Domain-Averaged Fermi Hole and Domain-Restricted Reduced Density Matrices: A Critical Comparison

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ABSTRACT: The knowledge of the properties and the applicability of domain-restricted matrices has provided important advances in the description of molecular electronic distributions. In this work, we perform a critical comparison between two different methods: the domain-averaged Fermi hole (DAFH) approach and the domain-restricted first-order reduced density matrix (DRRDM) one, focusing our study on both physical and mathematical points of view. Our results permit to show that both methods have a markedly different behavior at correlated wave function level: the DAFH approach provides information related with electron cloud localization and populations while the DRRDM is a true density matrix. To exemplify the theoretical discussion, we present a numerical test example and a simple analytical model that show such features. © 2010 Wiley Periodicals, Inc. Int J Quantum Chem 00: 000–000, 2010

Key words: reduced density matrices; population analysis

1. Introduction

The partitioning of electronic properties into contributions that are assigned to atoms or groups of atoms in a molecule has proven to be very powerful to describe molecular structures of systems with different kinds of bonding. The most extensively studied case is the partitioning of the N molecular electrons, known as population analysis [1–3]. To this end, two schemes attempting to perform this task have mainly been developed. Within the first scheme, the atoms are defined by means of one-electron basis functions centered at each nucleus; these methods constitute the techniques of partitioning in the Hilbert-space of atomic orbitals [1–5]. A second type of methodology is based on the partitioning of the three-dimensional physical space (3D), where an atom is defined as a nucleus surrounded by a surface. This surface can also be defined in different ways, that is, the "fuzzy" atom approach [6–9] uses atomic radii and "cutoff" parameters to partition the whole 3D physical space into atomic domains, while alternatively, the Bader's atoms in molecules (AIM) [10] and the electron localization function (ELF) [11, 12] models use topological properties of the electron distribution and the electron localization function to define these domains, respectively. The partitioning models implemented by means of the mentioned methodologies have been extended and applied to perform decompositions of other molecular properties usually expressed in terms of reduced density matrices [13, 14]. Examples of these types of studies are the decomposition of the number of electrons [15–22] and the partitioning of the molecular energy into one- and two-center contributions to describe quantitatively bonding energies and to provide a better insight of the interactions between the molecular groups and/or moieties [22–27]. Similarly, the partitioning of the squared-spin distribution $\langle S^2 \rangle$ [7, 28–32] gives rise to a wide and detailed chemical information.

Another case of interest to describe and analyze electronic structures is the partitioning of the electron density into meaningful chemical fragments. We will refer here to the partitioning of this density carried out in the 3D physical space. Within this scenario, we will analyze two previously reported models, the domain-averaged Fermi hole (DAFH) approach, which has been applied in the recent past to a wide-type of compounds [33, 34] and the domain-restricted first-order reduced density matrices (DRRDM) one [35–38], which has been recently developed, making special emphasis in the physical and mathematical requirements that a true density matrix must fulfill. The DAFH model in its correlated version, which requires the use of the second-order (2-RDM), has been implemented by some of us and reported in Ref. [39]. Nevertheless, to avoid the high computational cost of the 2-RDMs, Ponec and Cooper [34] have proposed a model, which approaches correlated DAFH by a symmetric DRRDM matrix, previously reported by us [35]. The central aim of this work is to perform a critical analysis of the differences between both models in the description of the electron distribution of a molecular system and hence to clarify their applicability.

The article is organized as follows. Section 2 is dedicated to summarize the decomposition of a reduced density matrix within the symmetric approach [35] to achieve the DRRDM and the derivation of the DAFH matrix for correlated wave functions in closed-shell systems [39]. We also show in this section that the so called pseudo-DAHF (pDAHF) in Ref. [33] is nothing but our previous published symmetric model approach for DRRDM. Section 3 is devoted to a theoretical and practical comparison and discussion of both the correlated DAFH and the DRRDM models from the mathematical and physical points of view, to show the consequences of their different physical nature [35, 36]. To this end, two simple examples are presented, which deal with the prominent essential differences between both methods and attempt to clarify their physical behavior. One of these examples shows the onset of negative eigenvalues for the correlated DAFH matrix even in simple systems [40] and the other one, of quasi-analytical character based on the valence bond (VB) method, compares the spatial localization of the electron cloud in both treatments. Finally, in the last section we report the concluding remarks.

