

Analytic Models of Domain-Averaged Fermi Holes: A New Tool for the Study of the Nature of Chemical Bonds

Robert Ponec,^{*,[a]} David L. Cooper,^[b] and Andreas Savin^[c]

Abstract: Simple analytical models are introduced that significantly enhance the ability to understand and rationalise the nature of bonding interactions depicted by domain-averaged Fermi hole (DAFH) analysis. The examples presented show that besides shedding new light on the role of electron-sharing in ordinary two-centre two-electron (2c–2e) chemical bonds that are well

represented by the classical Lewis model, the proposed approach also provides interesting new insights into the nature of bonding interactions that

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go beyond the traditional Lewis paradigm. This is, for example, the case of 3c–2e multicentre bonding, but a straightforward extension of the approach also reveals for direct metal–metal bonding the existence of a completely new type of bonding interaction that involves the mutual exchange of electrons between the lone pairs on adjacent metal atoms.

Introduction

The formulation of concepts is a vital and inescapable part of the human thought process and represents a crucial step in the development of science. As far as chemistry is concerned, the tenet of the chemical bond is such a key concept whose introduction crucially influenced our understanding of molecular structures and their transformations. A seminal contribution to understanding the nature of the chemical bond was made by Lewis^[1] who was probably the first to recognise correctly the electronic origin of the phenomenon. His basic idea that chemical bonds are usually formed by sharing electron pairs has become one of the cornerstones of the whole of modern chemistry. Reconciling the Lewis electron-pair model with the quantitative description provided by quantum mechanics^[2–33] continues to represent a chal-

lenge for contemporary chemical theory. A tribute to the role of Lewis in the development of our understanding of the nature of the chemical bond has recently been paid in the form of a special issue of the *Journal of Computational Chemistry*.^[34]

Although the parallel between quantum and classical chemical descriptions of chemical structures could relatively easily be demonstrated by using early approaches based on the analysis of approximate SCF wave functions,^[3,7,13–19] a similar “chemical” interpretation of more sophisticated wave functions, such as those resulting from contemporary high accuracy calculations, has proven to be more difficult. Among the existing tools for the analysis of arbitrary (both SCF and correlated) wave functions (or electron densities) it is possible to mention approaches such as the atoms-in-molecules (AIM) theory,^[23,24] electron localisation function (ELF),^[26–28] natural bond orbital (NBO) theory,^[33] various families of bond indices or populations^[14–17,35–50] and a range of other schemes.^[51–55]

Given that chemical bonding is often associated with notions of the sharing of electron pairs, the most straightforward approach to discerning the nature of the chemical bond could be expected to emerge from an analysis of correlated pair densities. The use of such analyses has received considerable attention recently, as evidenced from a wealth of studies.^[43–46] A procedure based on the analysis of the so-called domain-averaged Fermi holes (DAFH) can also be included in the framework of these approaches.^[56–58] This method aims to extract highly visual information about elec-

[a] Prof. R. Ponec
Institute of Chemical Process Fundamentals
Czech Academy of Sciences
Prague 6, Suchbát 2, 165 02 (Czech Republic)
Fax: (+420) 220-920-661
E-mail: rponec@icpf.cas.cz

[b] Dr. D. L. Cooper
Department of Chemistry, University of Liverpool
Liverpool, L69 7ZD (UK)

[c] Prof. A. Savin
Laboratoire de Chimie Théorique
Université de Paris VI and CNRS
place Jussieu, 75252 Paris (France)

tronic structure and bonding from one- and two-electron-density matrices. Various applications have demonstrated that it is indeed very useful for discerning the picture of bonding, especially for molecules with non-trivial bonding patterns, such as hypervalence and metal–metal bonding.^[59–64] Typically this approach has been applied at the restricted Hartree–Fock and/or Kohn–Sham level of theory to molecules close to equilibrium geometries. The formalism is, however, completely general and its extension beyond the scope of these approximations relies only on the availability of the correlated pair density.

