Electron pairing and chemical bonds. Molecular structure from the analysis of pair densities and related quantities

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The Fermi holes are presented as a new means of analysis and visualisation of molecular structure. Based on these quantities it is possible to get clear and highly visual insight into the structure of molecular fragments (functional groups) even in molecules with complex bonding patterns like multicenter bonding, hypervalence, etc. In addition to allowing the detection and localization of multicenter bonding, the new approach also brings some new interesting possibilities for the quantitative evaluation of molecular similarity.

1.   Introduction

The Lewis idea of electron pairing invented some eighty years ago represents one of the pivotal achievements in an effort to understand and to interpret the molecular structure and the proposal that chemical bonds are formed by shared electron pairs has become one of the cornerstones of the whole modern chemistry [18,27]. Despite being invented before the advent of quantum theory, this idea has correctly recognized the electronic nature of chemical bonding and the mutual relation of a Lewis and quantum mechanical picture of bonding represents a continuing challenge for the theory of the chemical bond. In spite of unceasing theoretical efforts at the reconciliation of both pictures of bonding [2,9–11,14–17,38], the role of electron pairs in chemical bonds is still not satisfactorily explained. The concept of chemical bond thus still eludes all attempts at simple and universally valid explanation. Our aim in this study is to contribute to the solution of this old but still active problem of the chemical theory. The basic quantity describing the behaviour of electron pairs in molecular systems is the so-called pair density [20,23] and in past years several studies has been published dealing with the analysis of this density in relation to chemical bonding [26,33,35,39,42,44]. Among these attempts it is possible to include also our recent studies based on the formalism of the so-called pair population analysis [3,8,28,29,34]. While the interpretative potential of this analysis was quite thoroughly explored in recent years, there also appeared some new possibilities based on the exploitation of some other quantities related to pair density. The most promising in this respect seems to be the use of conditional probabilities describing the distribution of one electron of the pair provided the position of the second, reference electron, is fixed in some point or

region. Using this approach it was possible, e.g., to monitor the detailed process of the scission of the bond during the dissociation [30]. Another quantity whose investigation seems to be able to throw some new light on the problem of the role of electron pairing in chemical bonds is the so-called Fermi hole. This quantity was first introduced by Wigner in the field of solid state physics [45] but during past years several authors have also discussed and analysed its possible relevance for chemistry [4,21,22]. In the framework of these studies can be included also our recent study [32] in which the Fermi holes were presented as a source of interesting and useful information about the structure of molecular fragments (functional groups), their valences and structural similarities. Our aim in this study is to pursue the general methodology presented in the previous study [32] and to demonstrate that Fermi holes represent a rich source of structural information whose analysis can contribute to the visualisation and the understanding of the molecular structure. For this purpose the formalism was applied to the investigation of bonding in several molecules which range from simple species well described by the classical Lewis model of two-center two-electron (2c-2e) bond to transition states and electron deficient systems with multicenter bonding and we would like to show that the methodology of this new analysis is universal enough to visualize even the structure

2. Theoretical

The basic quantity from which the Fermi holes $h_{r_2}(r_1)$ are derived is the conditional probability of finding one electron of the pair provided the position of the second, reference electron, is fixed in a point r_2. This conditional probability is given by

$$P_{r_2}(r_1) = \frac{2\rho(r_1, r_2)}{\rho(r_2)}, \tag{1}$$

in which the pair density $\rho(r_1, r_2)$ describes the joint probability of finding the first electron of the pair in a point r_1 and the second in the point r_2, and the probability of finding one single electron in a fixed point r_2 is given by the values of first-order density matrix $\rho(r)$ at r_2.

$$\rho(r_1, r_2) = \frac{N(N-1)}{2} \int \Psi^2(1, 2, \ldots, N)\, d\sigma_1\, d\sigma_2\, dx_3 \ldots dx_N, \tag{2}$$

$$\rho(r) = N \int \Psi^2(1, 2, \ldots, N)\, d\sigma_1\, dx_2\, d_3 \ldots dx_N. \tag{3}$$

In these equations $d\sigma$ and dx denote the integration over spin and spin/space coordinates, respectively. Based on these quantities, the Fermi hole associated with an electron fixed at r_2 is defined as

$$h_{r_2}(r_1) = \rho(r_1) - P_{r_2}(r_1). \tag{4}$$

The advantage of these holes is that by subtracting (1) from the ordinary density, the conditional probability is rectified from the contribution of single electron distribution so that they reflect the "net" effect of electron pairing. The properties of Fermi holes in molecular systems were studied by several groups [4,21,22] and this analysis clearly revealed that the second electron is usually predominantly distributed in the vicinity of the fixed electron. This predominance which clearly stresses the importance of electron pairing in chemical bonding can easily be demonstrated graphically since the holes, as the functions of 3 variables, can straightforwardly be displayed. Such a display, corresponding to Fermi hole associated for H_2O molecule with the reference electron fixed in the middle of one of the OH bonds, is given in the figure 1. As it is possible to see, the second electron is indeed strongly concentrated around the fixed electron which clearly shows the tendency of electrons in the OH bond to be paired.

In a similar way, it would be possible to analyze also any other molecule and in this way the role of electron pairing could in principle be evaluated. Such a point by point visualization of Fermi holes is not, however, a very efficient method for their analysis. This is due to the fact that the actual form of Fermi holes depends on the precise location of the reference electron and its fixation in different points generally yields different Fermi holes. This type of dependence was studied some time ago [21,22] by Luken who found that the hole usually moves with the reference electron and in order to characterize this movement the concept of Fermi hole mobility function was
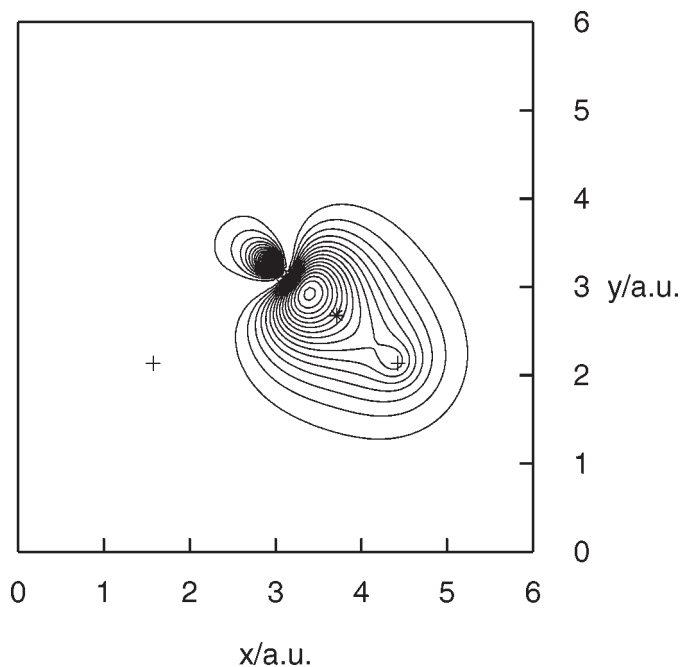

