Electron Pairing and Chemical Bonds: Pair Localization in ELF Domains From the Analysis of Domain Averaged Fermi Holes

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Received 8 February 2006; Accepted 2 March 2006
DOI 10.1002/jcc.20465
Published online 17 August 2006 in Wiley InterScience (www.interscience.wiley.com).

Abstract: This article reports the application of a recently proposed formalism of domain averaged Fermi holes to the problem of the localization of electron pairs in electron localization function (ELF) domains and its possible implications for the electron pair model of chemical bond. The main focus was on the systems, such as H₂O or N₂, in which the “unphysical” population of ELF domains makes the parallel between these domains and chemical bond questionable. On the basis of the results of the Fermi-hole analysis, we propose that the above problems could be due to the fact that in some cases the boundaries of the ELF domains need not be determined precisely enough.


Key words: chemical bonding; pair localization; ELF; domain averaged Fermi holes

Introduction

The Lewis model of chemical bond1 represents one of the pivotal achievements in the effort to understand and to interpret the molecular structure. Although invented before the advent of quantum theory, the idea that chemical bonds are formed by shared electron pairs has proved to be extremely fruitful and became the basis of classical structural theory. Because of immense debt which chemistry owes to the classical model of molecule as composed of directionally oriented and well localized chemical bonds, it is not surprising that a lot of effort was and still is devoted to its reconciliation with the quantum mechanical description in terms of delocalized wave functions.2–18 One of the promising procedures which indeed seem to provide the desired link between the classical and quantum chemical description of chemical bonding is the approach based on the so-called electron localization function (ELF).19–22 This function allows the unique partitioning of the molecule into disjunct domains, which indeed are reminiscent of classical chemical bonds. This parallel was also addressed in the recent study23 in which ELF domains were also found to represent reasonable approximation to the domains of minimum electron fluctuation,11 which were recently shown to coincide with the domains of maximum pair localization for the model of strictly localized orbitals.24 Although there is no doubt that the idea of ELF represents an important argument corroborating the localized nature of chemical bonds anticipated by the Lewis model, there are nevertheless examples, where the straightforward parallel between the ELF domains and chemical bonds is seriously questioned. The typical example of such a failure is the situation where the number of electrons in the domain dramatically deviates from the classical anticipations. An example in this respect can be, e.g., the molecule of N₂, where the ELF domain assumed to correspond to lone electron pair is populated by more than three electrons. This exaggerated population of lone pair domain is then compensated by complementary depletion of electrons from the domain corresponding to NN triple bond. Similar, albeit not so dramatic situation is also in molecules like NH₃ or H₂O. The possible reasons for such failure were recently discussed in the study.23 Our aim in this study is to address the problem of the questionable ELF domains, using a recently proposed approach based on the analysis of domain averaged Fermi holes but modified in a sense that averaging was performed over ELF rather than over originally used AIM domains. The results of such an analysis do indeed confirm the original claims23 that the exaggerated accumulation of electrons in some domains, as well as complementary depletion of electrons from the other domains, apparently arises from incorrectly determined boundaries of ELF domains in such questionable cases.
Theoretical

Domain averaged Fermi holes, introduced some time ago\textsuperscript{25–27} as a generalization of the original concept by Wigner and Seitz,\textsuperscript{28} have proved to represent a new and efficient tool for the interpretation of the nature of chemical bond, and numerous recent applications of this new methodology has clearly shown its usefulness for the elucidation of the picture of bonding, especially in molecules with nontrivial bonding pattern.\textsuperscript{29–34}

The domain-averaged Fermi holes can most straightforwardly be introduced by eq. (1) in which $\rho(r_1)$ and $\rho(r_2)$ are the pair and first order density, respectively, and the averaging (integration) is performed over the finite domain $\Omega$.

$$g_\Omega(r_1) = \rho(r_1) \int_\Omega \rho(r_2) \, dr_2 - 2 \int_\Omega \rho(r_1, r_2) \, dr_2.$$  \hspace{1cm} (1)

In the particular case of HF approximation to which was restricted most of the previous applications, the original formula reduces eq. (2)

$$g_\Omega(r_1) = 2 \sum_i^{occ} \sum_j^{occ} \langle \varphi_i | \varphi_j \rangle \varphi_i(r_1) \varphi_j(r_1)$$  \hspace{1cm} (2)

in which $\varphi_i$ and $\varphi_j$ represent occupied molecular orbitals, and $\langle \varphi_i | \varphi_j \rangle_\Omega$ denotes the overlap integral of orbitals $\varphi_i$ and $\varphi_j$ over the domain $\Omega$ [eq. (3)].

