Ab Initio SCF Nonlinear Pair Population Analysis. A New Means of Detection and Localization of Multicenter Bonding

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The nonlinear population analysis recently formulated at the level of semiempirical MO methods was generalized so as to be applicable to the *ab initio* SCF closed shell level of theory. The method provides a new, efficient means of visualization of molecular structure especially for molecules with complex bonding patterns such as multicenter bonding. The approach was applied to the visualization of bonding in several simple boranes like B_2H_6, B_4H_{10}, B_5H_9, and B_5H_{11}. In all cases the approach was able to detect and to correctly localize the three-center bonds in these molecules.

Introduction

Although the most general description of molecular structure looks at the molecule as composed of a set of mutually interacting electrons and nuclei, chemistry has created its own powerful language in terms of which molecular structure can be described and understood. The basic building blocks of this description are atoms and chemical bonds, and the behavior and properties of molecules can be interpreted in terms of atomic and bond contributions.[1]

The analysis of an *N*-particle state function which represents the most complete source of information about the structure of a system is, however, a rather complicated task, and in order to understand the molecular structure, some simplifying procedures are usually necessary. One of them is based on the elimination of redundant information present in the state function and in the subsequent introduction of the so-called reduced density matrices (RDM). Despite the considerable simplification introduced with density matrices, these matrices are still rather complex quantities, and in order for the desired information to be extracted from them, they have to be subjected to further mathematical processing. One of the most useful such approaches is so-called population analysis. The basic idea of this analysis is to decompose some molecular property into individual contributions which can be given a simple chemical or physical meaning. During the last several years many population schemes have been proposed[2−7] which can be divided into two main groups according to what type of density functional is actually analyzed. For linear functionals (irrespective of whether they are based on 1- or 2-RDM) we speak of linear population analysis. On the other hand, if other than linear density functionals are analyzed, we speak of nonlinear population analysis. An example in this respect is, e.g., the recently introduced analysis.[8−10] The most important feature of the analysis of 2-RDM is that in contrast to 1-RDM, which is sufficient for the description of such first-order bonding patterns as atomic shared and unshared populations, bond multiplicities, and valencies, the additional information included in the 2-RDM makes it possible to analyze also some more complex bonding situations like multicenter bonding frequently encountered in electron deficient compounds. The great advantage of such analysis is that, in addition to detecting the presence of multicenter bonding in a molecule, also its localization within the molecule is possible. This is an especially important and useful feature of the approach since, in contrast to direct localization schemes sometimes used for the same purpose, the population contributions are not sensitive to any mathematical transformation of the MO basis set and can be applied to any kind of system ranging from simple molecules to layer and crystalline systems of a solid state nature.[10,11] It can even be applied to the visualization of the distribution of electron spin in open-shell systems.[12,13]

Our goal in this study is to report the application of the nonlinear pair population analysis to the visualization of the structure of several electron deficient boranes for which the presence of multicenter bonding, which can be regarded as a second-order bonding pattern, is generally accepted. The study is divided into several parts. In the first, the formalism of the pair population analysis is briefly reviewed. After this review,

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the formalism, originally introduced at the semiempirical MO level, is applied to the level of *ab initio* SCF theory. In the third section, some numerical results obtained for several simple boranes are discussed.

Theoretical Background

In terms of irreducible representations of the S_2 group, the D (2-RDM) satisfying the normalization

$$\mathrm{tr}(D) = \binom{N}{2} \tag{1}$$

can be decomposed into components corresponding to singlet and triplet states of the electron pair

$$D = D^{(s)} + D^{(t)} \tag{2}$$

This allows us to write the multicenter populations as functions of the square of the matrix elements of the *two-particle matrix*

$$\frac{1}{64}\sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta}(d_{\alpha\beta}d_{\gamma\delta} + d_{\alpha\gamma}d_{\beta\gamma})^2 + \frac{3}{64}\sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta}(d_{\alpha\beta}d_{\gamma\delta} - d_{\alpha\gamma}d_{\beta\gamma})^2 = \binom{N}{2} \tag{3}$$