The ability to extract the correlated pair density from various modern valence bond (VB) and multi-configuration self-consistent field (MCSCF) (including complete active space self-consistent field (CASSCF)) wave functions has made it possible, amongst other things, to monitor the reorganisation of the pattern of electron-sharing during the making and breaking of chemical bonds.^[65,66] Useful information is retrieved from numerical values of the eigenvalues of the Fermi hole averaged over the chosen fragment (usually one of the atoms) involved in the splitting of a single or multiple bond and from the evolution of the shape of the corresponding eigenvector. We found for simple non-polar diatomic molecules that the observed systematic changes of the shape of the DAFH eigenvector straightforwardly reflect a monotonic decrease of the extent of electron-sharing with increasing nuclear separation R . On the other hand, polar bonds that dissociate to neutral atoms are more complicated because of the way in which the bonding electron-pair must undergo deeper reorganisation, as necessitated by the dramatic change in the character of the wave function with increasing R .

The purpose of this work was to show how the results of earlier DAFH studies can be rationalised in terms of simple analytical models. It proved possible not only to understand the reported variation of the eigenvectors of the Fermi holes during the splitting of chemical bonds, but important new insights into bonding interactions that go beyond the traditional Lewis model of shared electron pairs, which includes multicentre bonding and also certain metal–metal bonds, have also been obtained.^[62] A similar idea for rationalizing the results of DAFH analysis, albeit mostly at the restricted Hartree–Fock level with an emphasis on core electrons, was recently suggested by Matito and Salvador.^[67]

Theory

Domain-averaged Fermi holes g_{Ω} can most readily be introduced by Equation (1), in which $\rho(r_1, r_2)$ and $\rho(r_1)$ are diagonal components of the usual spinless two- and one-electron density, respectively, and the integration is performed over the finite domain Ω .

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

The form of the domain-averaged Fermi hole, as well as its information content, does of course depend on the shape and size of the chosen domain Ω , but we have shown in previous studies^[56–59] that particularly interesting and chemically relevant information can be extracted from g_{Ω} when Ω is identified with an AIM domain that results from virial partitioning of the total electron density. In addition to holes averaged over the domain of a single atom, it is also possible to analyse more complex domains formed by the union of several atomic domains that correspond to a particular molecular fragment or functional group.

The analysis of the holes defined by Equation (1) involves, in the first step, the construction of a matrix representation of g_{Ω} expressed in an appropriate basis. The basis is typically chosen to be the set of orthonormal natural orbitals that diagonalise the usual one-electron-density matrix. The matrix representation of g_{Ω} is then diagonalised and the resulting eigenvectors (and associated eigenvalues) are subsequently localised by using a so-called isopycnic transformation,^[68] which leaves $g_{\Omega}(r_1)$ unchanged. This isopycnic procedure transforms the original orthogonal eigenvectors to a generally non-orthogonal set that consists of somewhat more localised functions. These functions, which are usually reminiscent of localised orbitals, correspond to individual chemical bonds, lone pairs and other such classical chemical concepts in terms of which many chemists still prefer to describe molecular structures.

Although full details of the interpretation of the DAFH analysis have been described in numerous previous studies,^[56–59] it is useful to summarise here the basic ideas to the extent necessary for the purposes of this work. Analysis of a hole averaged over the domain of a single atom typically provides information about the number and the nature of electron pairs (bonds) whose formal splitting would be required to isolate a given atom from the rest of the molecule. Similar situations arise in the analysis of holes relating to more complex domains. In such cases the analysis also provides, in addition to information about the formally split electron pairs (“broken valencies”), information about the electron pairs (bonds and core and/or lone-electron pairs) that remain intact within the fragment. The nature of the electron pairs, as well as of the broken valencies, is then revealed in a straightforward manner by inspecting the form of the corresponding semi-localised functions (transformed eigenvectors) and the values of the corresponding transformed eigenvalues.