$$\langle \varphi_i | \varphi_j \rangle_\Omega \int_\Omega \varphi_i^*(r) \varphi_j(r) \, dr.$$  \hspace{1cm} (3)

The Fermi holes (1) satisfy the universal normalization condition (4)

$$\int g_\Omega(r_1) \, dr_1 = N_\Omega,$$  \hspace{1cm} (4)

which says that the integral of the hole over the whole space equals to the total number of the electrons in the domain $\Omega$. This general property has important implications which will be advantageously used in this study. The analysis of the holes is based, namely, on the diagonalization of the matrix which represents the hole of either molecular or atomic orbitals, followed by the subsequent isopycnic transformation.\textsuperscript{35} The desired structural information is then being retrieved from the nonzero eigenvalues and eigenvectors. Such analysis applied previously to holes averaged over the domains resulting from Bader’s virial partitioning of electron density (AIM),\textsuperscript{36} has shown that in the case of holes averaged over the domain associated with single atom, the approach straightforwardly provides the information about the valence state of that atom in a molecule. Valuable information can also be obtained from the holes averaged over composite domains formed by the union of several atomic domains corresponding, e.g., to functional groups and/or interesting molecular fragments where they reveal the electron pairs associated with chemical bonds and lone pairs retained in the fragment as well as about the free valences of broken bonds, whose formal splitting is required to isolate the fragment from the rest of the molecule.

Although the reported examples clearly demonstrated the usefulness of domain averaged holes for structural elucidations, the applicability of the approach is in no way restricted to the particular choice of AIM domains and one could in principle analyze the holes averaged over the domains of the arbitrary shape. Such a complete freedom in the choice of the shape of the domain is, of course, unlikely to provide any reasonable structural information, but the situation can be quite different in the case of domains introduced, such as AIM domains, on the basis of some sound physical ideas and models. This is just the case of domains resulting from the topological analysis of electron localization function (ELF). Similarly, as in the case of AIM partitioning, the ELF domains dissect the molecule into nonoverlapping domains, whose importance for structural elucidations arises from the fact that they are often very reminiscent of localized chemical bonds. The main goal of this study is to examine whether or to what extent the ELF domain does indeed characterize the domains of high localization of electron pairs and, consequently, to what extent they can be associated with chemical bonds and lone pairs of the classical structural formula. This can be especially interesting for puzzling systems such as H\textsubscript{2}O, N\textsubscript{2} etc, in which the ELF partitioning yields domains whose electron population considerably deviates from the classical anticipations and for which the association with classical concepts is questionable.

Computations

The suitability of ELF domains to represent in the molecules the regions of high localization of electron pairs was examined on a series of molecules ranging from simple model systems in which the satisfactory pair localization was possible (LiH) to puzzling systems (N\textsubscript{2}, H\textsubscript{2}O) in which the impossibility of sufficient pair localization results in “unphysical” electron population in ELF domains, which is apparently inconsistent with the traditional picture of the molecule as depicted by the classical structural formula. The above analysis required performing several types of calculations. First, it was necessary to generate the reliable wave functions for all the studied molecules. These calculations were performed using the Gaussian 98 series of programs\textsuperscript{37} at HF/6-31G* level of the theory. This level of the theory was chosen so as to correspond to the computational methods used in the previous studies\textsuperscript{11,23} to which we refer here. All the molecules were considered in completely optimized molecular geometries. After generating the wave functions and density matrices of the studied molecules, the subsequent analysis required first to perform the partitioning of the molecule into ELF domains. These calculations were performed using the TopMod program,\textsuperscript{38} modified so as to print in a separate file the matrix of overlap integrals of occupied molecular orbitals [eq. (3)] integrated over ELF domains. This file was then used, as an input for our own program FermiELF, which performed the analysis of the Fermi hole averaged over ELF domains. The results of the analysis are summarized in Tables 1–3 and Figures 1–3.
Results and Discussion

After having introduced the basic methodological background, let us discuss now the results of our calculations and let us start first with the molecule of LiH for which high localization of electron pairs in the domains corresponding to both core 1s² electrons and LiH bond was found in the previous study.²³