Figure 1. Calculated Fermi hole for H_2O molecule in the plane containing nuclei. The positions of atoms are denoted by crosses, the asterisk denotes the position of the reference electron.

introduced. In addition to sensitivity to the precise location of the reference electron, the above introduced analysis of Fermi holes suffers yet one important conceptual drawback. This drawback is that fixation of the reference electron in a single point is not very compatible with the quantum mechanical uncertainty principle. It is much more convenient and also more realistic is therefore to introduce the so-called integrated Fermi hole $h_\Omega(r_1)$ in which the reference electron is not fixed in a point but is allowed to move within a certain region Ω. The definition of this integrated hole is then given by

$$h_\Omega(r_1) = \rho(r_1) - P_\Omega(r_1), \tag{5}$$

where the integrated conditional probability $P_\Omega(r_1)$ is given by

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

The conditional probabilities satisfy the normalization

$$\int P_\Omega(r_1)\, \mathrm{d}r_1 = N - 1, \tag{7}$$

which holds for an arbitrary form of the region Ω. As a consequence of this universal normalization, the integrated Fermi holes satisfy

$$\int h_\Omega(r_1)\, \mathrm{d}r_1 = 1, \tag{8}$$

which again holds for the arbitrary form of the region Ω.

Although, as said above, normalizations (7) and (8) do not depend on how the form of Ω is actually chosen, there is a certain definition which is of special importance for chemistry. This definition is based on the virial partitioning of the charge density $\rho(r)$ proposed by Bader [1]. According to this partitioning the molecular space is divided into regions associated with individual atoms. Adopting this type of partitioning, the regions Ω are to be identified with the individual atomic regions of the Bader's partitioning. The first benefit resulting from associating the Fermi holes with the regions of individual atoms consists in allowing the simple definition of the valence state of the atom in a molecule. In addition to the analysis of Fermi holes associated with a single atom, it is also possible to analyze the holes associated with more complex forms of the region Ω. Such regions can naturally be formed by a union of individual atomic regions and one of our aims in this study is to show that especially the holes associated with the regions involving the classically bonded atoms (chemical bonds, molecular fragments, functional groups, etc.) represent a new extremely rich source of structural information. As it will be shown bellow, the picture resulting from such an analysis remarkably well corresponds with the classical expectation not only for molecules well described by localized 2c-2e bonds but also those, described by more complex bonding patterns like multicenter bonding, hypervalence, etc., can also correctly be detected by this approach. This opens the possibility of broader systematic

exploitation of Fermi holes and in the following part several examples of such analysis will be reported.

This analysis requires, however, to introduce yet some other auxiliary quantities and concepts. One of them is the concept of the so-called "charge-weighted" Fermi hole. This quantity is related to the "normal" Fermi hole by a simple proportionality

$$g_\Omega(r_1) = N_\Omega h_\Omega(r_1), \tag{9}$$

where the proportionality factor represents the number of electrons in a region Ω:

$$N_\Omega = \int_\Omega \rho(r_1)\,\mathrm{d}r_1. \tag{10}$$

The philosophy underlying the introduction of this concept is the following. The "normal" integrated Fermi holes are derived from the conditional probabilities describing the distribution of one electron of the pair provided the second, reference electron, is localized in a region Ω. Localization of one and only one electron in a region Ω is, however, a rather artificial act which does not reflect the fact that in a real molecule the region Ω is generally populated not by one but by N_Ω electrons. The proportionality factor in (9) is thus nothing but a statistical correction for the actual number of electrons in a region Ω.

As a consequence, the "charge-weighted" Fermi holes satisfy the normalization

$$\int g_\Omega(r_1)\,\mathrm{d}r_1 = N_\Omega. \tag{11}$$

The analysis of these quantities is based on the fact that like the ordinary density $\rho(r)$, these holes also are the functions of 3 variables only so that all methods used for the analysis of the first-order density can straightforwardly be used. Thus, e.g., if the hole $g_\Omega(r)$ is decomposed in the form of an ordinary expansion

$$g_\Omega(r) = \sum_{\mu\nu} G^\Omega_{\mu\nu} \chi_\mu(r)\chi_\nu(r), \tag{12}$$

the matrix G^Ω, which represents the hole in AO basis, can be diagonalized as ordinary charge density-bond order matrix and important information about how the electrons are actually distributed in a region Ω can be obtained from the inspection of resulting eigenvectors ("natural orbitals") and their corresponding eigenvalues (occupation numbers). Another possibility to extract the desired structural information from the matrices G^Ω consists in the straightforward application of the idea of standard Mulliken population analysis [25] to the dissection of the quantity N_Ω into contributions which can be associated with the bonds and free electron pairs of the corresponding structural fragment. In the following section the practical application of the above approach will be reported.

In order to demonstrate the broad universality of this approach, the systems we are going to analyze range from simple molecules and functional groups with classical well

localized 2c-2e bonds to nontrivial examples of molecules and fragments containing nonclassical multicenter bonds.

3.   Results and discussion

Although the above described methodology is formulated quite generally and can be applied at arbitrary level of theory, the practical applications reported in this study are based on some simplifying assumptions. The most important of them concerns the pair densities which were derived, similarly as in the previous introductory study [32], from semiempirical SCF wave functions. Another simplification concerns the integration over Bader's regions. Because the programs for the integration over these regions were not available to us we used an alternative approach in which the integration over the region is replaced by appropriately restricting the summations over the basis functions. Within this approach, the electron is assumed to be in a region of an atom A if it resides in an orbital centred on this atom. Using this approach, combined with the usual ZDO approximation used in semiempirical methods, the general formula for the conditional probability over the region Ω can be written as

$$P_\Omega(r_1) = \frac{2 \int_\Omega \rho(r_1, r_2)\, \mathrm{d}r_2}{N_\Omega}, \tag{13}$$

where N_Ω denotes the total electron density in a region Ω. The calculations were performed by a standard AM1 method [12] included in the MOPAC package [41] and all molecules were considered in completely optimized molecular geometries.

Having specified the technical details of the calculations let us discuss, in the following part, the results of the practical application of the above analysis. As a first example let us choose the CH_4 and H_2O molecules as a representatives of the systems well described by the classical Lewis model of 2c-2e bonds and let us analyze the Fermi holes associated with the regions Ω corresponding to CH_3-, $CH_2=$, $CH\equiv$, C and $OH-$ and $O=$ fragments, respectively.