In general, transformed eigenvalues (or “occupation numbers”) close to two typically correspond to chemical bonds within the fragment being analysed, to core orbitals or to lone pairs. Such an identification can be easily confirmed by examining the shapes of the corresponding transformed eigenfunctions (or DAFH functions). On the other hand, the DAFH functions derived for the different atomic domains contributing to a formally split two-electron bond often tend to have much the same shape and spatial extent as one another. This, together with the fact that the sum of the corresponding transformed eigenvalues tends to be close to two,

suggests that these occupation numbers can be regarded as the contributions of individual atoms to the shared electron pair of the formally split two-electron bond. We describe herein such a situation, in which the occupation numbers add to approximately two, as “near complementarity” of the eigenvalues.

Results and Discussion

Analytic models of DAFH: To understand better the DAFH results obtained from the analysis of the one- and two-electron densities associated with sophisticated ab initio wave functions, we propose simple analytical models of the DAFH analysis in this study. This allows a deeper insight into how electron correlation affects the extent of electron-sharing during the splitting of chemical bonds and into bonding interactions that go beyond the scope of the Lewis shared-electron-pair model. First of all, we will examine a simple model for the dissociation of a bonding electron pair in a homonuclear diatomic molecule.

Dissociation of the bonding electron pair in a homonuclear diatomic molecule: The proposed approach is based on the Fermi holes derived from the correlated electron-pair density resulting from the following classical VB wave function [Eq. (2)].

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

In this (normalised) wave function, Ψ_{cov} and Ψ_{ion} are the covalent and ionic components, respectively, which are constructed from atomic orbitals a and b that are localised on the individual atoms A and B, respectively [Eq. (3), in which Θ is the spin function for two electrons of opposite spin].

$$\begin{aligned} \Psi_{\text{cov}}(1,2) &= (1/\sqrt{2})[a(1)b(2)+b(1)a(2)]\Theta \\ \Psi_{\text{ion}}(1,2) &= (1/\sqrt{2})[a(1)a(2)+b(1)b(2)]\Theta \end{aligned} \quad (3)$$

The dissociation process is described straightforwardly in terms of Ψ_{VB} by means of the relative weights of the covalent and ionic components, Ψ_{cov} and Ψ_{ion} , as characterised by the value of ω in Equation (2). The pair density from which the Fermi holes are derived is in this case given by Equation (4) in which $\rho_{\text{cov}}(1,2)$ and $\rho_{\text{ion}}(1,2)$ denote the spinless contributions from the covalent and ionic components of the wave function, respectively, and $\rho_{\text{mix}}(1,2)$ is the corresponding cross term.

$$\begin{aligned} \rho(1,2) \equiv \int |\Psi_{\text{VB}}(1,2)|^2 d\sigma_1 d\sigma_2 &= \cos^2 \omega \rho_{\text{cov}}(1,2) \\ &+ \sin^2 \omega \rho_{\text{ion}}(1,2) + \sin 2\omega \rho_{\text{mix}}(1,2) \end{aligned} \quad (4)$$

To demonstrate the qualitative changes in the bonding interactions that accompany the splitting of the bonding electron pair, it is useful to focus first on the outcomes of sepa-

rate DAFH analysis of the purely covalent and purely ionic components of the wave function, for which the corresponding pair densities are as given in Equations (5a–c) in which we also show the corresponding cross term./>

$$\rho_{\text{cov}}(1,2) = 1/2[a(1)^2b(2)^2+b(1)^2a(2)^2+2a(1)b(1)a(2)b(2)] \quad (5a)$$

$$\rho_{\text{ion}}(1,2) = 1/2[a(1)^2a(2)^2+b(1)^2b(2)^2+2a(1)b(1)a(2)b(2)] \quad (5b)$$

$$\begin{aligned} \rho_{\text{mix}}(1,2) &= 1/2[a(1)^2a(2)b(2)+b(1)^2a(2)b(2) \\ &+ a(1)b(1)a(2)^2+a(1)b(1)b(2)^2] \end{aligned} \quad (5c)$$

We may now generate the “hole” g_{Ω} by inserting these expressions into the general definition [Eq. (1)] and performing the integrations over the chosen domain Ω .