LiH

The ELF partitioning dissects in this case the molecule into two domains. One of them is associated with core 1s² electron pair of Li and the other with the electron pair of LiH bond and as it was found in the previous study,²³ the extremely low values of domain fluctuations as well as near coincidence of domain populations to ideal value of 2 clearly confirm that the localization of electron pairs in these domains is indeed very high. This picture of bonding is then straightforwardly corroborated by the results of the Fermi-hole analysis (Table 1). Such analysis shows, for example, that the diagonalization of the hole associated with the ELF domain corresponding to 1s² electron pair and populated by 2.01 electrons yields two nonzero eigenvalues of which one is equal to 1.98 and the other to 0.03. The inspection of the form of the corresponding eigenvectors shows that the dominant contribution to electron pair in this ELF domain (Fig. 1a) does indeed corresponds to the original interpretation (1s² core electron pair on Li), but the existence of the second nonzero eigenvalue whose eigenvector is displayed in Figure 1b shows that the electrons in this domain are very slightly contaminated by the contribution from the electron pair of LiH bond. A similar situation, also for the second domain, is assumed to correspond to LiH bond. The dominant contribution to the total population of LiH bond domain (1.98 electrons) comes again from the first eigenvalue (1.95), (Fig. 1c), but the existence of the second nonzero eigenvalue (0.03), together with the form of the corresponding eigenvector (Fig. 1d) clearly suggest a small contamination of the electron pair of LiH bond by 1s² core electron pair on Li. Although the contaminating contributions are in this case at the limit of accuracy to which the integration over the ELF domains can be trusted, so that they can be neglected without any deeper impact on the final picture of bonding, the situation can be quite different in other molecules. As it will be shown, the contamination of electron population in individual ELF domains by the contributions from other domains is a general phenomenon, whose existence can provide not only the explanation for the increased domain fluctuation reported in the studies¹¹,²³ for molecules like BH₄(−) and CH₄, but also to reveal the origin of the “unphysical” electron population of ELF domains in molecules.

Table 1. Analysis of Fermi Holes Averaged Over ELF Domains for the Molecule of LiH and CH₄.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Domain</th>
<th>N_D (fluctuation)</th>
<th>Eigenvalue 1 (degeneracy)</th>
<th>Eigenvalue 2 (degeneracy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>C(Li)</td>
<td>2.01 (0.065)</td>
<td>1.98 (1×)</td>
<td>0.03 (1×)</td>
</tr>
<tr>
<td></td>
<td>V(LiH)</td>
<td>1.98 (0.065)</td>
<td>1.95 (1×)</td>
<td>0.03 (1×)</td>
</tr>
<tr>
<td>CH₄</td>
<td>C(C)</td>
<td>2.08 (0.24)</td>
<td>1.92 (1×)</td>
<td>0.04 (4×)</td>
</tr>
<tr>
<td></td>
<td>V(CH)</td>
<td>1.97 (0.61)</td>
<td>1.64 (1×)</td>
<td>0.11 (3×)</td>
</tr>
</tbody>
</table>

Figure 1. The eigenvalues and eigenvectors of the Fermi holes corresponding to ELF domains associated with core 1s² electron pair and electron pair of LiH bond in LiH.
such as H\textsubscript{2}O and N\textsubscript{2}. To demonstrate the applicability of our approach, let us first discuss the example of methane molecule.

\textit{CH\textsubscript{4}}

The localization of electron pairs in this molecule was first studied by Bader and Stephens\textsuperscript{11} who addressed the problem of pair localization in the domains of minimum electron fluctuation and concluded that this molecule represents the borderline example of the system for which the concept of localized electron pairs starts to lose its meaning. The existence of increased electron fluctuation was reported also in the recent study\textsuperscript{23} and although that study has shown that higher fluctuation in some domains does not require the complete omission of electron pair model of chemical bond, no real explanation for the observed increase was proposed. This can now be achieved using the analysis of ELF domain averaged Fermi holes.