2. Theoretical Background

In Ref. [35], we have reported a topological matrix decomposition of the spin-free first-order reduced matrix elements $^1D_j^i$, corresponding to an N-electron system described by a wave function Ψ as

$$^1D_j^i = \sum_\Omega {}^1D_j^i(\Omega) \qquad (1)$$

with

$$^1D_j^i(\Omega) = \sum_\sigma \sum_{k,l} \left({}^1D^{\frac{1}{2}} \right)_{k\sigma}^{i\sigma} S_l^k(\Omega) \left({}^1D^{\frac{1}{2}} \right)_{j\sigma}^{l\sigma}, \qquad (2)$$

where $i, j, \ldots$ are a set of orthonormal orbitals, σ is the spin coordinate (α or β) and $({}^1D^{\frac{1}{2}})^{i\sigma}_{k\sigma}$ means the elements of the positive square root matrix arising from the first-order reduced density matrix. $S^k_l(\Omega) = \langle k | l \rangle_\Omega$ are the overlap integrals over Bader domains Ω [10]. According to Bader's theory, the whole real space $\cup\Omega$, is partitioned into the domains Ω holding $\Omega \cap \Omega' = \emptyset$.

The elements ${}^1D^i_j(\Omega)$ in Eq. (2) define a DRRDM whose properties and foundations have been described in Refs. 35, 37. This matrix possesses similar features to those of the ordinary reduced density matrix; it is Hermitian and its trace is given by N_Ω, the number of electrons within the domain Ω. For singlets and other spin symmetry states having null spin projection, $S_z = 0$, the elements of the spin-free first-order reduced density matrix associated with the domain or region Ω can be calculated as [35]

$$ {}^1D^i_j(\Omega) = \sum_{k,l} \left({}^1D^{\frac{1}{2}} \right)^i_k S^k_l(\Omega) \left({}^1D^{\frac{1}{2}} \right)^l_j \qquad (3) $$

so that the spin coordinate σ can be ignored.

The same scenario permits to introduce the structure of DAFH at the correlated wave function level (correlated DAFH) $\Theta(\Omega)$, in the topological decomposition [39]. Regarding the spin-free structure of the ${}^2D$ (2-RDM) matrix for any arbitrary type of wave function, as [13, 41–45]

$$ {}^2D^{ik}_{jl} = \frac{1}{2} {}^1D^i_j {}^1D^k_l - \frac{1}{4} {}^1D^i_l {}^1D^k_j + \frac{1}{2} \Lambda^{ik}_{jl}, \qquad (4) $$

where Λ^{ik}_{jl} stands for the matrix elements of the 2-RDM cumulant [41–45], the matrix elements for $\Theta(\Omega)$ read [39]

$$ \Theta^i_j(\Omega) = \sum_{k,l} \left(\frac{1}{2} {}^1D^i_l {}^1D^k_j - \Lambda^{ik}_{jl} \right) S^k_l(\Omega) \qquad (5) $$

It is worthwhile to note that this magnitude does not refer to a particle density but to Fermi hole density coming from the fermion exclusion principle and from the interaction between the electrons. The structure of Eq. (5) permits to split the Θ matrix into two contributions [39]

$$ \Theta^i_j(\Omega) = \Theta^{(e)i}_j(\Omega) + \Theta^{(c)i}_j(\Omega), \qquad (6) $$

where

$$ \Theta^{(e)i}_j(\Omega) = \frac{1}{2} \sum_{kl} {}^1D^i_l {}^1D^k_j S^k_l(\Omega) $$

and

$$ \Theta^{(c)i}_j(\Omega) = -\sum_{kl} \Lambda^{ik}_{jl} S^k_l(\Omega). $$

The first term on the r.h.s. in Eq. (6) describes the exchange correlation while the last one represents the Coulomb correlation and both together constitute the correlated DAFH matrix. It may be noted that the exchange contribution $\Theta^{(e)i}_j(\Omega)$ is always present for any wave function. However, for a closed-shell wave function the irreducible many body effects represented through the cumulant term only appear in the case of correlated wave functions. All the cumulant elements vanish for a closed-shell Hartree–Fock wave function and hence both ${}^1D(\Omega)$ and $\Theta(\Omega)$ are coincident for this approach [35].