Usually, when we choose the domains in DAFH analysis to be those that arise in virial partitioning of the total ab initio electron density, we can straightforwardly integrate over the real AIM domains. However, in the present case, in which we have a model wave function instead, we need to adopt a much simpler strategy. For this purpose we can imagine that orbital a is localised on atom A and that orbital b is localised on atom B in the sense of being expanded only by using basis functions that are centred on the given atom, as is the case in classical VB theory. Instead of restricting the integrations in Equation (1) to particular regions of three-dimensional space, we could then use a Mulliken-like scheme in which appropriate summations are restricted so as to include only the contributions from those basis functions that are associated with the chosen domain.^[50] In the case of bonds of low polarity, such as those in homonuclear diatomics,^[65,66] we have found that the results of DAFH analysis obtained by using such an approximation were very similar to those obtained from the more expensive AIM-based analysis. On the other hand, much larger, and indeed unacceptable, differences were seen for very polar bonds. We do not consider any such examples in this study.

For the present case, the Mulliken-like scheme that we have adopted consists of applying the approximations given in Equations (6a–c):

$$\int_{\Omega_A} a(2)a(2)dr_2 \approx 1 \quad (6a)$$

$$\int_{\Omega_A} b(2)b(2)dr_2 \approx 0 \quad (6b)$$

$$\int_{\Omega_A} a(2)b(2)dr_2 \approx 0 \quad (6c)$$

in which we have neglected any overlap integrals between basis functions centred on different atoms. By using the approximations specified in Equation (6), the holes averaged

over the domain of atom A then take the form given by Equations (7a–c):

$$g_{A,\text{cov}}(1) \approx a(1)^2 \quad (7a)$$

$$g_{A,\text{ion}}(1) \approx b(1)^2 \quad (7b)$$

$$g_{A,\text{mix}}(1) \approx a(1)b(1) \quad (7c)$$

Equation (7) implies that the Fermi hole derived from the purely covalent component of the wave function remains localised on the atom over which the averaging was performed, whereas the one determined from the purely ionic component is localised instead on the other atom. This result is very interesting because it suggests in the case of the general wave function defined in Equation (2) that the hole will be delocalised over both atoms. This is indeed the case, and the corresponding expression for $g_A(1)$, shown in Equation (8), suggests that the hole is given by the square of the function $f_A(1)$, shown in Equation (9), which represents the eigenvector of the hole in this simple case.

$$g_A(1) \approx 1 \times [\cos \omega a(1) + \sin \omega b(1)]^2 \quad (8)$$

$$f_A(1) = \cos \omega a(1) + \sin \omega b(1) \quad (9)$$

As anticipated, the function $f_A(1)$ is indeed delocalised over both atoms with the relative contributions depending on the value of ω . It is also evident from Equation (8) that the corresponding population (eigenvalue) is equal to one irrespective of the value of ω , and so it is tempting to interpret $f_A(1)$ as a broken valence of the formally split bond.

We have previously reported studies^[65,66] in which the splitting of the bonding electron pair in the ground state of H_2 was monitored by examining the Fermi holes generated by ab initio CASSCF and even full configuration interaction (CI) wave functions. Such analyses have shown that the dissociation of the bonding electron pair is primarily reflected in systematic changes to the shape of the corresponding eigenvector of the Fermi hole, whereas the corresponding eigenvalue is always close to unity, which shows only marginal variation with nuclear separation R . Both of these features are well reproduced by the analytical model that we have presented, as will now be shown, starting with the splitting of the simple electron-pair bond in the ground state of the H_2 molecule.