The partitioning of methane molecule into ELF domains is quite straightforward and clearly reflects the parallel with classical structural formula. Consistent with this parallel, the partitioning yields five domains of which one, populated by 2.08 electrons, can straightforwardly be interpreted as corresponding to core 1s\textsuperscript{2} electron pair on carbon, and the other four, populated by 1.97 electrons, to electron pairs of CH bonds. Despite such a reasonably close coincidence of electron populations with the classical anticipations, the existence of increased electron fluctuation in these domains (Table 1) clearly implies that corresponding electron pairs cannot be localized in this case to such a degree as in the previous case of LiH. To reveal the origin of these increased fluctuations, it is useful to subject the corresponding domains to the formalism of the Fermi-hole analysis. The results of such analysis are summarized in Table 1 and Figure 2. Thus, for example, the analysis of the hole associated with core electron pair on C yields five nonzero eigenvalues of which the dominant one is equal to 1.92 and the rest to complete the total population of the domain (2.08 electrons) comes from the group of four degenerated eigenvalues each of which equals 0.04. The inspection of the corresponding eigenvectors shows that the dominant contribution to the population of core domain comes indeed from 1s\textsuperscript{2} electron pair on C, (Fig. 2a) but in addition to this, there are nonnegligible contributions arising from the contamination with electrons localized in four CH bonds (Fig. 2b). Similar contamination is then also clearly evident in the analysis of the hole associated with the ELF domain of a CH bond. Although the population of this bond is reasonably close to the ideal value of 2, so that there are apparently no complications with the association of these domains with localized electron pairs of CH bond, the analysis of the corresponding Fermi hole shows that the situation is nevertheless slightly more complex. This analysis shows, namely, that the total population of CH bond domain does not originate from the electrons localized in this particular domain only. The inspection of the Table 1 shows that although dominant contribution of 1.64 electrons is indeed due to electrons localized in the domain of the corresponding CH bond (Fig. 2c), there are

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
   & 1.92 & 0.04 \\
\hline
   & 1.64 & 0.11 \\
\hline
\end{tabular}
\caption{The eigenvalues of the Fermi hole averaged over the ELF domains associated with core 1s\textsuperscript{2} electron pair on C and the electron pair of CH bond.}
\end{table}
The ELF partitioning of this molecule is very simple and consistent with the expectations—it distributes 10 electrons into five domains. First of them, populated by 2.13 electrons, can evidently be associated with core electron pair on oxygen. The detailed Fermi-hole analysis based projection of the total population into individual contributions shows that dominant term (1.89) really comes from $1s^2$ core electron pair on oxygen, but the rest comes again from the interference with the two $\sigma_{\text{OH}}$ bonds ($2 \times 0.07$) and the lone pairs ($2 \times 0.05$). Similar but again nonnegligible contributions from electrons localized in the domains of remaining CH bonds ($3 \times 0.11$) (Fig. 2d).

This result is very important. It demonstrates, namely, that although the population of a given domain can still be plausibly close to the ideal value characteristic for localized electron pairs, the corresponding electrons do not behave statically but interfere with the electrons from other domains. Such interference is, of course, quite normal as it only reflects the well known fact that perfect localization of electron pairs into nonoverlapping domains is impossible, but what makes the situation of methane molecule slightly exceptional is the extent of the interference, which is much deeper than in the previous case of LiH molecule, and we believe that it is just here where the increased electron fluctuations reported for the methane molecule in previous studies\textsuperscript{11,23} come from.

To reveal the origin of the increased domain fluctuations it is, however, necessary to understand first the mechanism which is responsible for the interference of electrons from different domains. On the basis of the results of Fermi-hole analysis, we suppose that the main problem could be in the determination of the boundaries of individual ELF domains in some cases. The example of methane molecule is not in this respect very typical, since no indication of such a problem is evident from the values of domain fluctuations. Their values, namely, still remain plausibly close to ideal values anticipated for localized electron pairs, and it was only due to Fermi-hole analysis that the phenomenon of the interference of electrons from individual domains could be revealed. This, however, is not always the case and in the following part, we are going to discuss the examples of two systems ($\text{H}_2\text{O}$ and $\text{N}_2$), for which the possibility of the eventual incorrect determination of the boundaries of ELF domains is to be considered much more seriously. The results of the analysis for water molecule are summarized in Table 2.

### Table 2. Analysis of Fermi Holes Averaged Over ELF Domains for the Molecule of H$_2$O.

<table>
<thead>
<tr>
<th>Domain</th>
<th>$N_{\text{fl}}$ (fluctuation)</th>
<th>$\lambda_1$ (interpretation)</th>
<th>Eigenvalues 2 and 3 (interpretation)</th>
<th>Eigenvalues 4 and 5 (interpretation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(O)</td>
<td>2.13 (0.33)</td>
<td>1.89</td>
<td>0.07</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1s^2$ (O)</td>
<td>Lone pairs (O)</td>
<td>$\sigma_{\text{OH}}$</td>
</tr>
<tr>
<td>V(OH)</td>
<td>1.70 (0.77)</td>
<td>1.32</td>
<td>0.14</td>
<td>$\sigma_{\text{OH}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lone pairs (O)</td>
<td>0.09 and 0.01</td>
</tr>
<tr>
<td>V(O)</td>
<td>2.25 (1.04)</td>
<td>1.46</td>
<td>0.35</td>
<td>0.05 and 0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lone pair $2 \times \sigma_{\text{OH}}$</td>
<td>Second lone pair and $1s^2$ (O)</td>
</tr>
</tbody>
</table>

