Correlated holes and their relationships with reduced density matrices and cumulants

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This paper describes a matrix formulation for the correlated hole theory within the framework of the domain-averaged model in many electron systems (atoms, molecules, condensed matter, etc.). General relationships between this quantity and one-particle reduced density matrices for any independent particle or correlated state functions are presented. This formulation turns out to be suitable for computational purposes due to the straightforward introduction of cumulants of two-particle reduced density matrices within the quantum field structure. Numerical calculations in selected simple molecular systems have been performed in order to determine preliminary correlated values for such a quantity. © *2005 American Institute of Physics.*
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I. INTRODUCTION

The theory and features of Fermi holes were introduced long time ago in solid state physics[1,2] with the aim of describing the conduction model in a free electron gas. This concept has been exported to atomic and molecular physics in the development of the X_α approach[3] and the local density functional theories.[4] In Luken's works[5] the Fermi holes are derived from the conditional probability of finding one electron of a pair provided the position of the second one in a point of the space; a proper discussion of this procedure can be found in those references. A generalization of this tool has been reported taking into account topological atomic regions. This approach helps to extend the concept of Fermi hole depending on the position of an electron to domain-averaged Fermi hole, in which the reference electron is not fixed in any point but is allowed to move within a determined topological domain Ω.[6–8] The use of Fermi holes has enabled to carry out an appropriate description of electron pairing and chemical bonds at the Hartree–Fock level of theory,[9] as well as subsequent applications in molecular structure.[10] In these studies, the practical determination of Fermi holes has only required the use of the one-particle density; a brief and general review of these methods can be found in Ref. 11.

The main aim of this work is to go beyond the Hartree–Fock level of theory. For this purpose, a matrix formulation of the correlated hole theory is described. Within this approach the relationships between correlated holes, one-particle reduced density matrices (1-RDM) (Ref. 12) and *cumulant* matrices of two-particle reduced density matrices (2-RDM) (Refs. 13–16) are directly derived. This treatment allows us to incorporate correlation effects in a natural way,

as well as to analyze the influence of many-body effects over this quantity and over its applications.

The organization of this paper is as follows. Section II reports the main features of domain-averaged Fermi holes for Bader atomic regions and presents the matrix formulation of this concept. The obtained algorithms allow us to derive an explicit theoretical formulation for this quantity and to describe general relationships that provide accurate links between correlated holes, one-particle reduced density matrices, and cumulant matrices at any level of approximation in the state function. Section III is devoted to the numerical calculations performed to check the consequences of introducing many body effects in studies of electronic distribution. A discussion of the obtained results is also carried out. Finally, some remarks and conclusions are presented in the Sec. IV.

II. THEORY

The physical idea of correlated *holes* is based on the concept of conditional probability, which expresses the fraction of density excluded from a region of space because of the presence of other electron in that region.[5,6,11] We will distinguish two types of *correlation*: the *exchange correlation* and the *Coulomb correlation*.[17–20] The former (so called Fermi correlation) arises from the Pauli exclusion principle and it is always present in the description of an *N*-electron system even at the Hartree–Fock level. The Coulomb correlation only is taken into account when correlated state functions are used. Thus, in our terminology, the correlated holes include both effects.

The conditional probability of finding one electron provided the position of a second one, reference electron, is fixed in a point $\vec{r}_2$, irrespective of the spin of the particle, is given by[5,11]

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$$P_{\tilde{r}_2}(\vec{r}_1) = \frac{2\,{}^2\Gamma(\vec{r}_1\vec{r}_2|\vec{r}_1\vec{r}_2)}{{}^1\Gamma(\vec{r}_2|\vec{r}_2)}, \tag{1}$$

where ${}^1\Gamma(\vec{r}_2|\vec{r}_2)$ is the probability of finding the second electron at $\vec{r}_2$. ${}^2\Gamma(\vec{r}_1\vec{r}_2|\vec{r}_1\vec{r}_2)$ stands for the joint probability or pair probability density for first electron at $\vec{r}_1$ and second electron at $\vec{r}_2$. However, for practical reasons it turns out to be more convenient to normalize the conditional probability $P_{\tilde{r}_2}(\vec{r}_1)$ to $(N-1)$ electrons so that we define