where $d_{\alpha\beta}$ stands for the matrix element of the 1-RDM. Because of its four-index nature expression 3 can be rewritten in the form

$$\sum_{A}\Delta_{A} + \sum_{A<B}\Delta_{AB} + \sum_{A<B<C}\Delta_{ABC} + \sum_{A<B<C<D}\Delta_{ABCD} = \binom{N}{2} \tag{4}$$

which defines the partitioning scheme for the pair density into mono-, bi-, tri-, and tetraatomic contributions.

In a previous study[14] we demonstrated that instead of the original populations which are difficult to interpret it is useful to introduce the so-called effective pair populations[15] defined as the difference of the singlet (the first term on the left-hand side of eq 3) and one-third of the triplet population (the second term in the same equation):

$$\begin{aligned}\Delta_{A}^{eff} &= \Delta_{A}^{(s)} - (1/3)\Delta_{A}^{(t)}\\ \Delta_{AB}^{eff} &= \Delta_{AB}^{(s)} - (1/3)\Delta_{AB}^{(t)}\\ \Delta_{AB}^{(t)}\Delta_{ABC}^{eff} &= \Delta_{ABC}^{(s)} - (1/3)\Delta_{ABC}^{(t)}\\ \Delta_{ABCD}^{eff} &= \Delta_{ABCD}^{(s)} - (1/3)\Delta_{ABCD}^{(t)}\end{aligned} \tag{5}$$

The reasons for the introduction of *effective populations* have been discussed previously in refs 15 and 16, and so we consider it necessary to recall only that while the original populations Δ are normalized to

$$\binom{N}{2}$$

(total number of pairs), the effective populations are normalized to $N/2$, which for the molecule with N electrons is just the number of bonds plus free and/or core electron pairs.

$$\sum_{A}\Delta_{A}^{(eff)} + \sum_{A<B}\Delta_{AB}^{(eff)} + \sum_{A<B<C}\Delta_{ABC}^{(eff)} + \sum_{A<B<C<D}\Delta_{ABCD}^{(eff)} = \frac{N}{2} \tag{6}$$

Second, it turns out that these nonlinear effective pair populations are related, similarly to the previously introduced linear ones,[15] to classical bond multiplicities which are also well described by the so-called Wiberg's indices.[5] Here, however, it is worth mentioning that while linear effective pair populations[15] are exactly equal to half of Wiberg indices, no such simple straightforward relation exists for nonlinear ones even if a close parallel between them also exists.

As a consequence, the exact normalization can frequently be simplified to the form

$$\sum_{A}\Delta_{A}^{(eff)} + \sum_{A<B}^{\text{bonded}}\Delta_{AB}^{(eff)} \approx \frac{N}{2} \tag{7}$$

where the summation of biatomic terms runs not over all pairs of atoms but only over pairs which are classically bonded in the structural formula. The validity of this equation is thus a simple indicator of the extent to which the molecular structure is adequately represented by a classical Lewis formula. On the other hand, where the normalization is not satisfied with reasonable accuracy, the molecule can be expected to contain more complex bonding patterns such as multicenter bonds. In this connection it is, however, interesting to stress that the above population scheme not only brings the possibility of detecting the eventual presence of multicenter bonding but also allows us to determine its location in the molecule. This localization is based on the inspection of the values of three- and four-center pair populations. Generally it holds that the majority of these terms are very small and nonnegligible values are attained by these contributions only for certain very specific regions in the molecule, namely, those which coincide with the regions where the three-center or multicenter bonding is localized. As a consequence, the approximate normalization (7) can be rewritten in a more general form

$$\sum_{A}\Delta_{A}^{(eff)} + \sum_{A<B}^{\text{bonded}}\Delta_{AB}^{(eff)} + \sum_{A<B<C}^{\text{3-center}}\Delta_{ABC}^{(eff)} \approx \frac{N}{2} \tag{8}$$

which not only opens the possibility of visualizing the structure even for systems with complex bonding patterns but also makes it possible to estimate the accuracy of such a picture.