The first quantity characterizing the Fermi hole associated with some functional group is the total number of electrons N_Ω contained within the corresponding region. Such a global characterization is, however, rather trivial and gives only the crudest picture of bonding within the group. In order to get a more detailed insight into this structure, more sophisticated techniques of the analysis are necessary. One such technique is based on the diagonalization of the matrix G^Ω representing the Fermi hole associated with the fragment Ω. The main goal of this diagonalization is that it allows us to get the information about how electrons are internally distributed within a group. The information of this kind comes from the inspection of individual eigenvalues and eigenvectors resulting from the diagonalization of the Fermi hole. Generally, it holds that the diagonalization yields several non-zero eigenvalues and just from these non-zero eigenvalues (and the corresponding eigenvectors) the desired structural information can be extracted. Thus, e.g., if it happens that some of the eigenvalues are close to 2, then it is possible to expect that some of the total number of N_Ω

electrons contained within the group are coupled to pairs. The typical situation when this happens is where this happens is when there are some chemical bonds or free pairs within the group or fragment. Another frequently encountered situation is when some eigenvalues are close to 1. Such a situation is typical for systems where the formation of the fragment required to split some chemical bonds and such eigenvalues correspond then to what is classically known as the "free valence" of the group.

Let us attempt now to apply the above qualitative considerations to the above specified molecules and fragments. Thus, e.g., in all above cases it holds that irrespective of the actual form of the fragment, the diagonalization yields four non-zero eigenvalues η_i which satisfy the relation

$$\sum_{i}^{\text{non-zero}} \eta_i = N_{\Omega}. \tag{14}$$

Much more interesting than the global quantity N_{Ω} are, however, the individual eigenvalues η_i since they inform us about how the electrons are distributed within the group, or, in other words, about the structure of the group. Thus, e.g., for CH_3- and $OH-$ fragments, there are four non-zero eigenvalues of which three are very close to 2 and the remaining one is close to unity. This suggests that six of the total number of N_{Ω} electrons in these fragments are actually coupled in pairs and the remaining roughly one electron corresponds to single unsaturated free valence classically expected for these groups. Such an interpretation is quite straightforwardly supported by the inspection of the form of corresponding eigenvectors where it is possible to show that eigenvectors associated with paired electrons do indeed correspond to three CH bonds in a CH_3- group and/or one OH bond and two electron pairs of the OH group, respectively. The graphical display of one such CH bonds is shown in figure 2 and the eigenvector corresponding to the free valence of CH_3- group is in figure 3. In a similar way, it would be possible to analyze and to interpret the occupation numbers of the orbitals resulting from the diagonalization of the Fermi holes in any other case and it is possible to see from table 1 such an interpretation is in all cases consistent with the classical picture of functional group as consisting of bonds, free electron pairs and "free valences". In connection with such a simple picture it is necessary to say, however, that the eigenvectors (and eigenvalues) primarily resulting from the diagonalization of the matrices G^{Ω} do not reflect the equivalency of corresponding symmetry equivalent bonds, free pairs and free valences but rather they transform according to irreducible representations of the local symmetry of the fragment in a molecule. Thus, e.g., in the case of an isolated C atom in a CH_4 molecule, the degeneracy of the non-zero eigenvalues ($\eta_1 = \eta_2 = \eta_3 = 0.903$, $\eta_4 = 1.222$) suggests that the corresponding eigenvectors transform according to T_2 and A_1 irreducible representations of the T_d group. This, however, is not consistent with the classical picture of four equivalent tetrahedrally arranged free valences. We are thus in a similar situation invoked in the concept of hybridization as a linear combination of atomic orbitals. Here, however, we do not combine the atomic orbitals but the eigenvectors resulting from the
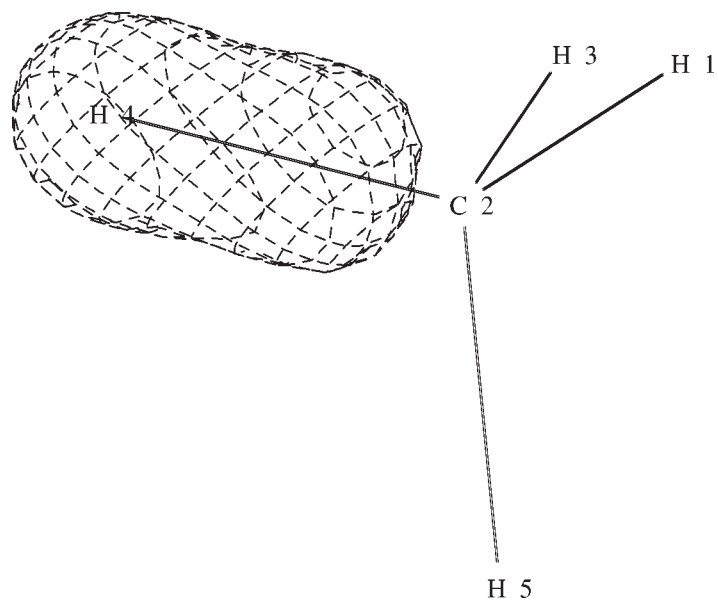
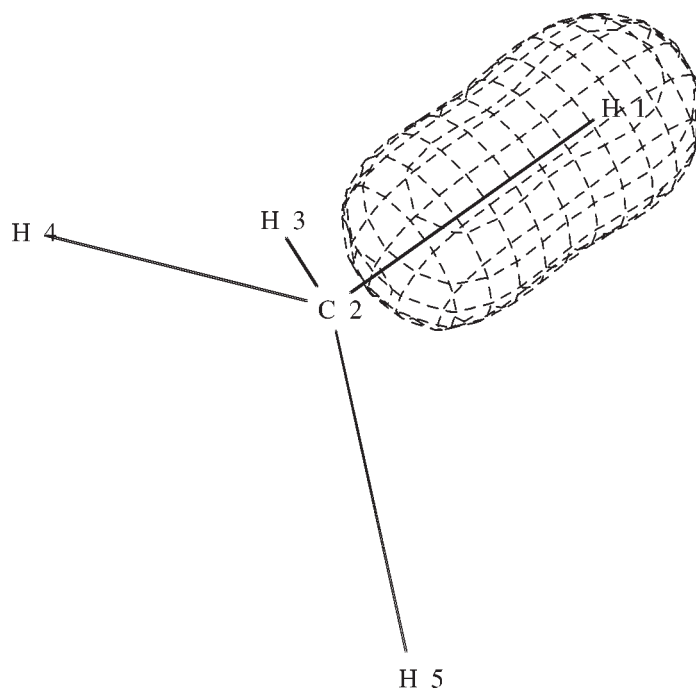Figure 2. Fermi hole associated with the CH_3- group in methane, eigenvector corresponding to one of CH bonds.