3. Comparison and Discussion of $\Theta(\Omega)$ and ${}^1D(\Omega)$ Models

Eqs. (3) and (5) express respectively the symmetric model for the domain-restricted first-order density matrix ${}^1D(\Omega)$ and the DAFH matrix $\Theta(\Omega)$, associated with a physical domain Ω. Both matrices have been proposed as tools for describing the electron distribution in a molecular system. The ${}^1D(\Omega)$ matrix is a true density matrix, that is, it is hermitian, positive semi-definite, bounded, has a finite trace [13], and is representable [37], which assures that there exists a wave function or a statistical ensemble, though unknown, from which it derives. The domains Ω define open systems, therefore, they may be described necessarily within the grand-canonical ensemble, and the necessary and sufficient conditions for a closed-shell system ${}^1D(\Omega)$ indicate that its eigenvalues, n^Ω_i must lie within the real interval $[0, 2]$, that is, $0 \leq n^\Omega_i \leq 2$ [37]. The $\Theta(\Omega)$ matrix is not positive semi-definite in the general case, which is also confirmed at local level of description [46]. Therefore, negative eigenvalues (populations) as well as populations greater than 2, which do not fulfill the Pauli principle, can appear for the correlated DAFH formulation and consequently this quantity is not physically acceptable as an electron density. Only for the closed shell Hartree–Fock approximation both ${}^1D(\Omega)$ and $\Theta(\Omega)$ are coincident and hence the DAFH proposal is equivalent to our symmetric approach, because then the density cumulant terms of ${}^2D$ vanish as indicated in the previous section.

In a recent article, a "one-electron approximation to DAFH" has been proposed to approximate

TABLE I

Negative eigenvalues and domain electronic populations in the domain-averaged correlated holes formalism for H_2O system in the SDCI treatment.

Domain	N_Ω	N_Ω^+	Eigenvalue	Degeneracy	$\langle i\|i\rangle_H$	$\langle i\|i\rangle'_H$	$\langle i\|i\rangle_O$
H	0.526	0.582	−0.014	1	0.122	0.014	0.864
			−0.018	2	0.010	0.050	0.940
					0.004	0.004	0.992

$\Theta(\Omega)$ matrices for correlated state functions; such approach has been denominated pseudo-DAFH [33]. To clarify the quality of this approximation, let us show first that the pseudo-DAFH is nothing but the model we called symmetric approach to $^1D(\Omega)$ in Ref. [35], defined by Eq. (3). Following the authors in Ref. [33], we will focus our attention on closed-shell wave functions. For that goal, we consider the elements of the positive square root matrix arising from the spin-free first-order reduced density matrix (1-RDM), $(^1D^{\frac{1}{2}})^i_j$ and the overlap $S(\Omega)^i_j = \langle i|j\rangle_\Omega$ in Eq. (3) in the natural basis set in which $^1D^i_j = n_i\delta^j_i$, where n_i and δ^i_j stand for the natural occupation numbers and the Kronecker delta, respectively. Therefore, the simple replacement of this form into Eq. (3) yields the symmetric form $G^i_j(\Omega) = n_i^{\frac{1}{2}} S^i_j(\Omega) n_j^{\frac{1}{2}}$ of Ref. [33] [cf. Eq. (2.9)], which is our symmetric $^1D(\Omega)$ model of Ref. [35]. The essential differences discussed earlier make $\Theta(\Omega)$ and $^1D(\Omega)$ matrices to be different entities; the former matrix is a Fermi correlation hole density matrix, which possesses positive and negative eigenvalues, whereas the latter one has only zero and positive eigenvalues and is representable. As a consequence of the earlier explanation, $\Theta(\Omega)$ may lead to inconsistencies arising from wrong assumptions of mathematical and physical nature. Therefore, it is important to state the limitations and consequences of its application. It is worthwhile to note that neither the symmetric approach $^1D(\Omega)$ nor the $\Theta(\Omega)$ one have a common basis of eigenvectors for all the Ω domains in the system, that is, the corresponding matrices are not diagonal in the same basis set [35, 39]. Therefore, calculating quantum chemical descriptors depending on the eigenvalues and eigenvectors of two domains may be considered as an approximation [47]. Nevertheless, this situation may be overcome within the $^1D(\Omega)$ models by use of the isopycnic approach to the domain-restricted decomposition of the first-order reduced density matrix in which all domains share a common eigenvector basis set [36].