In the following section the above methodology will be applied at the *ab initio* SCF level to several electron deficient boranes with three-center bonds.

Results and Discussion

Computational Details. In this study a series of simple boranes B_2H_6, B_4H_{10}, B_5H_9, and B_5H_{11} was investigated. The population analysis was performed by our own routine interfaced with the GAMESS program.[17] The calculations consisted first of normal SCF run to generate the density matrix which, in the second step, is subjected to the population analysis. The analysis itself is extremely fast and takes only a few seconds for systems of the studied size. The time-determining step is thus the generation of the state function and the density matrix in a standard quantum chemical run rather than the analysis itself. The routine perfoming the reported analysis can be obtained

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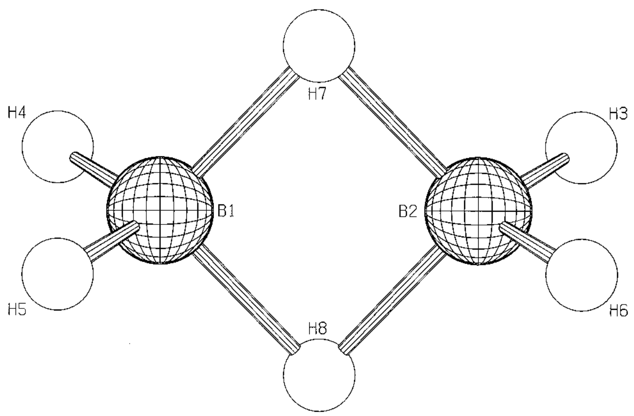

Figure 1. B_2H_6 diborane geometrical conformation (atoms H_7 and H_8 are out of plane).

Table 1. Three-Center Bonds (3-Bond) Population in B_2H_6

atom	Δ_A	3-bond	Δ_{ABC}	bond	Δ_{AB}
B(1)	1.159	B(1)H(7)B(2)	0.419	B(1)H(7)	0.198
H(4)	0.045	B(1)B(2)H(3)	0.027	B(1)B(2)	0.289
H(7)	0.022	B(1)H(4)H(5)	0.015	B(1)H(4)	0.814

upon request from the authors. The routine also exists for the same analysis at a semiempirical level of the theory, and it is also available upon request. The geometries of all systems have been fully optimized using a 6-31G** orthogonalized basis set with polarization d functions on heavy atoms and p functions on hydrogen atoms, and all of the structures have been checked to be the true minima on the potential energy hypersurface. In this connection it is necessary to mention the case of the B_5H_{11} molecule, for which the existence of two slightly different structures with C_s and C_1 symmetry was reported by previous *ab initio* calculations,[18,19] with C_1 being slightly more stable. The same order of stability was found also in our case; moreover, we found that the less stable C_s structure does not correspond to a minimum, but it is a saddle point. The only stable minimum was found for the structure with C_1 symmetry, and this structure was thus considered in all subsequent discussions. Basis sets orthogonalization has been carried out by means of Löwdin's procedure.[20]

Discussion. According to Lipscomb's rules[21] the structure of electron deficient boranes can be characterized by the so-called *styx* number where *s* is the number of three-center BHB bonds, *t* is the number of three-center BBB bonds, *y* is the number of two-center BB bonds, and *x* gives the number of BH_2 groups. Using this classification, the simplest borane B_2H_6 has the styx number 2002, which means that two BHB three-center bonds and two BH_2 fragments can be expected in this molecule. As we will see below, this is the picture which arises also from our analysis.