$$f_{\tilde{r}_2}(\vec{r}_1) = (N-1)P_{\tilde{r}_2}(\vec{r}_1) \tag{2}$$

or

$$f_{\tilde{r}_2}(\vec{r}_1) = \frac{2\,{}^2\mathbf{D}(\vec{r}_1\vec{r}_2|\vec{r}_1\vec{r}_2)}{{}^1\mathbf{D}(\vec{r}_2|\vec{r}_2)}, \tag{3}$$

where $N(N-1)\,{}^2\Gamma(\vec{r}_1\vec{r}_2|\vec{r}_1\vec{r}_2) = {}^2\mathbf{D}(\vec{r}_1\vec{r}_2|\vec{r}_1\vec{r}_2)$ stands for the diagonal element of the pair density or two-particle reduced density matrix (2-RDM) with $\mathrm{tr}({}^2\mathbf{D}) = \binom{N}{2}$, where $\binom{N}{2}$ is the binomial coefficient and tr the mathematical operation trace. $N\,{}^1\Gamma(\vec{r}_2|\vec{r}_2) = {}^1\mathbf{D}(\vec{r}_2|\vec{r}_2)$ is the diagonal element of the one-particle density matrix (1-RDM) which represents the particle density of the system. Hence, the normalization condition for this conditional probability is

$$\int f_{\tilde{r}_2}(\vec{r}_1)d\vec{r}_1 = N-1. \tag{4}$$

When the "source" electron is located in an atomic region Ω instead of in a single point $\vec{r}_2$, Eq. (3) can be written as[9]

$$f_\Omega(\vec{r}_1) = \frac{2\displaystyle\int_\Omega {}^2\mathbf{D}(\vec{r}_1\vec{r}_2|\vec{r}_1\vec{r}_2)d\vec{r}_2}{\displaystyle\int_\Omega {}^1\mathbf{D}(\vec{r}_2|\vec{r}_2)d\vec{r}_2}, \tag{5}$$

which also fulfills normalization condition (4). This scenario is useful to define the concept of *hole* as the difference between the actual density minus the fraction which has been considered as the conditional density, thus in the coordinate formulation this quantity reads

$$h_{\tilde{r}_2}(\vec{r}_1) = {}^1\mathbf{D}(\vec{r}_1|\vec{r}_1) - f_{\tilde{r}_2}(\vec{r}_1) \tag{6}$$

or, in the more useful topological approach,[9]

$$h_\Omega(\vec{r}_1) = {}^1\mathbf{D}(\vec{r}_1|\vec{r}_1) - f_\Omega(\vec{r}_1). \tag{7}$$

This expression is valid for any form of the region Ω and, consequently, domains of chemical interest as individual atomic regions as well as regions corresponding to atom sets (i.e., functional groups), can be included within this formulation. The integration of $h_\Omega(\vec{r}_1)$ over the whole space leads to

$$\int h_\Omega(\vec{r}_1)d\vec{r}_1 = 1.$$

One can now consider the number of electrons in the region Ω, N_Ω, where

$$N_\Omega = \int_\Omega {}^1\mathbf{D}(\vec{r}_1|\vec{r}_1)d\vec{r}_1, \tag{8}$$

which leads to the definition of *domain-averaged Fermi hole*[9]

$$g_\Omega(\vec{r}_1) = N_\Omega h_\Omega(\vec{r}_1) \tag{9}$$

and consequently

$$\int g_\Omega(\vec{r}_1)d\vec{r}_1 = N_\Omega.$$

Let us now to introduce the matrix notation in order to derive relations between these quantities and the corresponding reduced density matrices. Moreover, this matrix formulation will clarify the physical meaning of these concepts. Regarding the position variables $\vec{r}_1$ and $\vec{r}_2$ as continuous indices in the coordinate representation, it follows that the matrix elements of the conditional density are [cf. Eq. (3)]

$$F_{jl}^{ik} = \frac{2\,{}^2D_{jl}^{ik}}{{}^1D_l^k}, \tag{10}$$

where we have generalized the elements of the density matrices beyond the diagonal ones representing the densities (electron and pair populations) as well as off-diagonal components (electron and pair coherences). However, a physical singularity arises from the cases in which ${}^1D_l^k = 0\,(k \neq l)$ in Eq. (10) that stands for an incoherent relation between electron in the kth orbital and that of lth. Thus, in order to avoid such a singularity we will only consider that the "probe" electron is in the kth orbital and there is not interference terms $(k\,l)$. Hence, Eq. (10) reads

