Domain Averaged Fermi Hole Analysis for Open-Shell Systems

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The Article reports the extension of the new original methodology for the analysis and visualization of the bonding interactions, known as the analysis of domain averaged Fermi holes (DAFH), to open-shell systems. The proposed generalization is based on straightforward reformulation of the original approach within the framework of unrestricted Hartree−Fock (UHF) and/or Kohn−Sham (UKS) levels of the theory. The application of the new methodology is demonstrated on the detailed analysis of the picture of the bonding in several simple systems involving the doublet state of radical cation $NH_3^{(+)}$ and the triplet ground state of the O_2 molecule.

Introduction

There is probably no other concept that contributed to the development of chemistry so remarkably as the qualitative tenet of the chemical bond. The first who correctly recognized the electronic origin of the phenomenon of chemical bonding was Lewis,[1] and his idea that chemical bonds are formed by shared electron pairs has become one of the cornerstones of modern chemistry. Because of its immense impact for the description and the understanding of molecular structures, the classical Lewis model does not cease to represent an inspiration for the chemical theory, and a lot of effort was spent during the past years to reconcile the classical picture of the bonding in terms of structural formulas with the theoretical description provided by quantum chemistry.[2−35] A tribute to the role of Lewis in the development of our understanding of the nature of chemical bond has recently been paid in a special issue of *J. Comput. Chem.*[36]

Although the parallel between quantum chemical and classical chemical descriptions of chemical structures could relatively easily be demonstrated using early approaches based on the analysis of approximate SCF wave functions,[3,7,13−19] similar "chemical" interpretation of more sophisticated wave functions, such as those resulting from contemporary high accuracy calculations, has proved to be more difficult. For that reason, the development of new computational tools is accompanied by the parallel design of auxiliary tools and procedures, allowing one to "transform" the results of the abstract calculations back into the language close to classical chemical thinking.

Into the framework of such approaches can be included also the original methodology known as the analysis of domain averaged Fermi holes,[37,38] and various reported applications of this approach have demonstrated that it is indeed very useful for discerning the picture of the bonding, especially for molecules with nontrivial bonding patterns such as multicenter bonding, hypervalence, metal−metal bonding, etc.[39−48] In addition to reported successful examples of the elucidation of the structure of the molecules close to equilibrium geometries, for which the approach can reasonably be applied at Hartree−Fock and/or Kohn−Sham[49,50] levels of the theory, the approach was also recently generalized beyond the scope of the above approximations, and the analysis of explicitly correlated DAFH has provided new interesting insights into the details of electron reorganization during the splitting and/or formation of the chemical bonds.[51,52]

Although the above generalizations certainly extended the applicability of the DAFH analysis to effectively open-shell systems, the fact that the correct description of such systems relies on the knowledge of the correlated pair densities certainly represents an important obstacle for the application of the "exact" DAFH analysis to larger open-shell systems of real chemical interest. To remedy this computational drawback and to extend the applicability of the DAFH analysis to the study of the bonding arrangement in the equilibrium geometries of larger molecules with unpaired electrons, we report in this study the straightforward reformulation of the original approach within the framework of unrestricted Hartree−Fock (UHF)[53] and/or Kohn−Sham (UKS) levels of the theory. In addition to providing the necessary theoretical background of the above generalization, we also report examples of the application of the open-shell DAFH analysis to several selected molecules.

Theory

To demonstrate the main idea of the proposed generalization of the DAFH analysis to open-shell systems, it is useful to refer first to the definition of the DAFH for the closed-shell systems. In this simple case, the Fermi hole averaged over the finite domain of the space Ω is defined by the formula

$$g_\Omega(r_1) = N_\Omega \rho(r_1) - 2\int_\Omega \rho(r_1, r_2)\, dr_2 \tag{1}$$

where N_Ω denotes the number of electrons in the domain Ω, and $\rho(r_1)$ and $\rho(r_1,r_2)$ are the ordinary first order and pair density, respectively. In the case of the Hartree−Fock (and formally also Kohn−Sham) approximation, the above formula reduces to

$$g_\Omega(r_1) = 2\sum_i^{occ}\sum_j^{occ} \langle \phi_i|\phi_j\rangle_\Omega \phi_i(r_1)\phi_j(r_1) \tag{2}$$

where $\langle \varphi_i|\varphi_j\rangle_\Omega$ denotes the overlap integral of the molecular orbitals φ_i and $\varphi_j$over the domain Ω.

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$$\langle\phi_i|\phi_j\rangle_\Omega = \int_\Omega \phi_i(r)\phi_j(r)\,\mathrm{d}r \tag{3}$$

In view of the fact that the factor of 2 in eq 2 comes from the double occupancy of molecular orbitals in the wave function (Slater determinant) of the closed-shell systems, it seems natural to assume that in the case of UHF approximation, formula 2 can straightforwardly be rewritten in the form of (4):

$$\begin{gathered} g_\Omega(r_1) = \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{occ}} \langle\phi_i|\phi_j\rangle_\Omega \phi_i(r_1)\phi_j(r_1) + \\ \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{occ}} \langle\psi_i|\psi_j\rangle_\Omega \psi_i(r_1)\psi_j(r_1) \\ g_\Omega(r_1) = g_\Omega^\alpha(r_1) + g_\Omega^\beta(r_1) \end{gathered} \tag{4}$$

in which ϕ and ψ denote the (occupied) molecular orbitals for α and β spin, respectively. This equation suggests that in the case of open-shell systems, the DAFH is composed of two terms, which can be regarded as the contributions of (domain averaged) Fermi holes of individual α and β spin electrons, respectively. This implies that in the case of open-shell systems, the DAFH analysis is to be performed for α and β spin electrons independently, and the resulting final picture of the bonding emerges from the superposition of the two complementary analyses.

