26]. This agreement shows that there must exist a link between the DAFH analysis and the isopycnic localization procedure of Cioslowski, from which the \( P^{\Omega \Omega'} \)’s come from. This connection will be published elsewhere.49

### III. RESULTS AND DISCUSSION

We have considered several test cases to analyze the close relation between their DAFH occupation numbers \( n_i \) and EDFs. These include closed-shell molecules with an electronic ground state described by a single-determinant and two simple open-shell systems, the \( B_2 \) and \( O_2 \) molecules in their \( ^3\Sigma_g^+ \) and \( ^3\Sigma_u^- \) ground states, respectively. The chosen closed-shell systems are the homonuclear diatomic molecules \( A_2 \) (\( A = H, He, Li, Be, C, N, F \)), the second-row hydrides \( A_2H_n \) (\( A = Li, Be, B, C, N, O, F \)), the HCN molecule, and the \( C_2H_6 \) (\( n = 6, 4, 2 \)) molecules. All the electronic structure calculations have been performed with the GAMESS code at the Hartree–Fock level, using standard 6-311G(d,p) basis sets, except in \( N_2 \) and \( O_2 \) where a 6-311G(d,p++) basis was used, and the HCN and \( C_2H_6 \) (\( n = 6, 4, 2 \)) molecules, where the standard TZV(d,p)++ one was employed. All DAFH and EDF analyses have been obtained through our EDF code.

#### A. Diatomic molecules

We have collected in Table I the electronic states and configurations of the diatomics in which Hartree–Fock wave functions have been obtained. We will identify both nuclei with the \( A \) and \( A' \) labels. The results of our DAFH analysis are summarized in Table II, and may be best understood by examining the behavior of the \( \alpha \) and \( \beta \) subsets separately.

Let us start with \( H_2 \). Here, the \( \alpha \) and \( \beta \) sets have 1 electron, and the domain overlap matrix that has to be diago-

### Table I. Electronic configurations and states of homonuclear diatomic molecules used in the Hartree–Fock calculations.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}</td>
<td>(^1\Sigma_g^+)</td>
<td>( 1\sigma_g^+ )</td>
</tr>
<tr>
<td>He\textsubscript{2}</td>
<td>(^1\Sigma_u^+)</td>
<td>( 1\sigma_u^+ = KK )</td>
</tr>
<tr>
<td>Li\textsubscript{2}</td>
<td>(^1\Sigma_g^+)</td>
<td>( KK )</td>
</tr>
<tr>
<td>Be\textsubscript{2}</td>
<td>(^1\Sigma_g^+)</td>
<td>( KK\sigma_0^+ )</td>
</tr>
<tr>
<td>B\textsubscript{2}</td>
<td>(^3\Sigma_g^+)</td>
<td>( KK\sigma_0^+\sigma_1^+\sigma_1^+\sigma_1^+ )</td>
</tr>
<tr>
<td>C\textsubscript{2}</td>
<td>(^1\Sigma_g^+)</td>
<td>( KK\sigma_0^+\sigma_1^+\sigma_1^+\sigma_1^+ )</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>(^1\Sigma_g^+)</td>
<td>( KK\sigma_0^+\sigma_2^+\sigma_2^+\sigma_2^+ )</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>(^3\Sigma_g^+)</td>
<td>( KK\sigma_0^+\sigma_2^+\sigma_2^+\sigma_2^+\sigma_2^+ )</td>
</tr>
<tr>
<td>F\textsubscript{2}</td>
<td>(^1\Sigma_g^+)</td>
<td>( KK\sigma_0^+\sigma_2^+\sigma_2^+\sigma_2^+\sigma_2^+ )</td>
</tr>
</tbody>
</table>

\[ V_{xc}^{\Omega \Omega'} = \sum_{i,j} V_{xc}^{\Omega \Omega'}(ii). \]
TABLE II. DAFH orbital occupation numbers ($n_i$), delocalization indices [$\delta_{g}^{A}(i)$] and $p_{g}^{A}(n\sigma)$ ($\sigma=\alpha, \beta$) probabilities for $A_2$ ($A$ = H, He, Li, Be, B, C, N, O, F) molecules at their respective equilibrium geometries (except in He$_2$, $R_{He-He}=4.0$ bohr). $\alpha$ and $\beta$ data are identical, except when specified otherwise.