$$F_{jk}^{ik} = \frac{2\,{}^2D_{jk}^{ik}}{{}^1D_k^k}. \tag{11}$$

The "field" electron is expressed by the whole distribution (diagonal and off-diagonal terms) and the probe electron is described from its diagonal terms and thus the hole can be written by the matrix elements

$$H_{jk}^{ik} = {}^1D_j^i - F_{jk}^{ik}. \tag{12}$$

The spin-free matrix elements of 2-RDM can be expressed, for any arbitrary type of state function, as[13–16,20–22]

$${}^2D_{jl}^{ik} = \tfrac{1}{2}\,{}^1D_j^i\,{}^1D_l^k - \tfrac{1}{4}\,{}^1D_l^i\,{}^1D_j^k + \tfrac{1}{2}\Lambda_{jl}^{ik}, \tag{13}$$

where Λ_{jl}^{ik} stands for the matrix elements of the 2-RDM cumulant.[13–16,20–22] As is well known, all the elements of this cumulant matrix are zero in the particular case of a closed shell Hartree–Fock state function. Consequently, in a general case

$$H_{jk}^{ik} = \frac{{}^1D_k^i\,{}^1D_j^k}{2\,{}^1D_k^k} - \frac{\Lambda_{jk}^{ik}}{{}^1D_k^k}, \tag{14}$$

which allows us to define the matrix elements of the domain-averaged correlated holes

$$\Theta_j^i \equiv \sum_k H_{jk}^{ik} \, {}^1D_k^k \tag{15}$$

or, alternatively,

$$\Theta_j^i = \frac{1}{2}\sum_k {}^1D_k^i \, {}^1D_j^k - \sum_k \Lambda_{jk}^{ik} = {}^1D_j^i \tag{16}$$

and

$$\Theta_j^i = \sum_{k,l}\left(\frac{1}{2}\,{}^1D_l^i\,{}^1D_j^k - \Lambda_{jl}^{ik}\right)\delta_{kl}. $$

In this last equation, we will express the Kronecker delta as $\delta_{kl} = \Sigma_\Omega \langle k|l\rangle_\Omega$, where $\langle k|l\rangle_\Omega$ is the element of the overlap matrix between the molecular orbitals k and l over the Bader region Ω,[7] which leads to the topological partitioning

$$\Theta_j^i = \sum_\Omega \Theta_j^i(\Omega), \tag{17}$$

where

$$\Theta_j^i(\Omega) = \sum_{k,l}\left(\frac{1}{2}\,{}^1D_l^i\,{}^1D_j^k - \Lambda_{jl}^{ik}\right)\langle k|l\rangle_\Omega, \tag{18}$$

in which the trace of the weighted hole density is normalized to N, (Refs. 9 and 10)

$$\mathrm{tr}(\Theta) = N. \tag{19}$$

According to Eq. (16), this is equivalent to symmetric topological partitioning of 1-RDM matrix elements

$${}^1D_j^i = \sum_\Omega \Theta_j^i(\Omega). \tag{20}$$

Following the structure of Eq. (18) the Θ matrix for correlated holes can be split into the two components[21]

$$\Theta_j^i(\Omega) = \Theta^{(exch)i}{}_j(\Omega) + \Theta^{(cumul)i}{}_j(\Omega), \tag{21}$$

in which

$$\Theta^{(exch)i}{}_j(\Omega) = \frac{1}{2}\sum_{kl} {}^1D_l^i\,{}^1D_j^k \langle k|l\rangle_\Omega$$

and

$$\Theta^{(cumul)i}{}_j(\Omega) = -\sum_{kl}\Lambda_{jl}^{ik}\langle k|l\rangle_\Omega. $$

As has been above mentioned, the exchange contribution $\Theta^{(exch)i}{}_j(\Omega)$ is always present for any state function while the many-body effects, which are represented through the cumulant term, only appear in the case of correlated state functions. We can rigorously interpret the first term of Eq. (21) as the exchange correlation while the last one describes the Coulomb correlation and both together constitute the correlated hole.