Although formula 4 provides the complete recipe for the presented DAFH analysis of open-shell systems, we consider it useful to demonstrate that the above intuitive generalization can also be put on a safer theoretical basis. For this purpose, let us refer to the early studies,[37,38] in which the concept of DAFH was introduced from the straightforward generalization of the original definition of the Fermi hole[54] in terms of conditional probabilities (eqs 5−7):

$$P_{r_2}(r_1) = \frac{2\rho(r_1, r_2)}{\rho(r_2)} \tag{5a}$$

$$h_{r_2}(r_1) = \rho(r_1) - P_{r_2}(r_1) \tag{5b}$$

$$P_\Omega(r_1) = \frac{2\int_\Omega \rho(r_1, r_2)\,\mathrm{d}r_2}{\int_\Omega \rho(r_2)\,\mathrm{d}r_2} \tag{6a}$$

$$h_\Omega(r_1) = \rho(r_1) - \frac{2\int_\Omega \rho(r_1, r_2)\,\mathrm{d}r_2}{\int_\Omega \rho(r_2)\,\mathrm{d}r_2} = \rho(r_1) - \frac{2\int_\Omega \rho(r_1, r_2)\,\mathrm{d}r_2}{N_\Omega} \tag{6b}$$

$$g_\Omega(r_1) = N_\Omega h_\Omega(r_1) = N_\Omega \rho(r_1) - 2\int_\Omega \rho(r_1, r_2)\,\mathrm{d}r_2 \tag{7}$$

For this purpose, it is useful to rewrite the (spinless) pair and first-order density in terms of individual components[55] (eq 8):

$$\begin{gathered} \rho(r_1, r_2) = \rho^{\alpha\alpha}(r_1, r_2) + \rho^{\beta\beta}(r_1, r_2) + \rho^{\alpha\beta}(r_1, r_2) + \rho^{\beta\alpha}(r_1, r_2) \\ \rho(r_1) = \rho^\alpha(r_1) + \rho^\beta(r_1) \end{gathered} \tag{8}$$

Using the above partitioning, it is now possible to introduce the (domain averaged) conditional probabilities, characterizing the distribution of one electron of the pair provided the second (reference) electron of a given spin is localized in the domain Ω.

$$\begin{gathered} P_\Omega^\alpha(r_1) = \frac{\int_\Omega \rho(r_1, r_2)\,\mathrm{d}r_2^{(\alpha)}}{\int_\Omega \rho^\alpha(r_2)\,\mathrm{d}r_2} = \\ \frac{\int_\Omega (\rho^{\alpha\alpha}(r_1, r_2) + \rho^{\beta\alpha}(r_1, r_2))\,\mathrm{d}r_2}{N_\Omega^\alpha} \\ P_\Omega^\beta(r_1) = \frac{\int_\Omega \rho(r_1, r_2)\,\mathrm{d}r_2^{(\beta)}}{\int_\Omega \rho^\beta(r_2)\,\mathrm{d}r_2} = \\ \frac{\int_\Omega (\rho^{\beta\beta}(r_1, r_2) + \rho^{\alpha\beta}(r_1, r_2))\,\mathrm{d}r_2}{N_\Omega^\beta} \end{gathered} \tag{9}$$

In the case of UHF and/or UKS approximation, which is our main concern here, the above general formulas can be further simplified by taking into account the partitioning of the individual components of the pair density (eq 10):

$$\begin{gathered} \rho^{\alpha\alpha}(r_1, r_2) = \rho^\alpha(r_1)\rho^\alpha(r_2) - \rho_1^{\alpha\alpha}(r_1, r_2)\rho_1^{\alpha\alpha}(r_2, r_1) \\ \rho^{\beta\beta}(r_1, r_2) = \rho^\beta(r_1)\rho^\beta(r_2) - \rho_1^{\beta\beta}(r_1, r_2)\rho_1^{\beta\beta}(r_2, r_1) \\ \rho^{\alpha\beta}(r_1, r_2) = \rho^\alpha(r_1)\rho^\beta(r_2) \\ \rho^{\beta\alpha}(r_1, r_2) = \rho^\beta(r_1)\rho^\alpha(r_2) \end{gathered} \tag{10}$$

In this case, the integration of the pair density leads to eq 11:

$$\begin{gathered} P_\Omega^\alpha(r_1) = \rho(1) - \frac{\int_\Omega \rho_1^{\alpha\alpha}(r_1, r_2)\rho_1^{\alpha\alpha}(r_2, r_1)\,\mathrm{d}r_2}{N_\Omega^\alpha} \\ P_\Omega^\beta(r_1) = \rho(1) - \frac{\int_\Omega \rho_1^{\beta\beta}(r_1, r_2)\rho_1^{\beta\beta}(r_2, r_1)\,\mathrm{d}r_2}{N_\Omega^\beta} \end{gathered} \tag{11}$$

whose straightforward insertion into the general formula 12

$$\begin{gathered} h_\Omega^\alpha(r_1) = \rho(r_1) - P_\Omega^\alpha(r_1) \\ h_\Omega^\beta(r_1) = \rho(r_1) - P_\Omega^\beta(r_1) \end{gathered} \tag{12}$$