<table>
<thead>
<tr>
<th></th>
<th>H$_2$</th>
<th>He$_2$</th>
<th>Li$_2$</th>
<th>Be$_2$</th>
<th>B$_2(\alpha)$</th>
<th>B$_2(\beta)$</th>
<th>C$_2$</th>
<th>N$_2$</th>
<th>O$_2(\alpha)$</th>
<th>O$_2(\beta)$</th>
<th>F$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_1$</td>
<td>0.5000</td>
<td>0.0039</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td>$n_2$</td>
<td>0.9961</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>$n_3$</td>
<td>0.5000</td>
<td>0.0025</td>
<td>0.1555</td>
<td>0.1555</td>
<td>0.1869</td>
<td>0.0053</td>
<td>0.0051</td>
<td>0.0051</td>
<td>0.0054</td>
<td>0.0054</td>
<td></td>
</tr>
<tr>
<td>$n_4$</td>
<td>0.9975</td>
<td>0.8444</td>
<td>0.8444</td>
<td>0.8131</td>
<td>0.9947</td>
<td>0.9949</td>
<td>0.9949</td>
<td>0.9949</td>
<td>0.9949</td>
<td>0.9949</td>
<td></td>
</tr>
<tr>
<td>$n_5$</td>
<td>0.4998</td>
<td>0.5000</td>
<td>0.5000</td>
<td>0.0300</td>
<td>0.5000</td>
<td>0.139</td>
<td>0.9861</td>
<td>0.9861</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_6$</td>
<td>0.4998</td>
<td>0.5000</td>
<td>0.5000</td>
<td>0.9700</td>
<td>0.5000</td>
<td>0.9861</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_7$</td>
<td>0.5000</td>
<td>0.0300</td>
<td>0.5000</td>
<td>0.0139</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_8$</td>
<td>0.5000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_9$</td>
<td>0.5000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Turning to Li$_2$, each spin-block is 3 electrons in size. In the $1\sigma_g$, $1\sigma_u$, $2\sigma_g$ basis, the overlap matrix is

$$S^g = \begin{pmatrix} 0.5 & 0.5 & 0.0 \\ 0.5 & 0.5 & \approx 0.0 \\ 0.0 & \approx 0.0 & 0.5 \end{pmatrix}.$$  (28)

The two $\sigma_g$ orbitals are orthogonal in $\Omega$, and $1\sigma_u$ is almost orthogonal to $2\sigma_g$. The three eigenvalues of $S^g$ turn out to be $0.0 \approx 0.0$, $\approx 1.0$, and $\approx 0.5$. In the same order, $\phi_1$ and $\phi_2$ are the extremely localized $1s$ cores of Li and Li’, and $\phi_3$ almost coincides with the maximally delocalized $2\sigma_g$ canonical orbital. Only this function contributes to bonding.

This behavior is quite general. In Be$_2$, aside from the extremely localized $1s$ cores, we have a situation similar to He$_2$: there are two very localized almost $2s$ hybrids, $\phi_3$ and $\phi_4$, with eigenvalues close to 0 and 1, respectively, and a negligible overall delocalization index. Hence, in the DAFH image, H$_2$ and Li$_2$ are well described by a single bond, whereas He and He’, or Be and Be’, are only linked by a residual bond at the HF level. The $\delta_{g}^{A}(i)$ values in Table II corroborate this.
B₂ is the first open-shell determinant we examine. Except for φ₁ and φ₂, which do only exist in the α block, all the other DAFH orbitals are common to the α and β sets of electrons. The first two, φ₁ and φ₂, are again the extremely localized 1σ cores of both atoms, φ₁ = 1σₓ ± 1σᵧ, and do not contribute to δ₁B₂. Similarly, φ₃ and φ₄ are mainly given by φ₂ = 2σₓ ± 2σᵧ, although a small contamination of 1σₓ and 1σᵧ is needed to achieve simultaneously the three orthogonality conditions, ⟨φ₃∥φ₄⟩=⟨φ₁∥φ₂⟩₁ = 0. Contrarily to the Be₂ case, Pauli exclusion does not completely the valence electrons in B₂, and about 16% of φ₄ (φ₃) is localized on B(′). Thus, two symmetrical components contribute significantly (overall 0.5252) to δ₂B₂. These orbitals are essentially identical to the electrons. The first two, there are four different electron pairs contributing to bond-

EDF coming from DAFH orbitals φᵣ with nᵣ close to 0, 0, pᵣ = (0, 1), or to 1, 0, pᵣ = (1, 0), may thus be safely excluded on computing the direct product leading to the full EDF pᵣ = ⊗ pᵣ. Localized electrons, such as cores in standard chemistry, may be excluded from EDF computations. The total distribution turns out as a product of the subset of independent bonding pᵣ's. In our diatomics there are only two types of these one-electron bonding EDFs: either homopolar full bonds, φᵣ, nᵣ = 0.5, pᵣ = (0.5, 0.5); or a ν link partially localized on atom A, φᵣ, nᵣ = a > 0.5, pᵣ = (a, 1–a) which is necessarily accompanied by its symmetric counterpart, ν with nᵣ = 1–a < 0.5, this time partially localized on A′.