Let us make some comments on these results. On one hand, Eq. (18) represents the most general expression for correlated hole density matrix; it turns out to be valid for any kind of state function, i.e., particle independent or correlated models, and it also admits a general topological partitioning. On the other hand, the matrix structure of Θ is an appropriate tool for computational purposes since it is easy to express

this matrix into bonding terms (pairing or exchange) and many-body effect terms (nonpairing or unpaired) through the 2-RDM cumulant density. It is also worthwhile to note that according to Eqs. (16)–(20) the $\Theta(\Omega)$ matrix is the ^1D matrix defined in the region Ω, that is, $^1D(\Omega)$ and consequently the eigenvectors of $\Theta(\Omega)$ matrix may be interpreted as natural orbitals associated with the corresponding region. This constitutes a central point in this work since it reveals the nature of the correlated holes expressed by the $\Theta(\Omega)$ or $^1D(\Omega)$ matrix.

III. COMPUTATIONAL DETAILS, RESULTS, AND DISCUSSION

Numerical determinations have been carried out in order to test the above methodology evaluating several quantities of chemical and structural interest from correlated holes. For such a goal the series of hydrides of the second-row elements, in singlet ground states, has been chosen. Two types of calculations have been performed: at closed shell Hartree–Fock level and at correlated one so that the influence of the correlation can be analyzed. Configuration interaction (CI) state functions in their single and double expansion approximation (SDCI) have been used for all systems. The calculations were performed using a GAMESS98 code[23] from which first- and second-order reduced density matrices were generated while PROAIM code[24] was used to compute overlap matrices over atomic basins $\langle i|j\rangle_\Omega$. In all cases, we have employed the 6-31G** basis sets and all molecular geometries were optimized for these basis sets within SDCI used scheme. The Hartree–Fock calculations shared identical molecular geometries than those obtained from CI optimizations.

The diagonalization of the $\Theta_j^i(\Omega)$ matrix, written in Eq. (18), for a given Bader topological region Ω, leads to the determination of its eigenvalues and eigenvectors as well as their degeneracy. A wide and useful chemical information can be extracted from these quantities. Although the number of obtained eigenvalues is identical to the number of basis functions used, in practise, most of them turn out to be zero and consequently we can express the $\Theta(\Omega)$ matrix as

$$\Theta(\Omega) = \sum_I^{nonzero} n_I(\Omega)|I\rangle\langle I|, \tag{22}$$

in which $n_I(\Omega)$ and $|I\rangle$ are the nonzero eigenvalues and their corresponding eigenvectors, respectively. Hence, we can determine the number of electrons N_Ω in the region Ω approximately as

$$N_\Omega \approx \sum_I^{nonzero} n_I(\Omega). \tag{23}$$

A further isopycnic localization transformation is performed for the eigenvectors (orbitals) and the eigenvalues (populations) of $\Theta(\Omega)$ matrix to properly analyze the character and the symmetries of these orbitals.[25] Results of N_Ω for different Bader regions and the approximate values of the nonzero

TABLE I. Calculated eigenvalues (electronic populations) and eigenvectors (states) of domain-averaged correlated holes for molecular systems in the SDCI treatment.