For values of R close to the equilibrium bond length R_e , CASSCF and full CI descriptions of H_2 are dominated by the self-consistent field (SCF) wave function with a 1:1 mixture of covalent and ionic classical VB components. We note that the dominant eigenvector of the hole from such a full CI wave function for H_2 near equilibrium geometry is reminiscent of a $1\sigma_g$ molecular orbital. This is precisely the form suggested by Equation (8) for the case of covalent and ionic components present in equal weights, that is, $\omega = \pi/4$. The first eigenvector from the corresponding hole associated

with the other atom takes the form shown in Equation (10) [cf. Equation (9)].

$$f_B(1) = \sin \omega a(1) + \cos \omega b(1) \quad (10)$$

Although the eigenvectors in Equations (9) and (10) are in general different, the model does predict $f_A(1) = f_B(1)$ in the special case of $\omega = \pi/4$, consistent with calculations based on sophisticated ab initio wave functions and also with the notion of an ideally shared electron pair. Given that the SCF wave function corresponds (for all bond lengths) to $\omega = \pi/4$, this result is straightforwardly consistent with the findings of previous studies in which the best agreement with the classical Lewis description of molecular structure was obtained at the level of the SCF approximation.^[19,42,45]

A similar close parallel between the analytic model and the DAFH analysis of the full CI wave function is also observed as R is increased. As predicted by the model, we observe increasing localisation of the eigenvector onto the atom over which the averaging of the hole was performed. In the limit of complete dissociation, one recovers an electron in a 1s orbital localised on this atom (Figure 1). It is in-

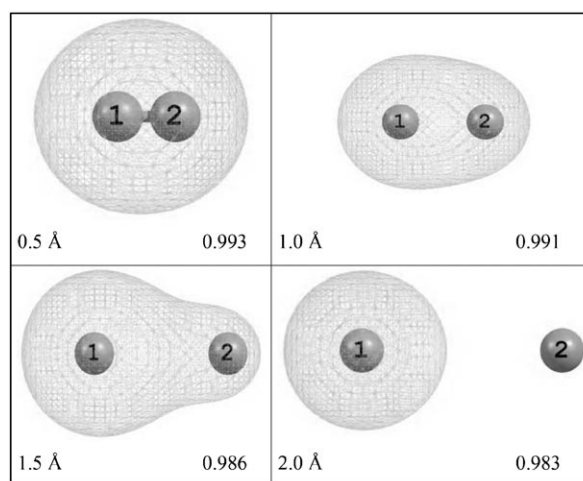


Figure 1. Dissociation of the electron pair of the H–H bond in H_2 , as monitored by the variation with R of the eigenvalues and eigenvectors of the Fermi hole averaged over the domain of atom H1. The figure was generated by using data taken from ref. [66] (AIM-based DAFH analysis at the full-CI/cc-pVTZ level of theory).

teresting to note in this context that close parallels between electron correlation, delocalisation and electron-sharing were also clearly demonstrated in a recent study by Ruedenberg and Schmidt.^[69]

Much the same analytic model as we have just described for H_2 also applies to the F_2 molecule except that instead of H(1s) functions, the bonding is based primarily on F(2p_z). We have seen for H_2 that the DAFH functions are highly symmetrical near the equilibrium geometry on account of the relative weights of the ionic and covalent classical VB components, but they become more asymmetric as the bond

dissociates (see Figure 1). In the case of F_2 , we have previously observed^[66] that the corresponding DAFH functions are already somewhat asymmetric, even near equilibrium geometry (see Figure 2), which suggests that the bond is partly dissociated (i.e., not fully formed) even at R_e , which is consistent with the known weakness of the F–F bond.