gives the final expressions for the spin-resolved (domain averaged) Fermi holes (eq 13):

$$\begin{gathered} g_\Omega^\alpha(r_1) = N_\Omega^\alpha h_\Omega^\alpha(r_1) = \int_\Omega \rho_1^{\alpha\alpha}(r_1, r_2)\rho_1^{\alpha\alpha}(r_2, r_1)\,\mathrm{d}r_2 = \\ \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{occ}} \langle\phi_i|\phi_j\rangle_\Omega \phi_i(r_1)\phi_j(r_1) \\ g_\Omega^\beta(r_1) = N_\Omega^\beta h_\Omega^\beta(r_1) = \int_\Omega \rho_1^{\beta\beta}(r_1, r_2)\rho_1^{\beta\beta}(r_2, r_1)\,\mathrm{d}r_2 = \\ \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{occ}} \langle\psi_i|\psi_j\rangle_\Omega \psi_i(r_1)\psi_j(r_1) \end{gathered} \tag{13}$$

which coincide with the expressions appearing in the intuitively introduced formula 4.

In addition to the above procedure, another alternative possibility of introducing the partitioning (eq 4) is via the (domain averaged) conditional probability of distributing one electron of the pair provided the reference electron of arbitrary spin is localized in the domain Ω.

$$P_\Omega(r_1) = \frac{\int_\Omega \rho(r_1, r_2)\,\mathrm{d}r_2}{\int_\Omega \rho(r_2)\,\mathrm{d}r_2} = \frac{\int_\Omega \rho(r_1, r_2)\,\mathrm{d}r_2}{N_\Omega^\alpha + N_\Omega^\beta} = \frac{\int_\Omega \rho(r_1, r_2)\,\mathrm{d}r_2}{N_\Omega} \qquad (14)$$

Taking now into account the partitioning of eqs 8 and 10, the above formula reduces to

$$P_\Omega(r_1) = \rho(r_1) + \frac{\int_\Omega \rho_1^{\alpha\alpha}(r_1, r_2)\rho_1^{\alpha\alpha}(r_2, r_1)\,\mathrm{d}r_2 + \int_\Omega \rho_1^{\beta\beta}(r_1, r_2)\rho_1^{\beta\beta}(r_2, r_1)\,\mathrm{d}r_2}{N_\Omega} \qquad (15)$$

which again straightforwardly leads to the equation for the partitioning of the total DAFH into spin-resolved components (eq 4).

Once the spin-resolved DAFHs are introduced, the whole subsequent analysis is exactly the same as in the case of DAFH for the closed-shell systems. First, it is necessary to specify the form of the domain, over which the averaging is performed. Here again, the choice of primary interest is the atomic domains resulting from the virial partitioning of the electron density[56] and/or the domains formed by the union of several atomic domains. After having generated the AOM matrices required for the generation of the corresponding (domain averaged) Fermi holes, the subsequent analysis consists of the diagonalization of the matrices that represent the holes (eq 13) and the subsequent inspection of the localized functions (and their occupation numbers) obtained by the isopycnic transformation[57] of the original eigenvectors resulting from the diagonalization. Such an inspection generally allows one to identify the bonds (and lone pairs) formed by the sharing of the electrons of different spin as well as to detect the localization of the unpaired electrons in the molecule. In addition to "exact" DAFH analysis in which the AOM matrices are calculated using integration over real AIM atomic domains, one can also use, as a cheaper alternative, the "approximate" form of DAFH analysis in which the integration over real AIM domains is replaced by the Mulliken-like approximation according to which the electron is in the domain of a given atom A if it is in an orbital localized at that atom.

To demonstrate the typical outcome of the open-shell DAFH analysis, we report in the following the results of the above approach on several simple examples. The first of them is represented by the doublet state of the $NH_3^{(+)}$ radical cation, and the other involves the triplet $^3\Sigma_g^-$ ground state of the O_2 molecule.

Computations

The reported analysis requires several types of the calculations. First, it is necessary to generate the wave functions of the studied molecules. These calculations were performed for completely optimized geometries of both of the studied molecules at the UB3LYP/6-311G* level of theory. Based on these wave functions, the second step involves the generation of the Fermi holes averaged over the selected fragment. Within the framework of the "exact" DAFH analysis, this requires the knowledge of the AOM matrices for the electrons of α and β spin (eq 4). These calculations were performed at the same level of the theory using the program AIMAll.[58] After having determined the necessary AOM matrices, the final step consists of the construction of the DAFHs for the selected fragment and in their subsequent analysis. This is performed using our own program WBaderO, which is available upon request. In the following, the results of the analysis for the studied two molecules are reported.

Results and Discussion

Doublet State of the Radical Cation $NH_3^{(+)}$. Before reporting the results of the analysis for this simple open-shell system, it is first useful to remind one of the basic structural information that can be extracted from the DAFH analysis of closed-shell molecules. In such a case, the analysis of the hole averaged over a certain domain Ω provides the information about the electron pairs (chemical bonds and/or core or lone electron pairs) that remain intact within the fragment, as well as about the free or broken valences generated by the formal splitting of the bonds required to isolate the fragment from the rest of the molecule. Exactly the same type of information is provided by the DAFH analysis also in the case of open-shell systems, but the fact that the analyzed molecule is now of open-shell type brings certain specificities that have to be taken into account in the interpretation of the results. The main difference concerns the fact that, consistent with eq 4, the analysis has to be performed for the holes generated independently for the electrons of α and β spin so that the final picture of the bonding emerges now from the superposition of the contributions from the electrons of individual spin.