System	Domain (Ω)	N_Ω	Eigenvalue	Degeneracy	Assignment	V_Ω
BeH_2	Be	2.275	1.998	1	$1s_{Be}$	0.548
			0.143	2	σ_{BeH}	
	H	1.862	1.349	1	σ_{BeH}	0.470
	BeH	4.138	1.993	1	$1s_{Be}$	0.497
			1.491	1	σ_{BeH} (inner H)	
			0.618	1	σ_{BeH} (outer H)	
BH_3	B	2.937	1.995	1	$1s_B$	1.587
			0.310	3	σ_{BH}	
	H	1.688	1.224	1	σ_{BH}	0.878
	BH	4.625	1.996	1	$1s_B$	1.453
			1.520	1	σ_{BH} (inner H)	
			0.568	2	σ_{BH} (outer H)	
CH_4	C	5.858	2.000	1	$1s_C$	3.987
			0.950	4	σ_{CH}	
	H	1.032	0.747	1	σ_{CH}	1.126
	CH	6.889	2.000	1	$1s_C$	3.224
			1.673	1	σ_{CH} (inner H)	
			1.000	3	σ_{CH} (outer H)	
NH_3	N	8.007	2.000	1	$1s_N$	2.855
			1.814	1	Lone pair	
			1.360	3	σ_{NH}	
	H	0.668	0.506	1	σ_{NH}	0.959
	NH	8.675	2.000	1	$1s_N$	2.082
			1.867	1	Lone pair	
			1.838	1	σ_{NH} (inner H)	
			1.431	2	σ_{NH} (outer H)	
H_2O	O	9.147	2.000	1	$1s_O$	1.590
			1.947	1	σ-lone pair	
			1.883	1	π-lone pair	
			1.605	2	σ_{OH}	
	H	0.427	0.284	1	σ_{OH}	0.699
	OH	9.573	2.000	1	$1s_O$	0.997
			1.961	1	σ-lone pair	
			1.933	1	π-lone pair	
			1.883	1	σ_{OH} (inner H)	
			1.693	1	σ_{OH} (outer H)	
HF	F	9.727	2.000	1	$1s_F$	0.733
			1.974	2	π-lone pair	
			1.945	1	σ-lone pair	
			1.758	1	σ_{FH}	
	H	0.273	0.222	1	σ_{FH}	0.479

eigenvalues n_I (electronic populations) as well as their degeneracy have been collected in Tables I and II. The degeneracy of each eigenvector also provides structural information since it allows us to know the number of identical bonding features within the region Ω and consequently it enables to assign electrons to different bondings (or to identify them as core electrons).

The physical meaning of the $\Theta(\Omega)$ matrix reported in Sec. II allows us to interpret its eigenvectors as natural orbitals of $^1D(\Omega)$. Therefore, in chemical language the eigenvectors are identified as inner shells, lone pairs, inner bonds inside the region Ω, and *broken bonds*, that is, those describing the bondings of the Ω region with the remaining regions of the system. Similarly, the corresponding eigenvalues are the electron population of such orbitals. In the present discussion we will focus the attention on the influence of many-body or correlation effects on such quantities describing the electron distribution, in comparison with results arising from Hartree–Fock state functions.

Another quantity that is described in these tables is the valence V_Ω associated with the Ω region of an atom (atomic valence) or with the Ω region of an atom group (group valence), which according to our previous studies[21] has been determined as

TABLE II. Calculated eigenvalues (electronic populations) and eigenvectors (states) of domain-averaged Fermi holes for molecular systems in the HF treatment.

System	Domain (Ω)	N_Ω	Eigenvalue	Degeneracy	Assignment	V_Ω
BeH_2	Be	2.252	1.990	1	$1s_{Be}$	0.507
			0.131	2	σ_{BeH}	
	H	1.873	1.844	1	σ_{BeH}	0.344
	BeH	4.125	1.995	1	$1s_{Be}$	0.344
			1.975	1	σ_{BeH} (inner H)	
			0.155	1	σ_{BeH} (outer H)	
BH_3	B	2.840	1.996	1	$1s_B$	1.447
			0.282	3	σ_{BH}	
	H	1.720	1.626	1	σ_{BH}	0.791
	BH	4.560	1.997	1	$1s_B$	1.274
			1.908	1	σ_{BH} (inner H)	
			0.328	2	σ_{BH} (outer H)	
CH_4	C	5.758	2.000	1	$1s_C$	3.920
			0.939	4	σ_{CH}	
	H	1.060	1.001	1	σ_{CH}	1.116
	CH	6.818	2.000	1	$1s_C$	3.076
			1.943	1	σ_{CH} (inner H)	
			0.958	3	σ_{CH} (outer H)	
NH_3	N	8.093	2.000	1	$1s_N$	2.627
			1.957	1	Lone pair	
			1.379	3	σ_{NH}	
	H	0.636	0.601	1	σ_{NH}	0.910
	NH	8.729	2.000	1	$1s_N$	1.785
			1.980	1	σ_{NH} (inner H)	
			1.971	1	Lone pair	
			1.389	2	σ_{NH} (outer H)	
H_2O	O	9.225	2.000	1	$1s_O$	1.265
			1.992	1	σ-lone pair	
			1.981	1	π-lone pair	
			1.626	2	σ_{OH}	
	H	0.388	0.369	1	σ_{OH}	0.639
	OH	9.612	2.000	1	$1s_O$	0.639
			1.996	2	σ-lone pair, σ_{OH} (inner H)	
			1.991	1	π-lone pair	
			1.631	1	σ_{OH} (outer H)	
HF	F	9.751	2.000	1	$1s_F$	0.440
			1.998	3	π-lone pair, σ-lone pair	
			1.762	1	σ_{FH}	
	H	0.249	0.239	1	σ_{FH}	0.440