Let us now present two examples of practical nature, which permit to exemplify the properties related above and turn out to be illustrative to understand the physical consequences of the use of $\Theta(\Omega)$ analysis in comparison with the use of the formalism of the domain-restricted reduced density matrices. At first, we propose a simple but enlightening example in which we calculate $\Theta(\Omega)$ matrix for H_2O molecule at the single–double configuration interaction level of approximation with the PSI 3.2 package [48], in the 6-31G basis set at the equilibrium geometry [49], to show the onset of negative eigenvalues of these matrices as a consequence of its non positivity. Table I shows the results of the diagonalization of $\Theta(\Omega)$ [Eq. (5)] for the H atomic domain. Only the most important negative eigenvalues are shown. The most negative (about ~ -0.02) is doubly degenerate in population. The term $\langle i|i\rangle_\Omega$ associated with a given domain Ω for the i-th orbital entering in the normalization condition $\sum_\Omega \langle i|i\rangle_\Omega = 1$ permits to estimate the degree of delocalization of the orbital over each domain [50, 51]. Therefore, the orbitals are slightly delocalized over the actual H domain and the other H' atom in the system and practically localized over the O atom. In the standard procedure of the correlated DAFH matrix analysis these negative eigenvalues (populations) are neglected [33, 34, 39] to perform the isopycnic orbital localization transformation [50] and hence to associate the eigenvectors to atoms and bonds. In case the negative populations become important, that is, their modulus are appreciable, it may lead to unphysical results. Also, the domain population is very different considering the negative eigenvalues ($N_\Omega = 0.527$) or neglecting them ($N_\Omega^+ = 0.582$), as shown in Table I. These difficulties are completely avoided within the framework of $^1D(\Omega)$ theory, as it can properly support an isopycnic transformation because all its eigenvalues are positive [35]. Therefore, it is clear that neglecting such eigenvalues of $\Theta(\Omega)$ matrices produces a different density and hence its integration over a domain does not keep the right population. These results may not be considered as unexpected, because as

indicated earlier, $\Theta(\Omega)$ issue form correlated wave functions are not true particle densities. Other example has been reported in advance for N_2 molecule in Ref. [40].

In the second example, a quasi-analytic VB model for a two-electron system is implemented to show in a graphic way the physical localization of the electron cloud. For that goal, we use a simple model [52], which has recently been subject of interest in studies of population analysis [53]. This model allows us to complement this critical discussion by analyzing the behavior of both densities in terms of the spatial localization of the electron cloud. We will consider a two-electron homonuclear diatomic molecular system, which has been used by the authors of Ref. [34, 54] to properly compare the behavior of both devices. The system VB wave function is expressed by,

$$\Psi_{VB}(1,2) = \cos(\omega)\Psi_{cov}(1,2) + \sin(\omega)\Psi_{ion}(1,2), \quad (7)$$

where the wave functions Ψ_{cov} and Ψ_{ion} stand for the covalent and ionic contributions respectively, and the trigonometric functions $cos(\omega)$ and $sin(\omega)$ are the VB expansion coefficients of each contribution, which read,

$$\Psi_{cov}(1,2) = \frac{1}{\sqrt{2}}[\mathbf{a}(1)\mathbf{b}(2) + \mathbf{b}(1)\mathbf{a}(2)]\Lambda;$$

$$\Psi_{ion}(1,2) = \frac{1}{\sqrt{2}}[\mathbf{a}(1)\mathbf{a}(2) + \mathbf{b}(1)\mathbf{b}(2)]\Lambda \quad (8)$$

where $\mathbf{a}$ and $\mathbf{b}$ are orthogonal atomic orbitals localized on the atoms $\mathbf{A}$ and $\mathbf{B}$ respectively, and Λ is the spin function for the two electrons with opposite spin. The spin-free second-order reduced density matrix ^2D (2-RDM) within this model in the coordinate representation is [13]

$$^2D(1,2|1',2') = \cos^2(\omega)^2 D_{cov}(1,2|1',2')$$
$$+ \sin^2(\omega)\,^2 D_{ion}(1,2|1',2') + \sin(2\omega)\,^2 D_{mix}(1,2|1',2')$$
$$(9)$$