After having briefly summarized the specificities of the DAFH analysis for open-shell systems, we report below the results for the simple example averaged over the NH fragment of the doublet state of the radical cation $NH_3^{(+)}$. As the unpaired electron can be in this simple case assumed to be localized on the central N atom, one can expect that besides the detection of the unpaired electron on that atom, the DAFH analysis of the hole averaged over the NH fragment will also confirm the existence of NH bond and the core electron pair on N that remain intact within the fragment as well as the presence of two broken valences formed by the formal spliting two NH bonds required to isolate the fragment from the rest of the molecule. As it will be shown, the above intuitive picture of the bonding is perfectly consistent with the results of the DAFH analysis summarized in Figure 1. The inspection of this figure shows that the analysis of the hole for α spin electron yields just five nonzero eigenvalues, while in the case of β spin electrons the number of nonzero eigenvalues drops to four. The detailed meaning of the above results for the structure of the studied fragment straightforwardly follows from the inspection of the graphical form of the corresponding eigenvectors also summarized in Figure 1. The most striking feature of this figure is that, besides the eigenvector corresponding to the unpaired electron (Figure 1i) that is localized, as expected, on the central N atom (Figure 1i), all of the remaining DAFH eigenvectors display remarkable resemblance for the electrons of both α and β spin.

This result is very important because it allows one to deduce the final picture of the bonding by straightforward superposition of the pictures for individual spins. Thus, the close resemblance of α and β spin eigenvectors 1a,1b and 1c,1d as well as the fact that the corresponding eigenvalues are close to 1 is straightforwardly consistent with the idea of the electron pairs ($1s^2$ core pair on N and electron pair of NH bond) formed by the sharing of the electrons of opposite spin. Similar close resemblance is also observed for the remaining two pairs of

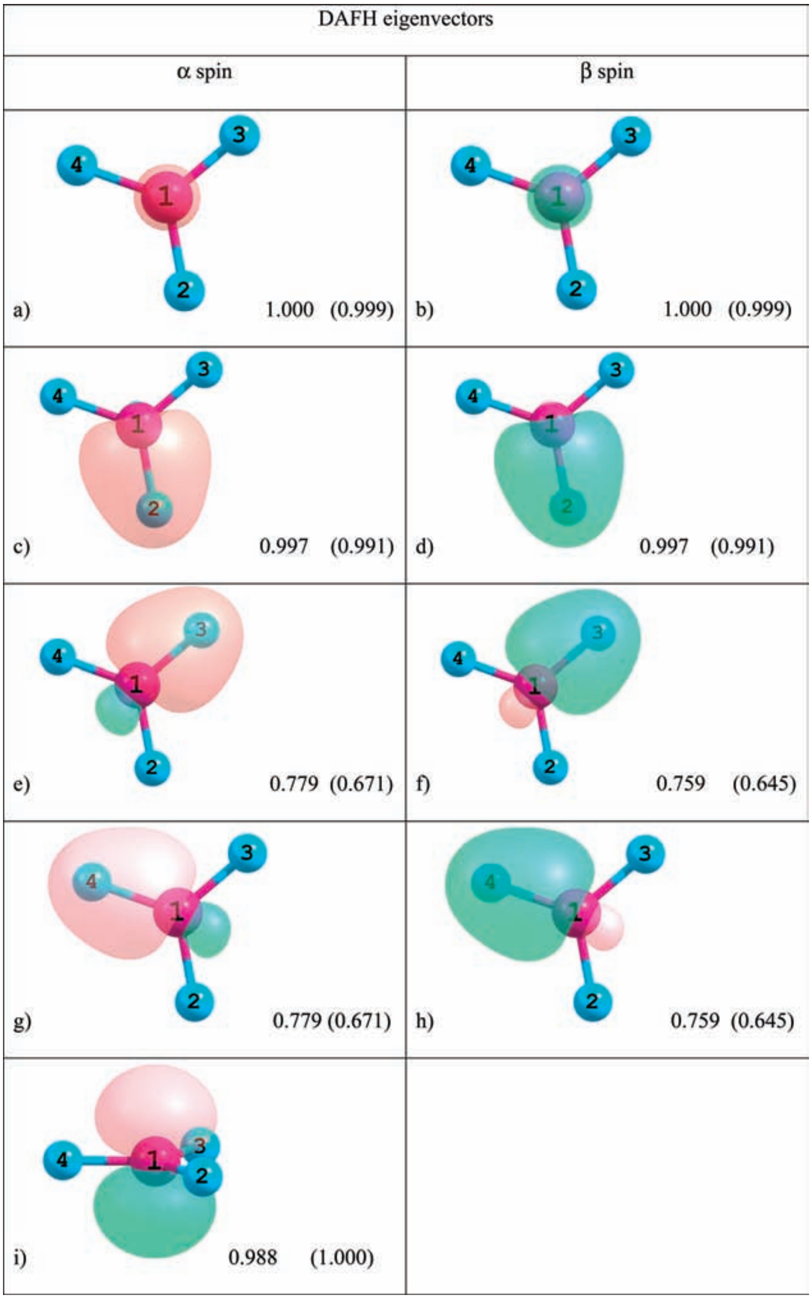


Figure 1. Eigenvalues and eigenvectors resulting from the DAFH analysis of the Fermi hole averaged over the fragment NH (the fragment involved atoms N1H2) of the radical cation $NH_3^{(+)}$. The numbers indicate the eigenvalues of the corresponding hole for the "exact" AIM form of the analysis, and the values in parentheses correspond to the "approximate" Mulliken-like approach.