$$V_\Omega = \sum_{\Omega' \neq \Omega} \sum_{ijkl} {}^1D_j^i \, {}^1D_l^k \langle i|l\rangle_\Omega \langle k|j\rangle_{\Omega'}$$
$$+ \sum_{ij} \left(2\,{}^1D_j^i - \sum_k {}^1D_k^i \, {}^1D_j^k\right) \langle i|j\rangle_\Omega, \tag{24}$$

in which the first term refers to the bondings which presents a determined region Ω with other regions Ω' (the bonding valence) and the last one means the remaining bonding capacity (or free valence) of the region Ω, which is described in terms of the elements of the effectively unpaired electron density matrix, that is, $2\,{}^1D_j^i - \Sigma_k \, {}^1D_k^i \, {}^1D_j^k$.[26]

According to the results reported in Tables I and II, the correlated and Hartree–Fock approaches lead to similar descriptions of the electron distributions in the studied systems.

However, it is possible to detect several correlation effects that deserve to be commented. A survey of the N_Ω values reported in Table I (calculated within correlated hole approach) and Table II (obtained at the Hartree–Fock level) shows that both treatments predict the ionic character of some compounds of the series according to the electronegativity of the central atom. In the BeH_2 and BH_3 hydrides the hydrogen atoms have a negative character while in the NH_3, H_2O, and HF molecules this character is positive (the CH_4 case is an intermediate situation). In relation with $\Theta(\Omega)$ matrix eigenvalues, it is interesting to point out that the Hartree–Fock procedure provides higher values for the eigenvalues corresponding to bondings than the correlated one in all the molecular fragments described (the σ inner values

for BeH, BH, CH, NH, and OH). Our interpretation of these results is that the Hartree–Fock approach describes a bonding as an even sharing of a pair of electrons by two centers and consequently the eigenvalues corresponding to bondings are closer to 2.0. However, lower bonding eigenvalues should be interpreted as an uneven sharing of the electron pair, pointing out the different electronegativities of the centers involved in bondings. In this sense, it must also be mentioned that, as the electronegativity of the X atom ($X = Be, \ldots, O$) increases, the eigenvalue associated with outer or broken σ_{XH} bonding becomes closer to the corresponding inner σ_{XH} one, i.e., less electron density involved in bonding is transferred to regions which does not contain the atom X. This effect is more evident is the SDCI treatment than in the Hartrre–Fock one. Another interesting feature is that, in the systems H_2O and HF, the use of correlated state functions splits the degeneracy which appears in the Hartree–Fock results. As can be observed, within these molecules, the topological regions corresponding to fragments OH and F present degenerate eigenvalues for σ-lone pair and σ_{OH} and for π-lone pair and σ-lone pair, respectively, at the Hartree–Fock level. These degeneracies are removed in the correlated hole treatment, providing a more realistic representation of those systems.

The total valence values V_Ω collected in the tables provide some addictional information about the influence of correlation on the molecular description. At correlated level the values of V_Ω turn out to be higher than the corresponding Hartree–Fock ones, particularly in the H_2O and HF molecules where the values 0.639 and 0.440 reported for the OH and F fragments (Table II) are too low. Our interpretation of this systematic behavior is that the Hartree–Fock model cannot properly describe the free valence of a determined region, due to the idempotency of the 1-RDM. This property causes that all the unpaired electron matrix elements $2\,{}^1D_j^i - \Sigma_k\,{}^1D_k^i\,{}^1D_j^k$, which appear in Eq. (24), are zero for closed shell systems in the Hartree–Fock treatment so that their free valence is null. Consequently, the total valence V_Ω is not appropriately evaluated within that procedure, which only takes into account the contribution related with bondings with other atoms or atomic groups, that is the so called bonding valences. However, in the correlated treatment the contribution to free valences arising from the partial split of electron pairs, that appear even in closed shell systems, is properly represented by that unpaired electron matrix.[26]