where $^2D_{cov}$, $^2D_{ion}$ and $^2D_{mix}$ become defined by

$$^2D_{cov}(1,2|1',2') = \frac{1}{2}[\mathbf{a}(1)\mathbf{a}(1')\mathbf{b}(2)\mathbf{b}(2')$$
$$+ \mathbf{b}(1)\mathbf{b}(1')\mathbf{a}(2)\mathbf{a}(2') + 2\mathbf{a}(1)\mathbf{b}(1')\mathbf{b}(2)\mathbf{a}(2')]$$
$$^2D_{ion}(1,2|1',2') = \frac{1}{2}[\mathbf{a}(1)\mathbf{a}(1')\mathbf{a}(2)\mathbf{a}(2')$$
$$+ \mathbf{b}(1)\mathbf{b}(1')\mathbf{b}(2)\mathbf{b}(2') + 2\mathbf{a}(1)\mathbf{b}(1')\mathbf{a}(2)\mathbf{b}(2')]$$
$$^2D_{mix}(1,2|1',2') = \frac{1}{2}[\mathbf{a}(1)\mathbf{a}(1')\mathbf{b}(2)\mathbf{a}(2')$$
$$+ \mathbf{b}(1)\mathbf{b}(1')\mathbf{a}(2)\mathbf{b}(2')$$
$$+ \mathbf{a}(1)\mathbf{b}(1')\mathbf{b}(2)\mathbf{b}(2') + \mathbf{a}(1)\mathbf{b}(1')\mathbf{b}(2)\mathbf{a}(2')] \quad (10)$$

Each orbital is centered at one of the nuclei denoted by A and B, which are defined by atomic domains Ω_A and Ω_B, respectively. To preserve the analytic character of the model, a Mulliken-like scheme of partitioning [1, 2], that is, identifying the atomic domains with the atomic orbital associated to each nucleus is used restricting the summation of the basis functions at each atom (one per atom in this case). Therefore, assuming the hypotheses,

$$\int_{\Omega_A} \mathbf{a}(x)\mathbf{a}(x)dx \approx 1 \quad \int_{\Omega_A} \mathbf{b}(x)\mathbf{b}(x)dx \approx 0$$
$$\int_{\Omega_A} \mathbf{a}(x)\mathbf{b}(x)dx \approx 0 \quad (11)$$

the overlap matrix of domain A (here in after we will use atom A for our goals) is

$$S_{\Omega_A} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

$^1D(\Omega)$ is directly calculated by application of Eq. (3) for domain A. $\Theta(\Omega)$ matrix [Eqs. (5)], may be evaluated by performing a partial trace over one variable, making $2 = 2'$ in Eqs. (9) and then integrating over the volume defined by Ω_A [39], that is, the basin defining the atom within AIM theory context [10]. Then, it is obtained

$$^1D(\Omega_A) = \begin{pmatrix} \dfrac{1}{2}(1 + |\cos(2\omega)|) & \cos(\omega)\sin(\omega) \\ \cos(\omega)\sin(\omega) & \dfrac{1}{2}(1 - |\cos(2\omega)|) \end{pmatrix}$$

and

$$\Theta(\Omega_A) = \begin{pmatrix} \cos^2(\omega) & \dfrac{1}{2}\sin(2\omega) \\ \dfrac{1}{2}\sin(2\omega) & \sin^2(\omega) \end{pmatrix},$$

respectively. From the above expressions, we calculate the density maps for $\Theta(\Omega_A)$ and $^1D(\Omega_A)$, which are shown in Figures 1 and 2, respectively. The horizontal axis indicates the linear space coordinate. Atom A, with an associated atomic function $\mathbf{a}(x)$, is placed on the right at the value 5.0 (arbitrary units), while atom B, with an associated atomic function $\mathbf{b}(x)$, is placed on the left of the figure at -5.0. The atomic functions used for the calculations are $1s$ Slater-type with unit exponent. The vertical axis represents the parameter ω defining the covalent and ionic mixing coefficients contributions of the VB wave function in Eq. (7). The zero or reference value of the map is placed just over the plane in