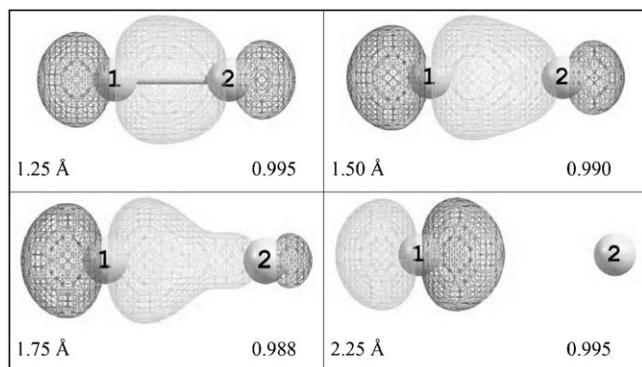


Figure 2. Dissociation of the electron pair of the F–F bond in F_2 , as monitored by the variation with R of the eigenvalues and eigenvectors of the Fermi hole averaged over the domain of atom F1. The figure was generated by using data taken from ref. [66] (AIM-based DAFH analysis at the full-valence-CASSCF/TZVP level of theory).

Three-centre two-electron (3c–2e) bonding: As is well known, the introduction of the three-centre two-electron (3c–2e) bonding concept^[70] opened the way to the elucidation of the structure of various classes of molecules, such as electron-deficient boron hydrides,^[71,72] non-classical carbon cations and small metallic clusters, for which the classical Lewis model of localised 2c–2e bonding fails. Much effort has been devoted over the last few years to the design of various auxiliary tools that aim to detect the presence of such multicentre bonding.^[35,36,45,73–78] In DAFH analysis, the existence of three-centre bonding involving atoms A, B and C is reflected in a near-coincidence of the first eigenvectors associated with each of $g_A(1)$, $g_B(1)$ and $g_C(1)$. These eigenvectors are indeed found to be delocalised over all three centres and the electron-pair nature of the bond is clearly demonstrated by the near complementarity of the corresponding eigenvalues, the sum of which is close to two (Figure 3).

Our aim here is to show that interesting qualitative insights into the nature of 3c–2e bonding, which confirm the picture of bonding obtained by DAFH analysis of ab initio wave functions, can be obtained by a simple approach that is based on further analysis of a simple qualitative model of 3c–2e bonding^[77] that is based on the earlier ideas of Longuet-Higgins.^[70] In terms of this model, a 3c–2e bond in the diborane molecule is characterised in a minimum basis set by a molecular orbital ψ expressed as a linear combination of three atom-centred functions, which corresponds to the contributions of two boron atoms (A and C) and the bridging hydrogen atom (B) [Eq. (11)] in which the coefficients

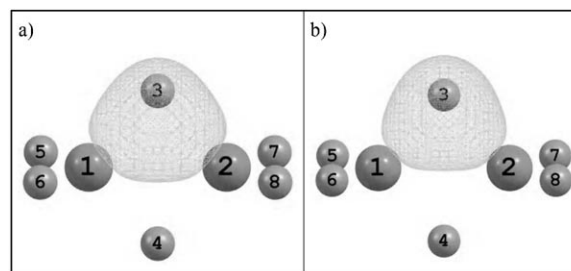


Figure 3. DAFH eigenvectors corresponding to the electron pair of one of the 3c–2e bonds in B_2H_6 , a) Averaged over boron atom 1 and b) averaged over hydrogen atom 3. The figure was generated by using data taken from ref. [45] (AIM-based DAFH analysis at the spin-coupled(4)/TZVP level of theory).

satisfy, for the sake of simplicity, the normalisation condition in Equation (12).

$$\psi(1) = a\chi_A(1) + b\chi_B(1) + a\chi_C(1) \quad (11)$$

$$2a^2 + b^2 = 1 \quad (12)$$

Based on this model, the electron pair of the 3c–2e bond can be characterised by a Slater determinant, which can be written in the usual shorthand as Equation (13):

$$\Psi(1,2) = |\psi\bar{\psi}| \quad (13)$$

It is then straightforward to write the pair density Equation (14), from which the corresponding domain-averaged Fermi hole can be easily obtained. By using the same simple Mulliken-like approximation as in the case of H_2 , the holes averaged over the domains of the individual atoms are given by Equations (15a–c).