IV. FINAL REMARKS AND CONCLUSIONS

This report has performed the extension of the Fermi hole concept at correlated level using a matrix formulation based on lower-order reduced density matrices and cumulants. This treatment allows us to evaluate the influence of the correlation on the description of selected topological regions within a determined molecule. One of the achievements of this paper is the formulation of the partitioning of the 1-RDM into $\Theta(\Omega)$ matrices according to Bader topological regions. Moreover, results at correlated level within this

scheme have been presented for the first time. The preliminary results found for closed shell systems show the deficiencies of the Hartree–Fock model since it predicts an excess of degenerate situations. Furthermore, the correlated results provide a higher resolution picture of the molecular structure showing that the Hartree–Fock numerical determinations leads to representations of bondings and valences which turn out to be too simple in some cases, while the description is improved in the correlated treatment. At this moment we are applying the correlated approach to systems with nonconventional bonding patterns. We are also studying the basis dependence over the results derived from the correlated hole approach. These aspects will be subject of forthcoming papers.

[1] E. P. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1934); **46**, 509 (1934).
[2] J. C. Slater, Rev. Mod. Phys. **6**, 209 (1934).
[3] J. C. Slater, *The Calculation of Molecular Orbitals* (Wiley, New York, 1979).
[4] R. A. Donnelly, J. Chem. Phys. **71**, 2874 (1979).
[5] W. L. Luken, Croat. Chem. Acta **57**, 1283 (1984), and references cited therein.
[6] M. A. Buijse, Thesis, Vrije University, Amsterdam, 1991, and references cited therein; web page: http://theochem.chem.rug.nl/publications
[7] R. F. W. Bader and M. E. Stephens, J. Am. Chem. Soc. **97**, 7391 (1975).
[8] R. F. W. Bader, *Atoms in Molecules* (Oxford University Press, Oxford, 1990).
[9] R. Ponec, J. Math. Chem. **21**, 323 (1997); **23**, 85 (1998).
[10] R. Ponec and X. Gironés, J. Phys. Chem. A **106**, 9506 (2002), and references cited therein.
[11] A. J. Thakkar, in *Density Matrices and Density Functionals*, Proceedings of A. John Coleman Symposium, edited by R. Erdahl and V. H. Smith, Jr. (Reidel, Dordrecht, 1987).
[12] E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic, New York, 1976), and references cited therein.
[13] D. A. Mazziotti, Chem. Phys. Lett. **289**, 419 (1998); Phys. Rev. A **57**, 4219 (1998); Chem. Phys. Lett. **326**, 212 (2000).
[14] L. Lain, A. Torre, R. C. Bochicchio, and R. Ponec, Chem. Phys. Lett. **346**, 283 (2001).
[15] W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **116**, 4787 (2002).
[16] L. Lain, A. Torre, and R. Bochicchio, J. Chem. Phys. **117**, 5497 (2002).
[17] J. G. Angyan, E. Rosta, and P. R. Surjan, Chem. Phys. Lett. **299**, 1 (1999).
[18] P. Karafiloglou, J. Phys. Chem. A **105**, 4524 (2001).
[19] P. Karafiloglou, Chem. Phys. Lett. **345**, 201 (2001).
[20] I. Mayer, Chem. Phys. Lett. **383**, 368 (2004).
[21] R. C. Bochicchio, L. Lain, and A. Torre, Chem. Phys. Lett. **374**, 567 (2003); **375**, 45 (2003).
[22] A. Torre, L. Lain, and R. Bochicchio, J. Phys. Chem. A **107**, 127 (2003).
[23] M. W. Schmidt *et al.*, J. Comput. Chem. **14**, 1347 (1993).
[24] F. W. Biegler-König, R. F. W. Bader, and T. H. Tang, J. Comput. Chem. **3**, 317 (1982).
[25] J. Cioslowski, Int. J. Quantum Chem. **S24**, 15 (1990).
[26] V. N. Staroverov and E. R. Davidson, Chem. Phys. Lett. **330**, 161 (2000), and references cited therein.