Figure 3. Fermi hole associated with CH_3- group in methane, eigenvector corresponding to unsaturated free valence.

Table 1
Calculated non-zero occupation numbers of the eigenvectors resulting from the diagonalization of Fermi holes for several simple molecular fragments.

Group	η_1	η_2	η_3	η_4
C	0.982	0.982	0.982	0.982
CH	2.000	0.982	0.982	0.982
CH_2	2.000	2.000	0.982	0.982
CH_3	2.000	2.000	2.000	0.982
O	2.000	2.000	1.163	1.163
OH	2.000	2.000	2.000	1.163

diagonalization of the Fermi hole. The natural criterion which such a transformation should satisfy is to leave the Fermi hole unchanged. This, however, is just the criterion introduced some time ago by Cioslowski [5] for the construction of localized natural orbitals. The method is known as the so-called isopycnic transformation and its application in our case does indeed lead to the formation of four equivalent eigenvectors directed, as expected to the corners of the tetrahedron and this equivalency finds its reflection also in the four-fold degeneracy of the corresponding eigenvalues ($\eta_1 = \eta_2 = \eta_3 = \eta_4 = 0.982$).

In a similar way it would be possible to analyze the structure of any other fragment and in all cases of molecules well described by classical Lewis model of 2c-2e bonds the resulting picture of bonding can straightforwardly be confronted with the classical expectation. Thus, e.g., in the case of C=C fragment in the ethene molecule, the diagonalization of the corresponding Fermi hole yields six non-zero eigenvalues of which two, corresponding to σ and π components of the C=C double bond are close to 2 ($\eta_1 = 2.000$, $\eta_2 = 1.996$) and the remaining four (after being subjected to an isopycnic transformation) are, consistent with the existence of four equivalent free valences corresponding to broken CH bonds, equal to 1.110. Similarly, if the region Ω is identified with one of the hydrogens, the diagonalization of G^H yields only one non-zero eigenvalue corresponding to the free valence of an isolated H atom from the broken CH bond.

After having demonstrated the applicability of the approach in the case of molecules well represented by the classical Lewis model let us report now the results of the application to more difficult cases. As an example of such systems let us choose first the electron deficient molecules with 3-center bonding and let us demonstrate that even such nontrivial feature as three-center bonding can straightforwardly be detected. As it is possible to expect, however, the picture of bonding resulting from the diagonalization of the Fermi holes will be a bit more complex in this case. The typical example of a molecule with 3-center bond is the diborane B_2H_6 and this is why the results for this molecule will be presented first. For this purpose let us start with the analysis of the Fermi hole associated with the region Ω involving one boron atom.

In this case the diagonalization of the matrix G^B, followed by the subsequent isopycnic transformation gives four non-zero eigenvalues of which two are close to unity ($\eta_1 = \eta_2 = 0.990$) and the remaining two are close to 0.5 ($\eta_3 = \eta_4 = 0.470$). The situation for the former eigenvalues is quite simple since as it is possible to expect they correspond to two free valences of broken BH bonds (figure 4). The existence of the eigenvalues close to 0.5 is, however, a completely new phenomenon and it was therefore of special interest to look at the type of bonding to which they correspond. One of the corresponding eigenvectors is shown in figure 5. As it is possible to see, the eigenvector is predominantly localized in the region involving *both* borons and the bridging hydrogen so that it clearly resembles the three-center bond whose presence is expected in the same region. The fact that the eigenvalue associated with this eigenvector is close to 0.5 can thus be interpreted in a sense that each boron atom
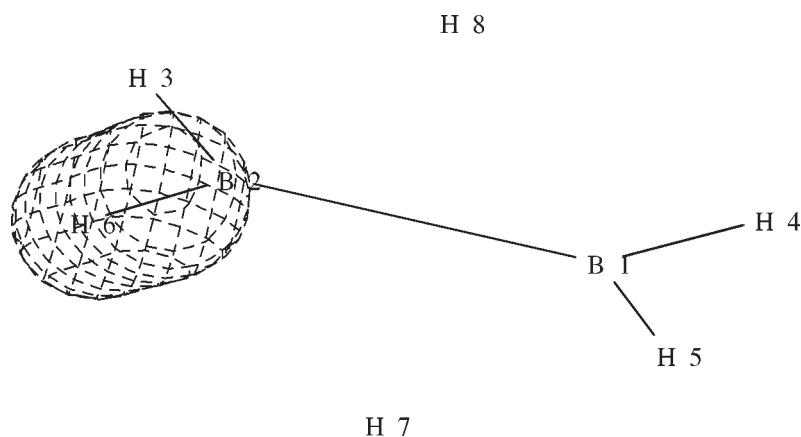

Figure 4. Fermi hole associated with one boron atom in B_2H_6, eigenvector corresponding to terminal BH bond.
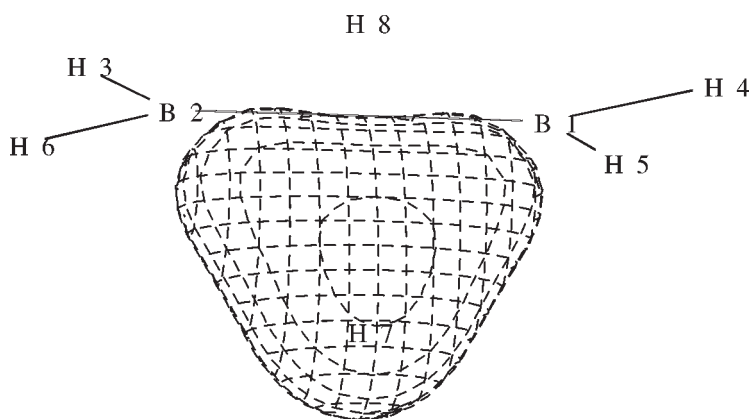

Figure 5. Fermi hole associated with one boron atom in B_2H_6, eigenvector corresponding to three-center BHB bond.

Table 2
Calculated eigenvalues of the Fermi hole associated with
the region involving both boron atoms in diborane.