$$\rho(1,2) = \psi(1)^2\psi(2)^2 \quad (14)$$

$$g_A(1) \approx 2a^2\psi(1)^2 \quad (15a)$$

$$g_B(1) \approx 2b^2\psi(1)^2 \quad (15b)$$

$$g_C(1) \approx 2a^2\psi(1)^2 \quad (15c)$$

This result reflects all of the basic features of the 3c–2e bonding reported in DAFH analyses at the Hartree-Fock and post-Hartree-Fock levels of theory (Figure 3). Thus, for example, the reported near-coincidence of the DAFH eigenvectors associated with individual AIM domains of the atoms involved in the fragment is evident from Equation (14), according to which the idealised form of these eigenvectors is identical to the delocalised molecular orbital ψ . Additionally, the anticipated eigenvalues ($2a^2$, $2b^2$ and $2a^2$) add to two because of the normalisation condition in Equation (12). As such, the primary mechanism in the formation of the 3c–2e bond is the same sort of electron-sharing that is anticipated in the original Lewis model except that this sharing now takes place across more than two centres.

Bonding interactions beyond the scope of the Lewis shared-electron-pair model: Although the sharing of one or more electron pairs certainly represents the most important and the most widespread mechanism of bonding interactions, recent systematic investigations have revealed that metal–metal bonding, for example, may require concepts that transcend the shared electron pair. Examples in this respect include various systems that are based on multiple metal–metal bonds between the elements of Groups IIIa and/or IVa (e.g., gallium, germanium, tin and lead). The peculiarity of such bonds was recognised in earlier studies,^[79–88] but further interesting insights into the nature of the bonding interactions were obtained from DAFH analysis^[62] in the particular case of the $[\text{PhGaGaPh}]^{2-}$ anion.

In the case of ordinary 2c–2e chemical bonds, DAFH analysis of holes averaged over individual atoms produces functions that can be interpreted as the broken valence of the bond that is formally being split. Furthermore, the corresponding functions usually resemble the eigenvector (with the eigenvalue close to 2) that results from DAFH analysis of the hole averaged over both atoms. A striking feature of the DAFH analysis of $[\text{PhGaGaPh}]^{2-}$ is that it does not follow this usual pattern. Analysis of the hole averaged over the domain comprising both gallium atoms suggests that the Ga–Ga bonding involves three pairs of electrons of which one corresponds to a Ga–Ga π bond and the remaining two, localised on individual gallium atoms, can be best characterised as polarised lone pairs. Such a static picture of bonding is, however, inconsistent with the results of the DAFH analysis performed for one of the PhGa fragments that result from the formal splitting of the molecule into two halves. Inspection of the DAFH eigenvectors and eigenvalues (Figure 4) shows that in addition to the anticipated broken

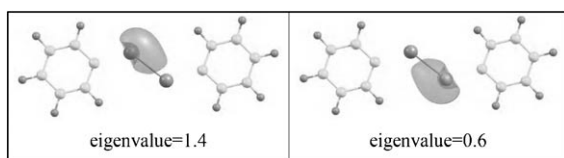
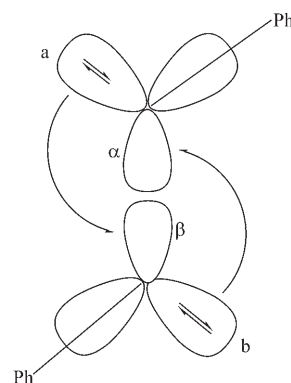


Figure 4. Key eigenvectors of the Fermi hole averaged over a PhGa fragment of the $[\text{PhGaGaPh}]^{2-}$ anion. The exchange of electrons between the lone pairs is demonstrated. The first eigenvector is localised on the gallium atom involved in the fragment, the second one is localised on the other gallium atom. The figure was generated by using data taken from ref. [62] (Mulliken-like DAFH analysis at the B3LYP/LANL2DZ level of theory).