which the figures are shown: white and grey colors indicate positive values while black color indicates zero value, respectively. It may be observed that the behavior of both densities is markedly different. The $\Theta(\Omega)$ density at domain Ω_A (Fig. 1) shows that at $\omega = 0$ (pure covalent structure) the DAFH density is completely localized on atom A, while at intermediate values in which both ionic and covalent structures contribute to the wave function, the ionic component begin to increase up to $\omega = \frac{\pi}{4}$ (Hartree–Fock state) in which this density at both atoms becomes identical. Finally, at $\omega = \frac{\pi}{2}$ (pure ionic structure) the domain-averaged Fermi hole density completely migrates to the other (complementary) domain, which defines atom B. This description is in agreement with the concept of the correlation hole so that it remains localized at domain A in the covalent case and is completely transferred to the complementary domain B in the ionic limit. This result has also been noted in Ref. [54]. The $^1D(\Omega_A)$ behavior is drastically different from the previous one, that is, the density remains localized over the domain Ω_A at all values of ω and it only shows a small charge transference to the complementary physical space defined by Ω_B domain at the Hartree–Fock state. This fact is due to the behavior of the eigenvalues and eigenvectors. For both densities the eigenvalues remain fixed and equal to 0 and 1, that is, they keep ω independent; the changes are only reflected on the eigenvectors
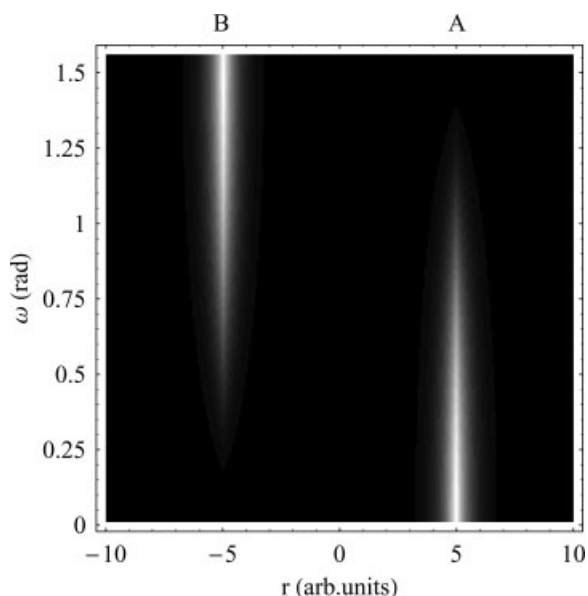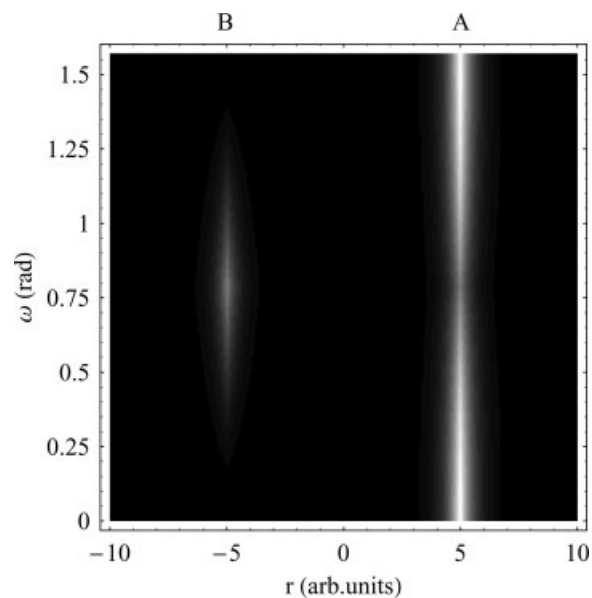

FIGURE 2. Density map for the domain-restricted first-order reduced density matrix $^1D(\Omega_A)$ in the Valence Bond model.

that remain localized on the center A for all values of the mixing coefficients for $^1D(\Omega_A)$, while for $\Theta(\Omega_A)$ the eigenvector is localized at center A for the covalent case and is transferred to center B for the ionic limit. Therefore, in spite of $\Theta(\Omega)$ density is positive definite in this particular example (cf., its matrix form), it shows a different behavior than the domain-restricted density matrix.

4. Concluding Remarks

The critical comparison between the DAFHs issued from correlated wave functions and DRRDM formulations from both mathematical and physical points of view permits to clarify the differences between these two schemes of description. The former one describes a Fermi correlation hole density, that is, it is not a strict electron density because it is not positive semi-definite, while the later one is a true density [37]. The examples in the previous section show both numerically and quasi-analytically, the nonpositivity of $\Theta(\Omega)$ by calculation of the eigenvalues of each matrix as well as the nonlocalized DAFH density picture in comparison with the localized one for $^1D(\Omega_A)$ within the simple VB model. Therefore, in general, because of those reasons, the DAFH model cannot be considered as a rigorous method for describing electron density in studies of molecular structure, except for the Hartree–Fock

FIGURE 1. Density map for the domain averaged-correlated hole $\Theta(\Omega_A)$ in the Valence Bond model.

approach in which the DAFH density coincides with a true-localized particle density.

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