Eigenvalue	Value	Localization
η_1	0.967	BHB
η_2	0.967	BHB
η_3	0.977	BH
η_4	0.977	BH
η_5	0.977	BH
η_6	0.977	BH

contributes roughly 0.5 electron to each of the three-center bonds. We can thus see that the analysis of the Fermi hole even for a rather arbitrarily chosen region Ω clearly reveals the existence of 3-center bonding in this molecule. The necessary condition for detecting the presence of such multicenter bonds is that the region Ω contains at least one atom involved in three-center bonding. If we accept this interpretation then it is possible to expect that for the region involving both boron atoms, the final picture of bonding should roughly correspond to the superposition of the pictures for individual borons. One can thus expect four eigenvalues close to unity (corresponding to four broken terminal BH bonds) and, since each boron atom contributes roughly 0.5 to each three-center BHB bond, the two eigenvalues associated with three-center BHB bonds should now be twice as large, i.e., they can be expected to be close to unity. The calculated eigenvalues resulting from the diagonalization of the corresponding Fermi hole are summarized in table 2 and as it is possible to see they closely parallel the above intuitive expectations.

The operation of such a superposition principle can quite convincingly be demonstrated by another example of the Fermi hole involving only bridging hydrogens. The diagonalization of the G^{HH} matrix yields in this case there are two non-zero eigenvalues close to unity, and the corresponding eigenvectors resemble again the three-center BHB bond (remember that bridging hygrogens are involved in three-center bonds). If we now realize, that similar eigenvectors with occupation numbers close to unity were detected also in the previous case of the Fermi hole associated with the region involving both boron atoms, then it is possible to expect that two eigenvalues close to 2 can be expected for the Fermi hole associated with the region involving both boron atoms and both bridging hydrogens. The actual calculations performed for this particular choice of the region Ω quite nicely correspond to the above simple expectations. The diagonalization of G^{BHBH} yields in this case six non-zero eigenvalues of which four, which are close to unity, correspond to four free valences of broken terminal BH bonds and the remaining two, which are close to 2 do indeed correspond to two-electron pairs of two three-center two-electron BHB bonds.

The limiting case of such an analysis corresponds to the situation when the region Ω involves all atoms. In this case the Fermi hole degenerates to the normal first-order density matrix so that its diagonalization leads to six doubly occupied molecular

orbitals. The effect of the isopycnic transformation is then to convert the canonical molecular orbitals to localized ones which, in the case of diborane, correspond to 4 terminal BH bonds and 2 BHB three-center bonds. The effect of the isopycnic transformation is thus in this case equivalent to usual orbital localization which is frequently used for the detection of three-center bonding in molecules [19]. The above approach thus provides a new theoretical rationale for the intuitive use of localization techniques sometimes employed for the detection of multicenter bonding. In view of the above analysis these localization techniques are nothing but the special case of the above presented general analysis of Fermi holes.

As a next example demonstrating the wide applicability of the presented approach for the analysis of three-center bonding let us discuss the case of the B_4H_{10} molecule. According to the Lipscomb rules [43] the molecule is expected to contain four BHB three-center bonds, one single BB bond and two BH_2 groups (figure 6). In order to test this theoretical prediction the molecule was recently subjected to the formalism of the so-called nonlinear pair population analysis [3,33]. Using this approach it was indeed possible to detect the presence of four three-center BHB bonds as well as one single BB bond and six terminal BH bonds consistent with the Lipscomb rules. At the same time, however, two non-negligible contributions corresponding to BBB three-center bonds were detected. In the original study [36] these contributions were
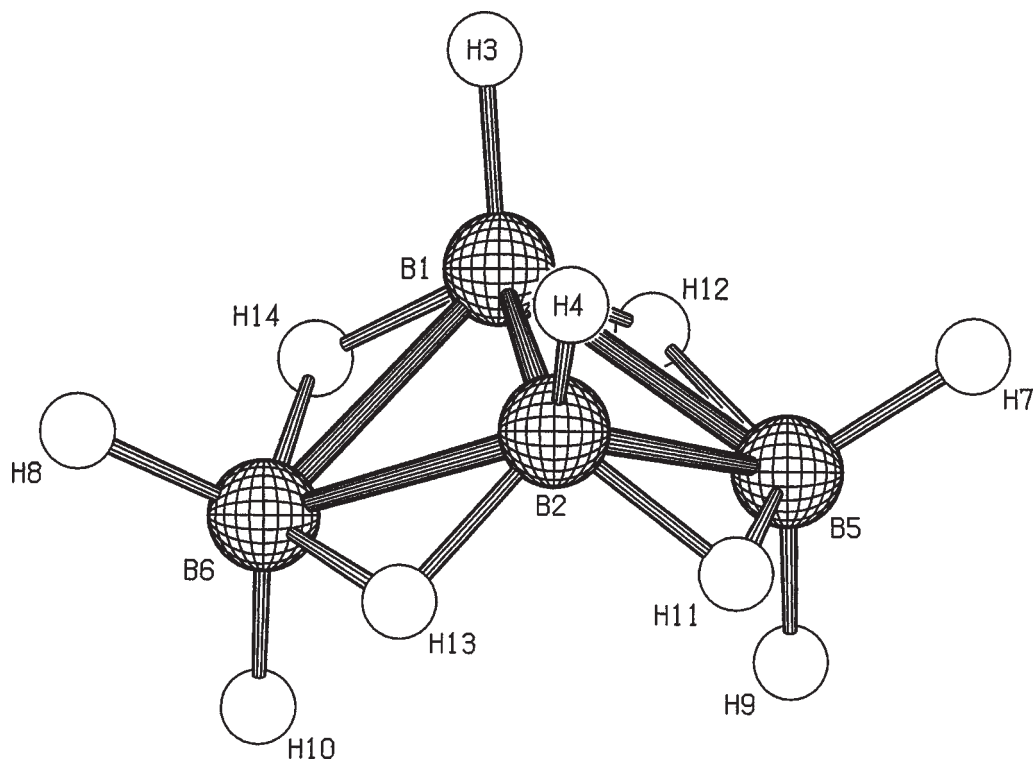

Figure 6. Structure of B_4H_{10}.

interpreted as fractional BBB bonds but after discussion with professor Lipscomb these contributions were reinterpreted as corresponding to partial delocalization from BB bond towards BH_2 terminal groups [3]. The fact that this interpretation is indeed to be preferred can straightforwardly be demonstrated using the above introduced analysis. For this purpose let us compose a region consisting of all four boron atoms and let us diagonalize the Fermi hole associated with this region. The diagonalization of this hole yields eleven non-zero eigenvalues of which one is close to 2 and the remaining ones close to unity. In light of what has been said above, this result can be regarded as an indication that there is one and just one electron pair in the BBBB fragment and the inspection of the form of the corresponding eigenvector clearly shows that it is strongly localized in the region of single BB bond (figure 7). The remaining 10 non-zero eigenvalues correspond to 10 unsaturated free valences. Six of them coincide with 6 broken BH terminal bonds and the remaining 4 with 4 three-center BHB bonds (remember that hydrogens were excluded from the region so that no complete pairs could be formed in BHB regions). We can thus see that the analysis of the Fermi hole conveniently complements the results of nonlinear population analysis [3] and unequivocally thus helps in the interpretation of the small BBB three-center pair populations.