eigenvectors 1e,1f and 1g,1h, but the fact that the sum of the associated eigenvalues now considerably deviates from 2 suggests to associate them with the two broken valences formed by the formal splitting of NH bonds. Such an interpretation is also straightforwardly corroborated by the results of the complementary DAFH averaged over the individual H atoms summarized in Figure 2. The inspection of this figure shows that the analysis yields in this case just one nonzero eigenvalue for each spin and, moreover, that the corresponding eigenvectors 2a,2b and 2c,2d always exhibit close resemblance with the corresponding counterparts 1e,1f and/or 1g,1h, respectively. This resemblance is not accidental, as a similar situation is also observed in the description of broken valences in closed-shell systems; the only difference here is that the contributions of individual atoms to shared electron pair of formally broken bond are again split into individual spin components. When taken together, these contributions for N and H atoms are 1.538 (0.779 + 0.759) and 0.458 (0.219 + 0. 239), respectively, which is consistent with the idea of uneven sharing of electron pair in polar NH bond. We can thus see that the picture of the bonding resulting from the DAFH analysis of this simple system does indeed correspond to the intuitive anticipations based on the qualitative considerations inherent to classical Lewis model. In this connection, it is, however, interesting to mention that the above picture of the bonding that resulted from the AIM-based formulation of DAFH analysis remains practically unchanged when the "exact" approach was replaced by the alternative approach based on the Mulliken-like approximation of the necessary integrals. This concerns above all the form of the corresponding eigenvectors that is visually non-distinguishable from the corresponding eigenvectors of the "exact" approach; the only slight differences can be observed in the

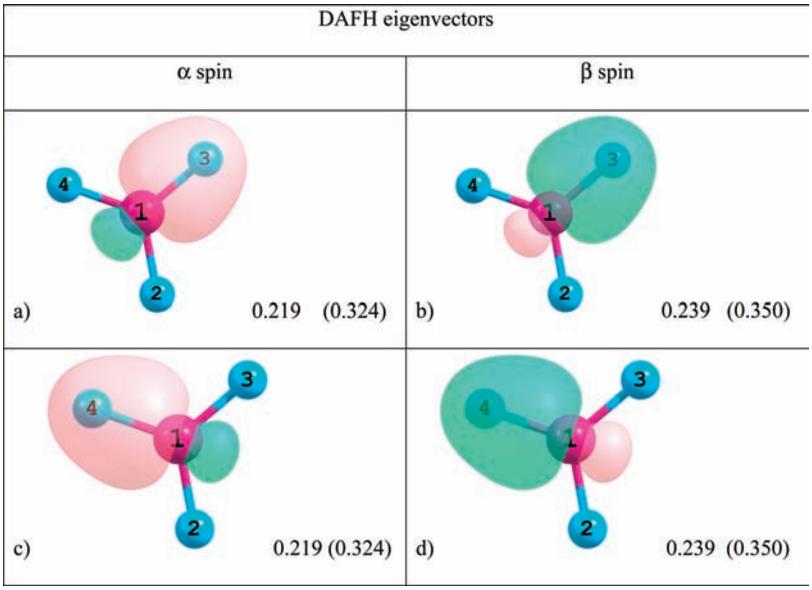
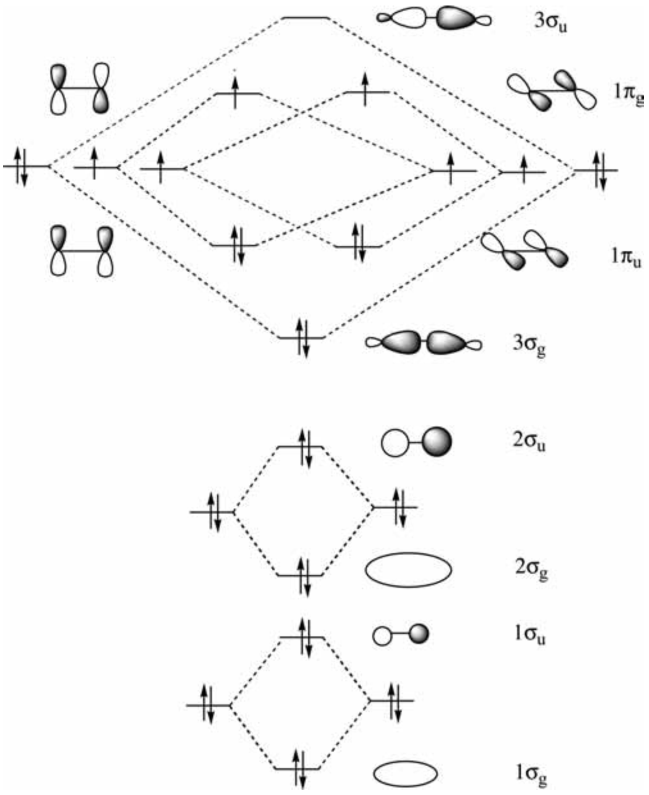


Figure 2. Eigenvalues and eigenvectors resulting from the DAFH analysis of the Fermi hole averaged over the individual H atoms (H3 and H4) of the radical cation $NH_3^{(+)}$. The numbers indicate the eigenvalues of the corresponding hole for the "exact" AIM form of the analysis; the values in parentheses correspond to the "approximate" Mulliken-like approach.

numerical values of the eigenvalues (also included in Figures 1 and 2), which in this case indicate, again in keeping with the expectation, slightly smaller polarity of NH bond than in the case of the AIM-based approach.