The direct product of ν independent pᵣ's EDFs in each spin-block gives rise to symmetric binomial distributions (BDs) pᵣ(ν) = ν!/[ν!(ν–n)!!]. For ν = 1, 2, 3 we obtain pᵣ(1·ν) = (0.5, 0.5), pᵣ(1·ν) = (0.25, 0.25, 0.25), and pᵣ(1·ν) = (0.25, 0.5, 0.5, 0.25). As seen in Table II [H₂, Li₂, O₂(α), F₂ with ν = 1; B₂(α), C₂ with ν = 2; and N₂, O₂(β) with ν = 3] our results follow this BD rather well. Only B₂(β) falls somewhat far from these BDs.

For closed-shells, we may also easily construct standard α, β pairs. In the case of homopolar links, each of them results to a spinless two-electron BD pᵣ = (0.25, 0.5, 0.25, 0.25), which is classified as a noncorrelated homopolar normal bond in a statistical classification reported earlier. Similarly, the set of four DAFH spin orbitals coming from a ν link ends up in two equivalent bonds with the following two-electron EDF: pᵣ = [a(1–a), 1–2a(1–a), a(1–a)]. Each of these links is a correlated homopolar normal bond that contributes to δ with 4b, b = a(1–a), and with correlation factor f = (1–2b)/2b(1–b). Bonding in a general closed-shell diatomic in this view comes from a number of isolated uncorrelated α, β pairs and a set of pairs of correlated bonds due to incompletely localized (or delocalized) pairs of electrons.

B. AHₙ hydrides

For all the AHₙ hydrides, except LiH and HF, the fragments Ω and Ω' can be defined in several ways. The results of our DAFH and EDF analysis using Ω=H and Ω' =AHₙ₋₁ are summarized in Table III. We notice in this table that only the φ₁ DAFH orbital has a non-negligible delocalization in both fragments, let us call it the valence bonding orbital (VBO). Its degree of localization in H decreases from LiH to HF (see row labeled n₁ in the table). Let us also skip
the rest of residual delocalizations, effectively considering that bonding in these cases is due to a single α, β pair, and study the effects of this simplification.

This DAFH image corresponds to a single polar bond between Ω and Ω′, with 0.949 electrons transferred from Li to H (which almost becomes a H− anion) in LiH, and more than 0.881 electrons transferred from H to F (which is almost a F− anion) in HF; i.e., the VBO evolves from a strong polarization toward the H atom in LiH, passing through a practically unpolarized covalent situation in CH₄ (n₁=0.489), toward a strongly F-polarized situation in HF. Notice that, were our simplification strictly true, the average number of electrons of each spin in H should be identical to n₁, the occupation number of the VBO. This is seen to be approximately true, the residual charge on this atom due to the rest of orbitals being always smaller than 0.044 electrons, the value found in BH₃. According to the above arguments δ₁=2n₁(1−n₁) gives, by far, the greatest contribution to δ₁^O^0 , so following the arguments posed in Sec. II, CH₄ displays the greatest δ₁^O^0 , since this hydride has the closest to 0.5 value of n₁.

With the assumption that n₁≠0 and n₁≠1, pₜ^H(n²) takes the values 1−n₁, n₁, 0,..., for n²=0,1,2,... These approximate probabilities are compared with the exact ones in Table III. The agreement is reasonably good, confirming again that, to a good precision, the H and AH₃−₁ fragments are linked through the delocalization of a single pair of electrons. Although this single bond model describes pretty well the bonding properties of these systems, it can be improved by assuming that the n₁≠1 are not zero, although much smaller than n₁. Calling ε=Σₙ=1^n,m, the improved probabilities pₜ^H(n²), up to first order in ε, are (1−ε)(1−n₁), n₁+ε(1−2n₁), εn₁,0,... for n²=0,1,2,3,... They add up exactly to 1.0 and their values, not shown in Table III, are equal to the exact results up to four decimal figures.