As a next example demonstrating the universality and the usefulness of the above presented analysis of the Fermi holes let us discuss the molecule of pentaborane B_5H_9 (figure 8). For this molecule the Lipscomb rules predict the existence of four BHB, one BBB and 2 BB bonds and the structure thus could be schematically depicted by
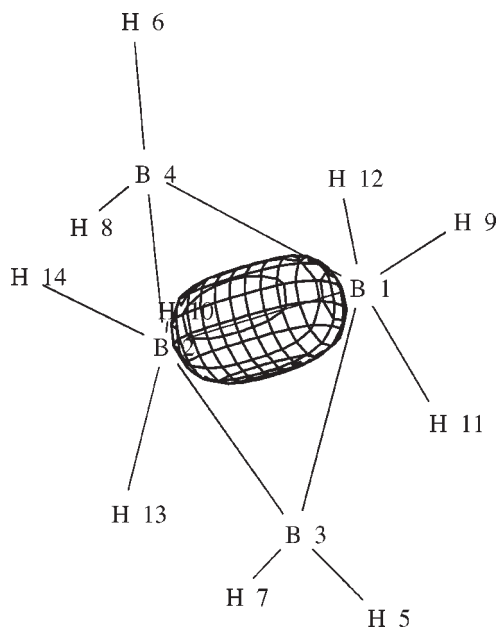

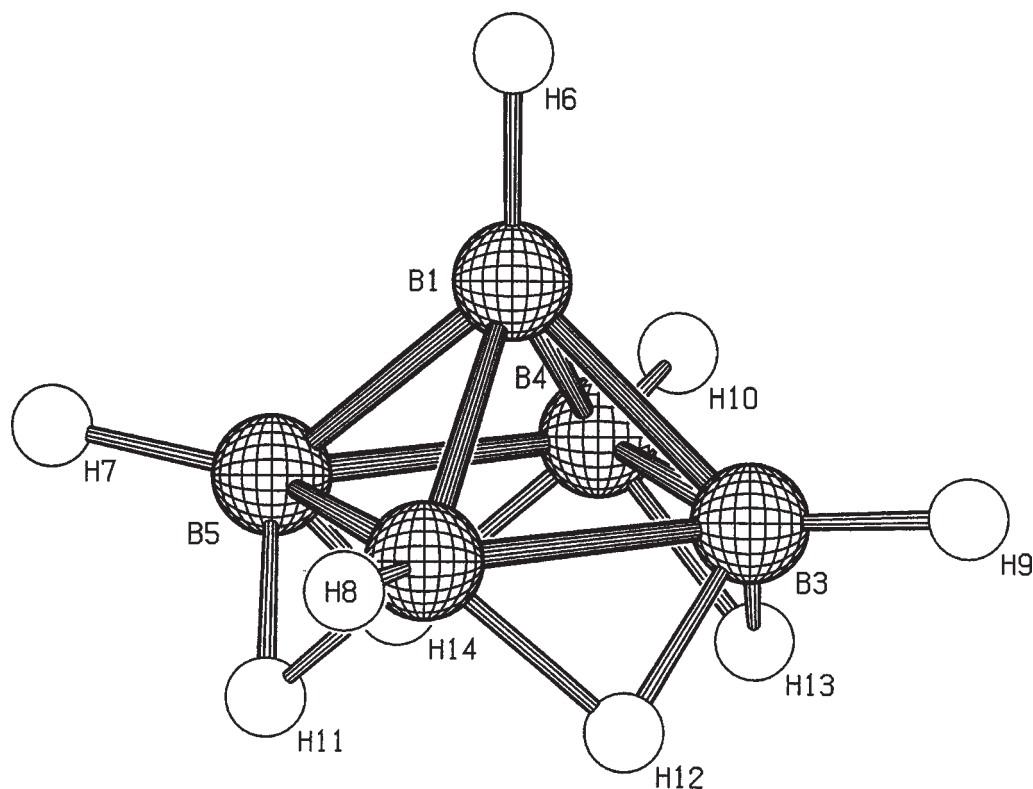Figure 7. Fermi hole associated with BBBB fragment in B_4H_{10}, eigenvector corresponding to 2c-2e BB bond.

Figure 8. Structure of B_5H_9.

figure 9. The correctness of the schematic structure can straightforwardly be confirmed also by the results of the analysis of the Fermi hole. For this purpose let us analyze the Fermi hole associated with the fragment consisting of all five boron atoms. The selected results of the diagonalization of the matrix G^Ω are collected in table 3. There are in this case 12 non-zero eigenvalues of which 3 (included in the table) are close to two and the remaining 9 close to unity. The detailed inspection of the form of corresponding eigenvectors suggests that of the nine eigenvectors occupied by roughly one electron, five correspond to the free valences of five broken terminal BH bonds and the remaining four to four non-completely filled three-center BHB bonds. Much more interesting than these free valences are, however, the eigenvectors corresponding to electron pairs. This information can again be obtained from the inspection of the form of corresponding eigenvectors, and such an analysis shows that they quite closely correspond to two 2c-2e B_1B_5 and B_1B_2 bonds and to one 3c-2e $B_1B_3B_4$ bond. This result is very interesting since it completely corresponds to the expectations of the Lipscomb rules ($styx$ = 4120) and to the schematic formula (figure 9). We can thus see that the above formalism does indeed reflect the basic structural features of this molecule correctly even if the standard localization techniques usually used for the visualization of bonding fail in this case [19]. Here it is, however, necessary to
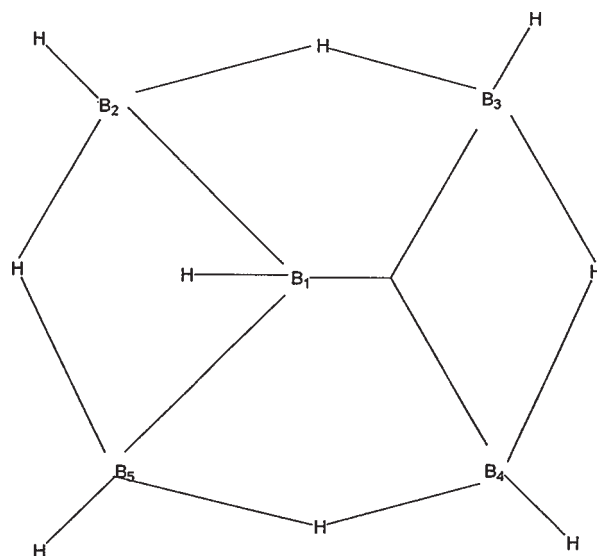
Figure 9. Schematic visualization of the bonding in B_5H_9.