valence of the formally split Ga–Ga π bond, there are two further eigenvectors associated with complementary eigenvalues, which are close to 1.4 and to 0.6. The function with an eigenvalue close to 1.4 is localised on gallium atom A belonging to the PhGa fragment over which the averaging was performed and the other is localised on the second gallium atom (B), which does not belong to this fragment. Both of these functions resemble the lone pairs detected in the

DAFH analysis involving averaging over the GaGa fragment, but the fact that the population of the eigenvector localised on the gallium atom of the PhGa fragment deviates from the ideal value of two, which is typical for the lone pair, and at the same time, the complementary fraction of electrons populates the second eigenvector localised on the gallium atom of the other PhGa fragment, implies the existence of partial charge transfer from one atom to another. Of course, the overall symmetry of the system then requires compensation of the above charge transfer by an equivalent transfer in the opposite direction so that the net result is that each of the gallium lone pairs effectively carries two electrons, as detected in the analysis of the GaGa hole. These results are very interesting because they demonstrate that the lone pairs on the two gallium atoms interact such that there appears to be an exchange of electrons (cf. Scheme 1) which is very reminiscent of the orbital diagrams considered in earlier studies.^[85,87]



Scheme 1.

Having summarised the peculiarity of this metal–metal bond, we can now attempt to elucidate the origin of the observed bonding interactions by using a simple analytical DAFH model analogous to those we used for H_2 and diborane. For this purpose it is necessary first to suggest the form of the approximate wave function whose analysis might lead to the observations of an actual DAFH analysis. A natural choice for such a wave function is in the form of a CI expansion that involves the ground state and two monoexcited configurations [Eq. (16)], which allows for the mutual charge transfer depicted in Scheme 1.

$$\Psi = \cos \omega |a\bar{a}b\bar{b}\rangle + \frac{1}{2} \sin \omega (|a\bar{a}b\bar{a}\rangle + |a\bar{a}a\bar{b}\rangle + |\beta\bar{a}b\bar{b}\rangle + |a\bar{\beta}b\bar{b}\rangle) \quad (16)$$

Based on this wave function it is possible to determine the corresponding pair density, and consequently, the form of the domain-averaged Fermi holes. By using the same Mulliken-like approximation as in the previous examples, the hole averaged over the domain of atom A is given by Equation (17):

$$g_A(1) \approx (1 + \cos^2 \omega) a(1)^2 + \frac{1}{2} \sin^2 \omega [b(1)^2 + \beta(1)^2] + \sin 2\omega a(1)\beta(1) \quad (17)$$

This result demonstrates that the hole averaged over single atom A does indeed have two eigenvectors of which one is localised on the same atom and the remaining one, roughly complementing the electron count to the complete pair, is localised on adjacent atom B. This picture of bonding, characteristic of the partial charge transfer between individual gallium atoms, is exactly what was observed in the DAFH analysis.^[62] The importance of the above analytical model is in that it reveals the origin of the mutual exchange of electrons between the lone pairs on adjacent gallium atoms, and moreover, that it demonstrates that such an exchange is qualitatively different from the electron-sharing considered in the original Lewis model.

The full spectrum of bonding interactions is clearly much richer than was anticipated on the basis of the traditional model of electron-sharing, and especially in the realm of metal–metal bonding, one must be ready to encounter new, unusual patterns of bonding. We believe that analytical DAFH models of the type presented in this report will prove to be of significant utility as general tools for revealing the peculiarities of metal–metal and other unusual bonds.

Conclusions

The various examples presented in this work demonstrate the utility of simple analytic models not only for the a posteriori rationalisation of the outcomes of domain-averaged Fermi hole (DAFH) analysis, but also as efficient tools for providing interesting new insights into the nature of bonding interactions. Especially encouraging is the ability of such analytical models to provide useful information on systems that can transcend the traditional Lewis model of the bond as a shared electron pair, such as those with metal–metal bonding. It seems likely that analogous DAFH models will also prove useful for revealing the nature of other unusual bonding types.

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