C. C₂Hₙ (n=6,4,2) hydrocarbons

The results of our DAFH and EDF calculations for C₂H₆, C₃H₄, and C₄H₂ are collected in Table IV. As it is evident from the n₁’s, all the DAFH MOs except φ₉ in C₂H₆, φ₇ and φ₅ in C₃H₄, and φ₅ and φ₃ in C₄H₂ are almost fully localized in Ω or Ω′. Thus the classical image of a single, double, and triple bond between the CH₃, CH₂, CH groups, respectively, emerges.

The delocalized DAFH MO φ₅ in C₂H₆ results from the mixture of the fully delocalized canonical MOs 2a₁, 3a₁, φ₅=0.512×2a₁+0.859×3a₁. The two MOs in each of the pairs (φ₁,φ₂), (φ₅,φ₆), and (φ₅,φ₆) are approximately given by the sum and the difference of only two canonical MOs, one of them gerade and the other ungerade, 1a₁±1a₂w for (φ₁,φ₂), 1eₓ±1eₙ for (φ₅,φ₆), and 2eₓ±2eₙ (degenerated with 1eₓ and 1eₙ) for (φ₃,φ₅). This result is analogous to that found in the diatomic molecules studied here (except H₂), where φ₁=1eₓ±1eₙ. Finally, φ₁ and φ₄ are given by linear combinations of the gerade 2a₁, and 3a₁, and the ungerade 2a₂, canonical MOs.

In C₃H₄, as in our previous diatomics, φ₁ and φ₂ coincide with the 1s cores of C and C’. They are the first two eigenvectors of the overlap matrix in the 1a₂, 2a₃, 3a₃, 2b₃, 3b₃ occupied basis, although both are practically given by φ₁=1b₁₃−1a₁, and φ₂=1b₁₃+1a₁. The pair (φ₅,φ₆), with φ₅ mainly localized along the C−H axis of one CH₂ and φ₆ localized along the C−H axis of the other, is obtained after diagonalizing the 2×2 block of the overlap matrix in the basis 1b₁₃, 1b₂₃. The delocalized orbital φ₅ is directly the fully delocalized 1b₁₃ canonical MO that forms an independent 1×1 block in the overlap matrix, and corresponds to

| TABLE III. α=β DAFH orbital occupation numbers (n₁), delocalization indices [δ₁=|^H^n|=i(1)], and pₜ^H(n²) (α=α, β) probabilities for the second-row hydrides AH₃ at their respective equilibrium geometries using Ω =H and Ω′=AH₃−₁. For each pₜ^H(n²), the exact (exact) and the approximate (approx.) value assuming that AH₃ has a single α (or β) valence electron are given. N^H is the number of electrons with spin σ (α=α, β) in H. |
|-----------------------------------------------|
|           |   LiH  | BeH₂  | BH₃   | CH₄   | NH₃   | H₂O   | HF     |
| n₁        | 0.9490 | 0.9129 | 0.8043 | 0.4890 | 0.3057 | 0.1880 | 0.1186 |
| n₂        | 0.0036 | 0.0114 | 0.0337 | 0.0131 | 0.0115 | 0.0059 | 0.0029 |
| n₃        | 0.0021 | 0.0097 | 0.0131 | 0.0060 | 0.0041 | 0.0029 | 0.0029 |
| n₄        | 0.0006 | 0.0022 | 0.0015 | 0.0012 | 0.0010 | 0.0000 | 0.0000 |
| N^H       | 0.9491 | 0.9264 | 0.8482 | 0.5175 | 0.3247 | 0.1993 | 0.1255 |
| δ₁        | 0.0987 | 0.1591 | 0.3148 | 0.4998 | 0.4245 | 0.3053 | 0.2091 |
| δ₂        | 0.0072 | 0.0225 | 0.0651 | 0.2599 | 0.2288 | 0.1118 | 0.0059 |
| δ₃        | 0.0043 | 0.0191 | 0.0259 | 0.119 | 0.083 | 0.0058 | 0.0058 |
| δ₄        | 0.0012 | 0.0045 | 0.0030 | 0.0024 | 0.0020 | 0.0000 | 0.0000 |
| δ₅        | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| δ₆        | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| δ₇        | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| δ₈        | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| δ₉        | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| δ₁₀       | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| δ₁₁       | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
the classical π bond of ethene. The other delocalized orbital ($\phi_3$), third eigenvector of the overlap matrix with negligible contributions from the 1a, 1b, and 2b orbitals, represents a C–C σ bond. Finally, $\phi_1$ is very localized on one CH group, and $\phi_2$ is very localized on the other.