Table 3
Calculated eigenvalues of the Fermi hole associated with the electron pairs contained in the region involving all five boron atoms in B_5H_9.

Eigenvalue	Value	Localization
η_1	1.973	B_1B_5
η_2	1.973	B_1B_2
η_3	1.971	$B_1B_3B_4$

be aware of the fact that even if the pair localization could be obtained within our analysis, the resulting set of bonds corresponds to one limiting structure and in order to satisfy the requirements of symmetry of the molecule, the resonance of several limiting structures has to be invoked.

After having discussed several examples of molecules with three-center bonding, let us demonstrate, as a next example, the applicability of the approach to the visualization of bonding in some other systems with unclear bonding patterns. Such systems can be represented, e.g., by the transition states of chemical reactions and in the following part one example of such an application will be reported. The system analyzed is the thermally allowed conrotatory cyclisation of 1,3-butadiene to cyclobutene. In keeping with the allowed nature of the process the reaction can formally be regarded as a cyclic shift of bonds [31]. Such a classical picture of electron reorganization is, however, rather crude and gives us no idea of how the structure of the corresponding transition state should look. For that reason and in view of the success of the above approach in visualizing the bonding in other complex systems we decided to apply the

analysis of the Fermi holes also in this case. The first problem which we encounter here is how to choose the form of the region Ω properly. A certain guide which can help us with the choice of this region is that only CC bonds are actively involved in the process so that it seems natural to choose the region Ω as a union of the regions of individual C atoms. Having specified the form of the region the whole subsequent analysis is quite straightforward and consists first in the determination of the form of the Fermi hole associated with the CCCC region for the transition state of the reaction. The structure of the transition state is then deduced from the eigenvectors and eigenvalues resulting from the diagonalization of the matrix G^{Ω} representing the Fermi hole in AO basis. This diagonalization yields 11 non-zero eigenvalues of which 6 are very close to unity and the remaining 5 are close to two. The inspection of the form of corresponding eigenvectors shows that six singly occupied eigenvalues clearly correspond to the free valences of the 6 broken CH bonds. Much more interesting than these free valences are, however, the doubly occupied eigenvectors since they are just these quantities which inform us about the distribution of electron pairs (chemical bonds) in the CCCC fragment. The detailed analysis of these eigenvectors shows that three of them are localized in three σ bonds belonging to butadiene σ skeleton. The graphical display of one of such eigenvectors is shown in figure 10. If we look similarly also at the remaining two doubly occupied eigenvectors then it is possible to show that one of them strongly resembles the π component of cyclobutene double bond and the remaining one is highly reminiscent of distorted σ bond of cyclobutene (figures 11 and 12). We can thus see that instead of the intuitively expected picture of fractional CC bonds delocalized over the whole CCCC skeleton the structure of the transition state clearly resembles the structure of the final cyclobutene. This result is very interesting since the classification of transition states in terms of similarity to either reactant or the product is well known in organic chemistry as the so-called Hammond postu-
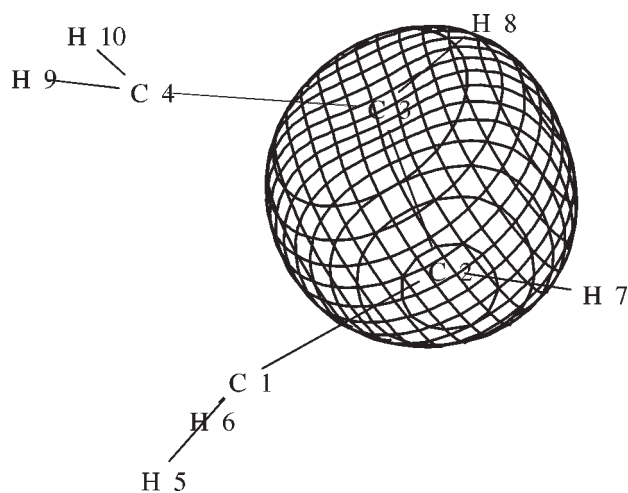

Figure 10. Fermi hole associated with CCCC region for the transition state of butadiene to cyclobutene rearrangement. Eigenvector corresponding to one of the CC σ bonds of butadiene skeleton.
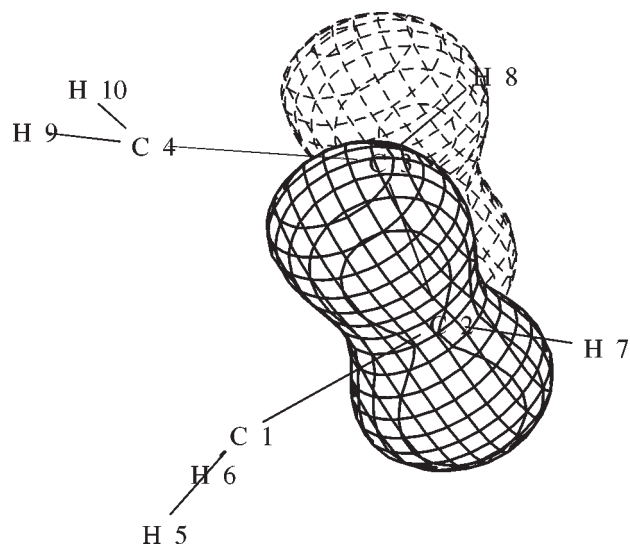
Figure 11. Fermi hole associated with CCCC region for the transition state of butadiene to cyclobutene rearrangement. Eigenvector corresponding to newly formed CC π bond.
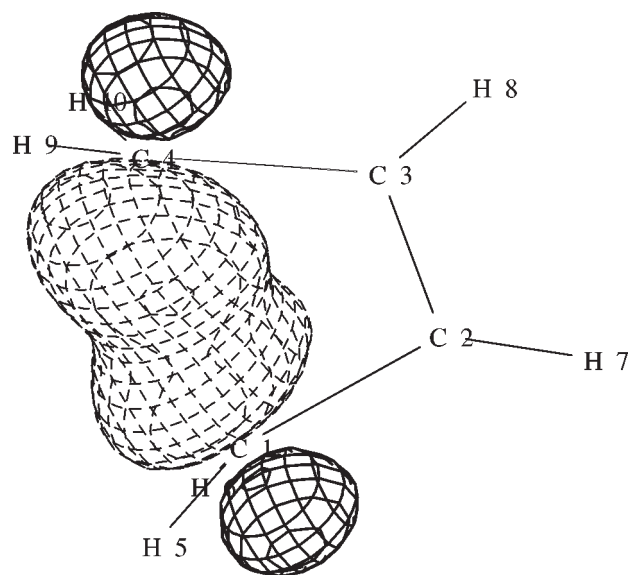