much deeper interference also contributes to the electron population of ELF domain associated with OH bonds and the lone pairs. Increased importance of the interference is in this case clearly evident already from the values of domain populations, whose values start to deviate from the ideal value of 2 quite considerably. These deviations are then also accompanied by much higher domain fluctuations, especially in the case of lone pairs. To reveal the origin of these increased fluctuations, it is again useful to invoke the results of Fermi-hole analysis. Thus, for example, in the case of the domain associated with one OH bond, the overall population of this domain (1.70 electrons) is indeed composed of the dominant contribution arising from the ELF domain of this particular OH bond (1.32 electrons), but the contributions from the two lone pairs (0.14 each) and the second OH bond (0.09) clearly suggest that the interference of electrons from various domains is in this case indeed increasingly important. This tendency of increasing importance of interference of electrons from various domains is even more strongly evident in the results of the Fermi-hole analysis for the domains associated with the lone pairs. The population of these domains exceeds this ideal limit of 2 and the actual value is around 2.25 electrons. The inspection of Table 2 shows the terms that contribute to the total electron population of this domain. The most important of them is, of course, the population of the corresponding lone pair domain itself (1.46 electrons), but the contaminating contributions from other domains, namely, the domains of both OH bonds (0.35 each), the domain of the second lone pair (0.05 electrons) and even the domain of $1s^2$ core electron pair on O (0.04 electrons) are in this case so important that the final population of the domain exceeds the idealized value of 2 quite considerably.

What can be deduced from these results? The problem of the primary importance is not in the existence itself of the interference of electrons from various domains, but again the extent of this interference is so large that considerable deviations of values of the domain populations from the idealized limits really suggest the possibility of the incorrect determination of the boundaries of the corresponding ELF domains. This possibility seems to be corroborated also by the fact that the increase of the population in some domains is more or less compensated by the complementary decrease of the population of other domains. In our case, such a complementarity primarily concerns OH bond and lone pair domains. A similar situation is also observed for other molecules in which the complementary deviations of the actual domain populations are even much more important, so
that the parallel between ELF domains and localized electron pairs is really seriously questioned. The typical example in this respect is the molecule of N₂.

\[ N_2 \]

The fact that ELF partitioning in this molecule does not follow the straightforward parallel with the classical structural formula is clearly evident already from the fact that in spite of involving 14 electrons, the ELF partitioning yields only five domains. Two of them, populated by roughly 2.10 electrons are again easy to interpret. The detailed inspection of the Fermi hole averaged over this domain shows that the dominant contribution (1.91) to the total population of this domain comes from core 1s² electron pair on N. Nevertheless, similarly as in all previous cases, the Fermi-hole analysis reveals again the interference with other domains, which finds its reflection in the contaminating contribution (0.06 electrons) from the lone pair domain localized on the same N atom, the contributions from the two \( \pi \) components (0.04 electrons each) and the one \( \sigma \) component (0.05 electrons) of NN triple bond. This extent of the contamination is thus quite similar to what was observed for core domains in previous cases, so that the identification of this domain is completely straightforward. The situation is not, however, much more complicated with remaining three domains (Table 3). One of them, interpreted on the basis of topological analysis of ELF as the domain of NN triple bond is, namely, populated by only 3.54 electrons. This is so much different from the ideal limit of 6, which would correspond to three electron pairs of such bond, that any reasonable parallel with classical structural formula is practically impossible. The same problem is then also for two remaining domains whose population (3.12 electrons each) again strongly deviates from the ideal limit of 2 anticipated on the basis of their assignment to lone pairs. In previous examples, we have repeatedly met with the situation where electron population, in particular ELF domain, deviates from the classical expectations and these deviations were shown to originate from the interference of the electron population of a given domain with the electrons localized in other domains. This general mechanism is, of course, operating here as well; only the extent of the deviations is in this case so deep that even the very parallel between ELF domains and localized chemical bonds is in this case practically