The Hartree–Fock electronic configuration of C2H3 is $1\sigma^2_1 1\sigma^2_2 2\sigma^2_3 3\sigma^2_4 1\pi^2_{1u} 1\pi^2_{2u}$. The π orbitals do not mix with the σ ones and become directly the two maximally delocalized DAFH orbitals $\phi_1$ and $\phi_2$, each one contributing with 0.5 to $\delta_{\sigma}^{\Omega \Omega'}$. The σ orbitals form a $5 \times 5$ block. However, $1\sigma_1$ and $1\sigma_2$ have negligible overlaps with the other three and, in practical terms, form an independent $2 \times 2$ box, with the four elements equal to 0.5, as in H2. As before, its diagonalization leads to $n_1 = 0$ and $n_2 = 1$, and $\phi_1$ and $\phi_2$ are practically equivalent to the atomic 1s cores of carbon atoms. Neglecting them, the third maximally delocalized DAFH orbital ($\phi_3$) and the very localized $\phi_4$ and $\phi_5$ ones arise from diagonalizing the overlap matrix in the basis $2\sigma_3^2 3\sigma_4^2 4\sigma_5^2$. $\phi_3$ concentrates along the C–C axis and represents a σ bonding orbital between both CH fragments. $\phi_1$ ($\phi_2$) is highly concentrated on C(C') and (with an opposite sign) along the axis connecting this atom to H(H').

As shown, the homopolar EDFs for $N$ statistically independent electrons, Eqs. (16)–(19), are (0.5,0.5), (0.25,0.5,0.25), and (0.125,0.375,0.375,0.125) for $N=1$, 2, and 3, respectively. We can see in Table IV that the full EDFs for C2H6, C2H4, and C2H2 are very well reproduced by the above three model EDFs This recovers the classical 1, 2, and 3 bonding pairs. The small differences are due to contamination coming from electrons highly localized in $\Omega$ or $\Omega'$. The final image is clear: the DAFH effective electrons are self-localizing entities that map traditional chemical bonding ideas into quantitative pictures of bonding. When they are fully localized in a fragment (core electrons or/and electrons forming part of a lone pair or an intrafragment chemical bond) they are irrelevant in computing the EDF and the $\Omega-\Omega'$ delocalization index of the system. Electrons described by partially or fully delocalized DAFH orbitals contain the information needed to analyze interfragment chemical bonds. Besides this, in the DAFH view, these electrons are fully statistically independent.

**D. The HCN molecule**

The EDF and DAFH results for HCN with the partitions ($\Omega, \Omega'$)=(H,C,N) and ($\Omega', \Omega$)=(H,C,N) are collected in Table V. According to the first one, a single DAFH MO ($\phi_0$) is partially localized on H, $\phi_2$ and $\phi_5$ are very localized on CN, and the rest are almost fully localized also on this group. $\phi_0$ represents a H–N σ bond polarized toward CN, and $\phi_2$ and $\phi_5$, which contribute marginally to the H–CN bonding, are basically the $\pi_s$ and $\pi_y$ C–N valence orbitals. As corresponds to an unique delocalized orbital, the exact EDF is