Triplet Ground State ($^3\Sigma_g^-$) of O_2. Another example, demonstrating the application of the DAFH analysis of open-shell systems we are going to report, concerns the description of the ground triplet $^3\Sigma_g^-$ state of the O_2 molecule. According to elementary MO considerations, the electron structure of this molecule is described by the configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$, which is characterized by the presence of two unpaired electrons in two mutually perpendicular π^* orbitals (Scheme 1).

SCHEME 1



As it will be shown, the qualitative MO picture also provides a simple rationale for the picture of the bonding resulting from the DAFH analysis. The analysis was performed for the fragment averaged over one of the oxygen atoms, whose formation thus requires formal symmetrical splitting of the molecule. The results of this analysis are summarized in Figure 3. The inspection of this figure shows that the analysis of the holes yields for the electrons of both α and β spin 5 essentially nonzero eigenvalues, but the distribution of the eigenvalues between the electrons of different spin is quite different. Thus, four eigenvalues are close to 1 and one is close to 0.5 for the electrons of α spin, while for the electrons of β spin there are only two eigenvalues close to 1 and three close to 0.5. In view of the universal normalization satisfied by the individual spin components of DAFHs (eq 16):

$$\int g_\Omega^\alpha(r_1)\, \mathrm{d}r_1 = N_\alpha$$
$$\int g_\Omega^\beta(r_1)\, \mathrm{d}r_1 = N_\beta \qquad (16)$$

the above result reflects the well-known result that of the 8 electrons that each O atom contributes to the molecule, 4.5 is effectively of α and 3.5 of β spin.[59] To reveal the physical meaning of the above distribution of electrons, it is useful to confront the above numerical results with the actual shapes of the associated eigenvectors. The simplest situation is with the first two pairs eigenvectors associated with the eigenvalues close to 1 (Figure 3a,b and c,d); they evidently describe the electrons involved in the shared core $1s^2$ electron pair and slightly polarized $2s^2$ electron pair localized on one of the O atoms (the one over which the Fermi hole was averaged). A similarly simple situation is also with the pair of eigenvectors 3e,3f, which are reminiscent of the localized $3\sigma_g$ orbital of OO bond but whose populations suggest that they correspond to contributions of α and β spin electrons to the broken valence formally split OO σ bond. A bit more complex situation is, however, with the remaining two pairs of eigenvectors (3g,3h and 3i,3j) whose form for α and β spin electrons considerably differs from each other. However, as surprising as this result may seem to be, we are going to show that the picture of the bonding it implies is

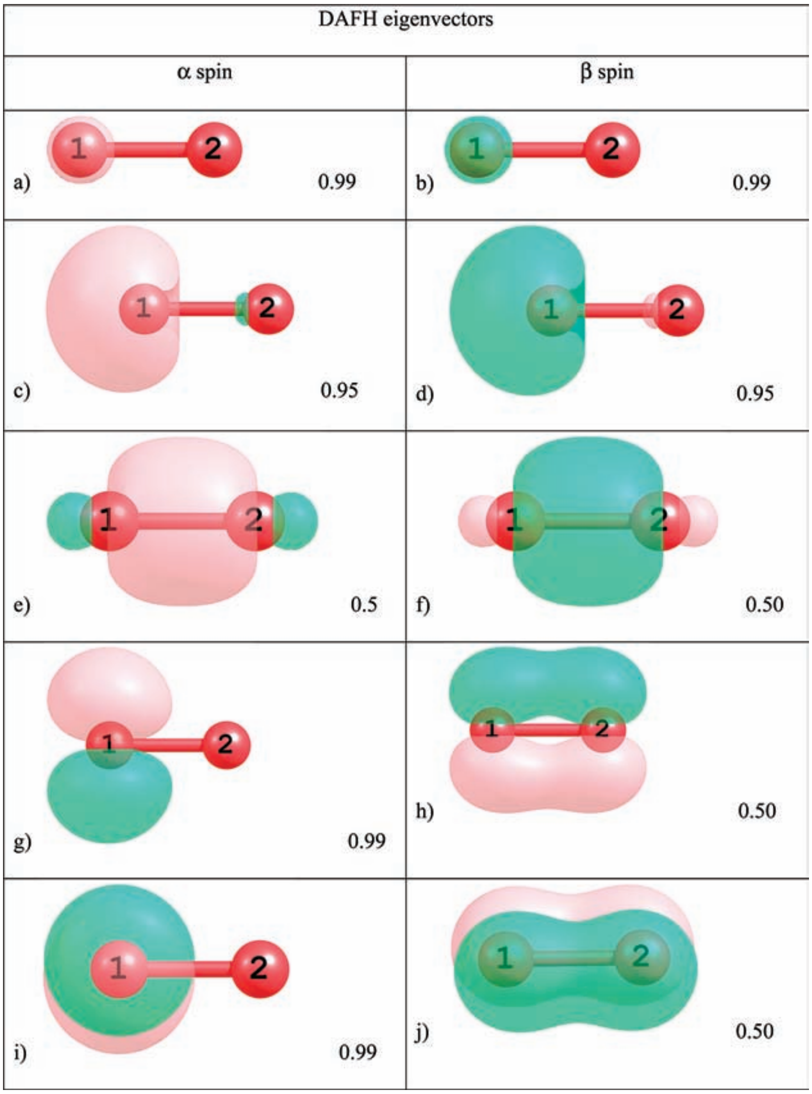
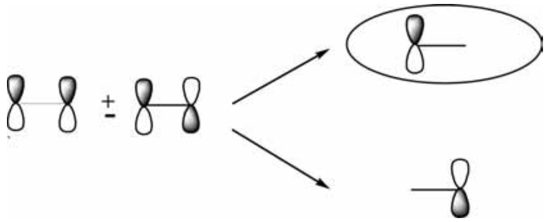