Figure 12. Fermi hole associated with CCCC region for the transition state of butadiene to cyclobutene rearrangement. Eigenvector corresponding to newly formed CC σ bonds.

late [13,24]. This empirical postulate characterizes the transition states as reactant- or product-like on the basis of the exothermicity of the process. Exothermic reactions are expected to have reactant-like transition states while product-like transition states are typical for endothermic reactions. Although widely accepted and frequently used,

this postulate has the disadvantage of all empirical rules which is that it lacks solid theoretical justification. The importance of the above introduced approach is in that it opens the possibility of theoretical justification of this postulate. Such a justification is quite straightforward since if we compare the calculated heats of formation of butadiene and cyclobutene it is possible to see that the reaction written in the direction butadiene → cyclobutene is endothermic so that the Hammond postulate requires the transition state to be product-like and this is indeed the case. In this connection it is, perhaps, worth recalling that quite recently another independent attempt at the theoretical justification of the Hammond postulate in terms of the so-called similarity indices was reported [6,7,37,40] and the results of both these independent approaches are completely consistent. This result is extremely important since it demonstrates that the analysis of Fermi holes is not only able to visualize and to interpret the structure of the species with complex bonding patterns but also it opens the new possibility of the quantitative characterization of similarity of molecules and molecular fragments. For both these reasons we believe that further systematic studies of Fermi holes are worth pursuing and some such investigations, aiming, e.g., at a new look at the problem of group valence and hypervalence are currently being performed in our laboratories and their results will be reported elsewhere.

Acknowledgements

References

[1]   R.F.W. Bader, *Atoms in Molecules. A Quantum Theory* (Clarendon Press, Oxford, 1994).
[2]   R.F.W. Bader and M.E. Stephens, J. Am. Chem. Soc. (1975) 7391.
[3]   R. Bochicchio, R. Ponec and F. Uhlik, Inorg. Chem. 36 (1997) 5363.
[4]   R.J. Boyd and C.A. Coulson, J. Phys. B 7 (1974) 1805.
[5]   J. Cioslowski, Int. J. Quantum Chem. S24 (1990) 1833.
[6]   J. Cioslowski, J. Am. Chem. Soc. 113 (1991) 6756.
[7]   J. Cioslowski, J. Sauer, J. Hetzenegger, T. Karcher and T. Hierstetter, J. Am. Chem. Soc. 115 (1993) 1353.
[8]   D.L. Cooper, R. Ponec, T. Thorsteinsson and G. Raos, Int. J. Quantum Chem. 57 (1996) 501.
[9]   C. Coulson and W.E. Moffitt, Phil. Mag. 40 (1949) 1.
[10] R. Daudel, R.F.W. Bader, M.E. Stephens and D.S. Borrett, Can. J. Chem. 52 (1974) 1310.
[11] R. Daudel, S. Odiot and H. Brion, J. Chim. Phys. 51 (1954) 74, 358, 553.
[12] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy and J.J.P. Stewart, J. Am. Chem. Soc. 107 (1985) 3902.
[13] G.S. Hammond, J. Am. Chem. Soc. 77 (1955) 334.

[14] A. Julg and P. Julg, Int. J. Quantum Chem. 13 (1978) 483.
[15] E. Lennard-Jones, J. Chem. Phys. 20 (1952) 1024.
[16] G. Leroy, D. Peters and M. Tihange, J. Mol. Struct. (Theochem) 123 (1985) 243.
[17] M. Levy, J. Am. Chem. Soc. 98 (1976) 6849.
[18] G.N. Lewis, J. Am. Chem. Soc. 38 (1916) 762.
[19] W.N. Lipscomb, Accounts Chem. Res. 6 (1973) 257.
[20] P.O. Löwdin, Phys. Rev. 97 (1955) 1474.
[21] W. Luken, Croat. Chem. Acta 57 (1984) 1283.
[22] W. Luken and D.N. Beratan, Theoret. Chim. Acta 61 (1982) 265.
[23] R. McWeeny and B.T. Sutcliffe, *Methods of Molecular Quantum Mechanics* (Academic Press, London, 1969) chapter 4.
[24] L. Melander, Spec. Publ. Chem. Soc. 16 (1962) 119.
[25] R.S. Mulliken, J. Chem. Phys. 23 (1955) 1833.
[26] R. Parrondo, P. Karafiloglou and E.S. Marcos, Int. J. Quantum Chem. 52 (1994) 1127.
[27] L. Pauling, *The Nature of Chemical Bond* (Cornell Univ. Press, Ithaca, 1960).
[28] R. Ponec, Coll. Czech. Chem. Comm. 54 (1994) 505.
[29] R. Ponec, Croat. Chem. Acta 67 (1994) 55.
[30] R. Ponec, Croat. Chem. Acta 70 (1997) 745.
[31] R. Ponec, Int. J. Quantum Chem. 62 (1997) 171.
[32] R. Ponec, J. Math. Chem. 21 (1997) 323.
[33] R. Ponec and R. Bochicchio, Int. J. Quantum Chem. 54 (1995) 99.
[34] R. Ponec and K. Jug, Int. J. Quantum Chem. 60 (1996) 75.
[35] R. Ponec and M. Strnad, Int. J. Quantum Chem. 50 (1994) 43.
[36] R. Ponec and F. Uhlik, Croat. Chem. Acta 69 (1996) 941.
[37] R. Ponec, G. Yuzhakov and J. Pecka, J. Math. Chem. 19 (1996) 265.
[38] K. Ruedenberg, Rev. Mod. Phys. 14 (1962) 326.
[39] L. Salem, Nouv. J. Chem. 2 (1978) 559.
[40] M. Sola, J. Mestres, R. Carbo and M. Duran, J. Am. Chem. Soc. 116 (1994) 5909.
[41] J.J.P. Stewart, MOPAC 6, QCPE 455, Indiana University, Bloomington (1993).
[42] M. Strnad and R. Ponec, Int. J. Quantum Chem. 49 (1994) 35.
[43] K. Wade, *Electron Deficient Compounds*, Studies in Modern Chemistry (T. Nelson and Sons, 1971).
[44] J. Wang and V.H. Smith, Jr., Int. J. Quantum Chem. 49 (1994) 147.
[45] E. Wigner and F. Seitz, Phys. Rev. 43 (1933) 804.