<table>
<thead>
<tr>
<th>$\Omega, \Omega' = \text{(H,C,N)}$</th>
<th>$\Omega', \Omega = \text{(H,C,N)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma \equiv \beta$ DAFH orbital occupation numbers ($n_i$), delocalization indices [$\delta_i = \delta_{\sigma}^{\Omega \Omega'} (i)$], together with the number of $\sigma$ electrons in $\Omega$ ($n^\sigma$) and their $p_{\sigma}^{\Omega}(n^\sigma)$ probabilities for HCN at the equilibrium geometry. Two different definitions of $\Omega$ and $\Omega'$ are used.</td>
<td>$\sigma \equiv \beta$ DAFH orbital occupation numbers ($n_i$), delocalization indices [$\delta_i = \delta_{\sigma}^{\Omega \Omega'} (i)$], together with the number of $\sigma$ electrons in $\Omega$ ($n^\sigma$) and their $p_{\sigma}^{\Omega}(n^\sigma)$ probabilities for HCN at the equilibrium geometry. Two different definitions of $\Omega$ and $\Omega'$ are used.</td>
</tr>
</tbody>
</table>
| $\begin{array}{cccccc}
 i & n_i & \delta_i & n^\sigma & p_{\sigma}^{\Omega}(n^\sigma)_{\text{exact}} & p_{\sigma}^{\Omega}(n^\sigma)_{\text{apprx}} \\
 1 & 0.0000 & 0.0000 & 0 & 0.6131 & 0.6218 \\
 2 & 0.0073 & 0.0145 & 2 & 0.3819 & 0.3782 \\
 3 & 0.0073 & 0.0145 & 3 & 0.0000 & 0.0000 \\
 4 & 0.0000 & 0.0000 & 4 & 0.0000 & 0.0000 \\
 5 & 0.0000 & 0.0000 & 5 & 0.0000 & 0.0000 \\
 6 & 0.3782 & 0.4704 & 6 & 0.0000 & 0.0000 \\
 7 & 0.0003 & 0.0006 & 7 & 0.0000 & 0.0000 \\
\end{array}$ | $\begin{array}{cccccc}
 i & n_i & \delta_i & n^\sigma & p_{\sigma}^{\Omega}(n^\sigma)_{\text{exact}} & p_{\sigma}^{\Omega}(n^\sigma)_{\text{apprx}} \\
 1 & 0.0000 & 0.0000 & 0 & 0.0000 & 0.0000 \\
 2 & 0.0073 & 0.0145 & 2 & 0.6940 & 0.4247 \\
 3 & 0.0073 & 0.0145 & 3 & 0.6940 & 0.4247 \\
 4 & 0.0000 & 0.0000 & 4 & 1.0000 & 0.0000 \\
 5 & 0.0000 & 0.0000 & 5 & 0.0012 & 0.0025 \\
 6 & 0.3782 & 0.4704 & 6 & 0.0115 & 0.0228 \\
 7 & 0.0003 & 0.0006 & 7 & 0.9995 & 0.0010 \\
\end{array}$ |
relatively well reproduced by considering exclusively this orbital and ignoring the rest (compare columns 5 and 6 of Table V).

Regarding the second partition, $\phi_1$ represents a $\sigma$ orbital 80.6% localized on N and 19.4% on the HC group, whereas the equivalent $\phi_2$ and $\phi_3$, 69.4% localized on N and 21.6% on HC, coincide with the $\pi_x$ and $\pi_y$ canonical C–N bonding orbitals, not mixed with $\sigma$ ones in the overlap matrix. It is interesting to notice how each $\pi$ orbital, less polarized toward the N atom than the $\sigma$ orbital $\phi_1$, gives a larger contribution to $d_{\text{ECN}}$. Finally, as the last two columns of Table V show, the exact and approximate (this time considering only $\phi_1$, $\phi_2$, $\phi_3$) $P^0_{ij}(n^\alpha)$'s are very similar, confirming the existence of a triple bond between the HC and N fragments.

IV. SUMMARY AND CONCLUSIONS

We have shown in this paper how for single-determinant wave functions the molecular orbitals derived from the diagonalization of DAFHs, expanded in the canonical orbitals basis, provide statistically independent domain-averaged one-electron states. With them, full EDFs for space partitions containing two domains become direct products of one-electron contributions. This establishes a connection between two seemingly unrelated fields.

DAFH eigenvalues, frequently called occupation numbers of the DAFH orbitals, are given a novel statistical interpretation. We show that they determine the contribution of these one-electron states to the chemical bonding between the real space fragments in which the space is divided. Eigenvalues either close to 1.0 or to 0.0 correspond to DAFH orbitals almost fully localized on a real space domain or on its complementary, and do not contribute to bonding between the fragments. On the other hand, eigenvalues close to 0.5 correspond to maximally delocalized orbitals that participate significantly in the bonding.

Orbitals highly localized in a fragment, generally associated to core electrons or lone pairs of this fragment, can safely be ignored in the determination of the EDFs. Contrarily, delocalized orbitals, usually associated with valence electrons, suffice to determine with reasonable accuracy the final EDF of the system.

Tracing back the origin of the statistical independence of electrons when a single-determinant wave function is expressed in terms of DAFH orbitals, we are presently studying how to simplify the calculation of the EDFs. We are also exploring the relationship, if any, between DAFHs and EDFs beyond the single-determinant level, as well as in cases where the space partitioning contains any number of fragments.

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