<table>
<thead>
<tr>
<th>Domain (fluctuation)</th>
<th>( \bar{N} \Omega )</th>
<th>Eigenvalue 1 (interpretation)</th>
<th>Eigenvalues 2 and 3 (interpretation)</th>
<th>Eigenvalues 4 and 5 (interpretation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(NN) 3.54 (1.47)</td>
<td>1.69</td>
<td>0.82 (2 \times)</td>
<td>( \sigma_{NN} \times 2 \times \bar{\sigma}_{NN} )</td>
<td>2 \times \bar{\sigma}_{NN} lone pairs</td>
</tr>
<tr>
<td>V(N) 3.12 (1.10)</td>
<td>1.86</td>
<td>0.55 (2 \times)</td>
<td>( \bar{\sigma}_{NN} \times 0.11 ) and 0.05</td>
<td>( \sigma_{NN} ) and 1s² (N)</td>
</tr>
</tbody>
</table>

**Figure 3.** Eigenvalues and eigenvectors of the Fermi holes averaged over ELF domain associated with one of the lone pairs and NN bond in N₂ molecule.
impossible. In this situation, it is therefore of primary interest to consider again the role of individual domains in the interference and, especially, to identify the dominant contributions which the total domain population comes from. Such an insight can straightforwardly be deduced from the Fermi-hole analysis of the corresponding holes and the results of this analysis are summarized in Table 3. Let us discuss first the results for the domain of NN bond. This domain is populated by 3.54 electrons and the Fermi-hole analysis yields 5 nonzero eigenvalues. The largest of them is equal to 1.69 and the inspection of the corresponding eigenvector shows that it corresponds to $\sigma$ component of NN bond (Fig. 3a). In addition to this primary contribution, there is a pair of degenerated eigenvalues (0.82 each) which correspond to two $\pi$ components of NN bond (Fig. 3b). These dominant contributions thus account for about 90% of the electron population in this domain. The rest comes from the degenerated pair of contributions (0.10 each), corresponding to lone pairs on N atoms (Fig. 3c). This result is very interesting, since it demonstrates that the dominant contribution to the population of this domain really comes from $\sigma$ and $\pi$ components of NN bond, so that the association of this domain with NN bond is qualitatively correct. What, however, is really puzzling, is why the total amount of electrons contributed to the population of this domain from $\sigma$ and $\pi$ components of NN bond is so low. To understand the origin of this inconsistency, it is useful to inspect also the results of the analysis of the Fermi hole averaged over the domain of the lone pair. Such analysis yields again 5 nonzero eigenvalues of which the largest is equal to 1.86 and the inspection of the corresponding eigenvector shows that it is indeed very reminiscent of $\sigma$ lone pair. This dominant contribution is not in fact too much different from the idealized limit anticipated for the lone pair but again it strongly interferes with other contributions, owing to which the final domain population dramatically exceeds the idealized limit. The most important of these contaminating contributions come from the pair of degenerated eigenvalues equal to 0.55, whose inspection shows that they are very reminiscent of two $\pi$ components of NN bond (Fig. 3d). These contributions form the dominant part of the population of this domain and the rest comes from the interference of $\sigma_{NN}$ bond (0.11 electrons, Fig. 3e) and 1$s^2$ core electron pair (0.05 electrons, Fig. 3f) on the corresponding N atom.

The existence of the strong interference between the electrons in these two domains’ results suggests that possible clue to the solution of the problem of “unphysical” domain populations could be found in the near complementarity of the domain populations, which is reflected in the fact that depletion of electron population from the domain of NN bond is more or less compensated by the complementary increase of the population of lone pair domains. This result is thus very similar to what was observed already in the case of water molecule, only the extent of the deviations of the populations of bond and lone pair domains is much deeper, so that the possibility of incorrect determination of the boundaries of the corresponding domains is to be in this case considered even more seriously. Such a possibility seems to be also corroborated by the fact that in the linear molecule of $N_2$ both bond and lone pair domains are of the same cylindrical symmetry. As a consequence, there are no symmetry constraints that could prevent the interactions of $\sigma$ and $\pi$ components of NN bond with the lone pairs, and the absence of such constraints can be the main reason why the determination of the domain boundaries is in this case more difficult. In this connection it is, nevertheless, possible to ask whether the dramatic failure to yield realistic domain populations could not be, at least in part, due to particular form of ELF and whether other localization functions or procedures could not give “better” results.

In this connection, it is necessary to mention the recent studies by Savin and coworkers who proposed the partitioning into the so-called maximum probability domains and it is interesting that even in the “difficult” case of $N_2$ molecule, the population of lone pair and NN bond domains was indeed satisfactorily close to the classical expectations. This result is really very important and it would be therefore really interesting to subject these holes to the same scrutiny of the Fermi-hole analysis to see to what extent they are really able to improve the possible imperfections of ELF partitioning.

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