Figure 3. Eigenvalues and eigenvectors resulting from the DAFH analysis of the Fermi hole averaged over the atom O1 in the O_2 molecule.

nevertheless straightforwardly consistent with the qualitative MO diagram of Scheme 1. For this purpose, let us first focus on the electrons of β spin. In this case, the associated eigenvectors (Figure 3h,j) are reminiscent of the pair of occupied bonding π_u orbitals, and because of their populations it seems natural to interpret them as the β-spin components of the broken valences of formally split OO π bonds. If this is the case, one has to ask, however, why the form of the complementary α spin components is so much different and why one does not observe the α-spin eigenvectors complementary to broken valences of the OO π bond as in the case of β-spin electrons. To understand this dramatic difference, it is useful to take into account the factors underlying the construction and analysis of the DAFHs. As it has been said above, the important step of the DAFH analysis is the isopycnic localization whose goal is to transform the original canonical molecular orbitals into localized functions that can more easily be interpreted in chemical terms. While in the case of the closed-shell systems such functions can usually be straightforwardly associated with the classical chemical concepts of bonds and/or core or lone electron pairs, etc., in the case of open-shell systems the analysis of the DAFH performs the isopycnic localization for the molecular orbitals of α- and β-spin separately, and it is just here where the difference in the final outcome of the analysis comes from. The clue to understanding is closely tied with the different possibilities localization of π-molecular orbitals in the MO Scheme 1. As it is possible to see from this scheme, there are two β-spin electrons in two occupied π_u molecular orbitlas, but because of localization in different planes, these orbitals cannot be mixed in the isopycnic localization, and this impossibility is reflected in that the corresponding DAFH eigenvectors still keep the form of the original canonical molecular orbitals. A slightly different situation is, however, in the case of α-spin electrons, because in addition to the pair of bonding π_u orbitals, there is in this case another pair of antibonding π_g orbitals, of which each is occupied by one electron. This implies that in this case there is a possibility of mixing of these orbitals during the isopycnic localization (Scheme 2).

SCHEME 2



This mixing results in two new singly occupied localized orbitals, of which one is detected among the DAFH eigenvectors averaged over the analyzed fragment; the other would be observed in the DAFH analysis of the DAFH averaged over the complementary domain of the second O atom.

This result is very interesting as it implies that the possibilities of localization and/or delocalization of α- and β-spin electrons in O_2 molecule are dramatically different. As a consequence, the π components of OO bonds cannot be regarded as ordinary shared electron pair bonds, but the delocalization, which is the prerequisite for the sharing, in fact involves only the electrons of β-spin. The electrons of α-spin remain localized on the O atoms. The above peculiar picture of the bonding is thus straightforwardly consistent with the conclusions of the earlier study,[59] in which the prevailing localization of α-spin electrons was deduced from the analysis of the delocalization indices (SEDI),[60] but in contrast to the numerical evidence of that study, the present study also provides a simple qualitative insight into the origin of the observed peculiar differences.

Conclusions

This Article reports the extension of the formalism of the so-called domain averaged Fermi hole analysis beyond the scope of closed-shell systems. The applicability of the proposed generalization has been demostrated by the detailed analysis of the two model systems, the doublet state of $NH_3^{(+)}$ and the ground triplet state of O_2 molecule. The picture of the bonding resulting from the above analyses has been shown to be completely consistent with the conclusions of earlier computational approaches, but in contrast to these approaches that rely only on the numerical values of various auxiliary indices, the proposed approach provides simple qualitative insights, allowing one to rationalize the structure of the systems with unpaired electrons in visual terms close to classical chemical thinking. This allows us to believe that the proposed generalization of DAFH analysis could hopefully represent a new attractive tool for the elucidation of the structure and bonding especially in open-shell molecules with a nontrivial bonding pattern. An example in this respect is represented by the triplet state of the dication $C_2O_4^{(2+)}$, whose existence has been recently detected in a study.[61] The analysis of this and some other related molecules is being pursued in our laboratory, and the results will be reported elsewhere.

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References and Notes

(1) Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762.

(2) Pauling, L. *The Nature of Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(3) Coulson, C. A. *Valence*, 2nd ed.; Oxford University Press: New York, 1961.

(4) Lennard-Jones, J. *Proc. R. Soc. London, Ser. A* **1949**, *198*, 14.

(5) Hurley, A. C.; Lennard-Jones, J.; Pople, J. A. *Proc. R. Soc. London, Ser. A* **1953**, *220*, 446.

(6) Lennard-Jones, J.; Pople, J. A. *Proc. R. Soc. London, Ser. A* **1950**, *02*, 166.

(7) Lennard-Jones, J. *J. Chem. Phys.* **1952**, *20*, 1024.

(8) Berlin, T. *J. Chem. Phys.* **1951**, *19*, 208.

(9) Ruedenberg, K. *Rev. Mod. Phys.* **1962**, *14*, 326.

(10) Hund, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 87.

(11) Julg, J.; Julg, P. *Int. J. Quantum Chem.* **1978**, *3*, 483.

(12) Levy, M. *J. Am. Chem. Soc.* **1976**, *98*, 6849.

(13) Gopinathan, M. S.; Jug, K. *Theor. Chim. Acta* **1983**, *68*, 497–511.

(14) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

(15) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270.

(16) Sannigrahi, A. B. *Adv. Quantum Chem.* **1992**, *23*, 301.

(17) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142.

(18) Ponec, R.; Strnad, M. *Int. J. Quantum Chem.* **1994**, *50*, 43.

(19) Ponec, R.; Uhlik, F. *J. Mol. Struct. (THEOCHEM)* **1997**, *391*, 159.

(20) Daudel, R.; Bader, R. F. W.; Stephens, M. E.; Borrett, D. S. *Can. J. Chem.* **1974**, *52*, 1310.

(21) Salem, L. *Nouv. J. Chim.* **1978**, *2*, 559.

(22) Giambiagi, M. S.; Giambiagi, M.; Jorge, F. E. *Theor. Chim. Acta* **1985**, *68*, 337.

(23) Bader, R. F. W. *Atoms in Molecules-A Quantum Theory*; Oxford University Press: Oxford, UK, 1990.

(24) Bader, R. F. W.; Johnson, S.; Tang, T. H.; Popelier, P. L. A. *J. Phys. Chem.* **1996**, *100*, 15398.

(25) Bader, R. F. W.; Stephens, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 7391.

(26) Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397.

(27) Savin, A.; Becke, A. D.; Flad, J.; Nesper, R.; Preuss, H.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *30*, 409.

(28) Silvi, B.; Savin, A. *Nature (London)* **1994**, *71*, 683.

(29) Gillespie, R. J.; Popelier, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3331.

(30) Savin, A. *Reviews of Modern Quantum Chemistry. A celebration of the contributions of R. G. Parr*; World Scientific: Singapore, 2002; pp 43−62.

(31) Kohout, M. *Faraday Discuss.* **2007**, *35*, 43.

(32) Gatti, C.; Lasi, D. *Faraday Discuss.* **2007**, *135*, 55.

(33) Scemama, A.; Cafarel, M.; Savin, A. *J. Comput. Chem.* **2007**, *28*, 442.

(34) Pendas, A. M.; Francisco, E.; Blanco, M. A. *J. Phys. Chem. A* **2007**, *111*, 1084.

(35) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(36) Frenking, G.; Shaik, S. *J. Comput. Chem.* **2007**, 28.

(37) Ponec, R. *J. Math. Chem.* **1997**, *21*, 323.

(38) Ponec, R. *J. Math. Chem.* **1998**, *23*, 85.

(39) Ponec, R.; Roithová, J. *Theor. Chem. Acc.* **2001**, *105*, 383.

(40) Ponec, R.; Cooper, D. L.; Savin, A. *Chem.-Eur. J.* **2008**, *14*, 3338.

(41) Ponec, R.; Girones, X. *J. Phys. Chem.* **2002**, *106*, 9506.

(42) Ponec, R.; Cooper, D. L.; Yuzhakov, G. *Theor. Chem. Acc.* **2004**, *112*, 419.

(43) Ponec, R.; Yuzhakov, G.; Carbó-Dorca, R. *J. Comput. Chem.* **2003**, *24*, 1829.

(44) Ponec, R.; Yuzhakov, G.; Gironés, X.; Frenking, G. *Organometallics* **2004**, *23*, 1790.

(45) Ponec, R.; Yuzhakov, G.; Sundberg, M. *J. Comput. Chem.* **2005**, *26*, 447.

(46) Ponec, R.; Lendvay, G.; Sundberg, M. R. *J. Phys. Chem. A* **2008**, *112*, 2008.

(47) Ponec, R.; Chaves, J.; Lendvay, G. *J. Comput. Chem.* **2008**, *29*, 1287.

(48) Ponec, R.; Yuzhakov, G. *Theor. Chem. Acc.* **2007**, *118*, 791.

(49) Kohn, W.; Sham, J. *Phys. Rev. A* **1985**, *140*, 1133.

(50) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, 136.

(51) Ponec, R.; Cooper, D. L. *Faraday Discuss.* **2007**, *135*, 31.

(52) Ponec, R.; Cooper, D. L. *J. Phys. Chem. A* **2007**, *111*, 11294.

(53) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.

(54) Wigner, E.; Seitz, F. *Phys. Rev.* **1933**, *43*, 804.

(55) McWeeny, R. *Rev. Mod. Phys.* **1960**, *32*, 335.

(56) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990.

(57) Cioslowski, J. *Int. J. Quantum Chem.* **1990**, *S24*, 15.

(58) Keith, T. A. *AIMAll (Version 08.11.06)*; 2008; aim.tkgristmill.com.

(59) Fradera, X.; Solà, M. *J. Comput. Chem.* **2002**, *23*, 1347.

(60) Ponec, R.; Cooper, D. L. *J. Mol. Struct. (THEOCHEM)* **2005**, *727*, 133.

(61) Roithová, J.; Ricketts, C. L.; Schröder, D.; Price, S. D. *Angew. Chem., Int. Ed.* **2007**, *46*, 9316.

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