Diborane B_2H_6. In Table 1 the selected values of nonlinear pair populations from our *ab initio* calculations are collected. Let us attempt now to discuss these data. For this purpose let us base our consideration on the classical structural formula (Figure 1) and let us assume first that there is no three-center bond in a molecule. In this case the approximate normalization (7) gives

$$\sum_{A}\Delta_{A}^{(\mathrm{eff})} + \sum_{B-H}^{\text{terminal}} \Delta_{BH}^{(\mathrm{eff})} + \sum_{B-H}^{\text{bridging}} \Delta_{BH}^{(\mathrm{eff})} = 6.59$$

As it is possible to see, the resulting value is quite far from the ideal limit ($N/2 = 8$). This suggests that the molecule is not well described by a set of 2c−2e bonds only so that the presence of multicenter bonding can be expected.

According to Lipscomb's rules the three-center bonds should be localized in the region of the boron atoms and the bridging hydrogens so that, if the analysis is correct, there should be two nonvanishing BH_bB three-center bond populations. As it is possible to see, this is indeed the case, and it is interesting that they are the only significantly nonvanishing three-center terms. If we now take this three-center term into account, the approximate normalization (4) can be improved to the form (8)

$$\sum_{A}\Delta_{A}^{(\mathrm{eff})} + \sum_{B-H}^{\text{terminal}} \Delta_{BH}^{(\mathrm{eff})} + \sum_{B-H}^{\text{bridging}} \Delta_{BH}^{(\mathrm{eff})} + \sum_{BHB}^{3c}\Delta_{BHB}^{(\mathrm{eff})} = 7.428$$

As it is possible to see, the inclusion of this three-center term considerably improves the accuracy of the approximate normalization, but the deviation from the ideal limit 8 is still quite large. A more detailed inspection of the possible cause of this deviation shows that there is still some nonnegligible and so far nonconsidered pair population which corresponds to the interaction of two classically nonbonded boron atoms. If this interaction is taken into account, the normalization sum improves to 7.717.

Tetraborane B_4H_{10}. This molecule with C_{2v} symmetry has the styx number 4012, which means that there should be four three-center BHB bonds, one two-center BB bond, and two BH_2 fragments (Figure 2a). Let us now look at how these expectations correlate with the theoretically calculated pair populations. The corresponding symmetry unique values are summarized in Table 2. As it is possible to see, the only nonnegligible two-center pair populations correspond to (a) four B−H bonds representing two BH_2 fragments, (b) one BB bond, and (c) two terminal B−H bonds.

In addition to this there are also four three-center BHB populations which correspond to four BHB three-center bonds. Combined together, this leads to the final formula (see Figure 2b), which exactly reflects the structure expected on the basis of Lipscomb's rules.

In order to check the accuracy of such a picture of bonding, the approximate normalization (8) can be used, which in this case gives

$$\sum_{A}\Delta_{A}^{(\mathrm{eff})} + 4\Delta_{B_1H_{12}}^{(\mathrm{eff})} + 4\Delta_{B_5H_{12}}^{(\mathrm{eff})} + 2\Delta_{B_1H_3}^{(\mathrm{eff})} + 4\Delta_{B_5H_7}^{(\mathrm{eff})} + \Delta_{B_1B_2}^{(\mathrm{eff})} + 4\Delta_{B_1B_5}^{(\mathrm{eff})} + 4\Delta_{B_1H_{12}B_5}^{(\mathrm{eff})} = 13.78$$

As it is possible to see, this normalization describes well the localization of the majority of electron pairs, but the nonnegligible deviation from the ideal limit 15 suggests that there are still some additional bonding interactions not reflected by the styx number. An inspection of Table 2 reveals that there are indeed two symmetry equivalent three-center BBB populations. If their contributions are taken into account, the normalization sum is improved to:

$$\sum_{A}\Delta_{A}^{(\mathrm{eff})} + 4\Delta_{B_1H_{12}}^{(\mathrm{eff})} + 4\Delta_{B_5H_{12}}^{(\mathrm{eff})} + 2\Delta_{B_1H_3}^{(\mathrm{eff})} + 4\Delta_{B_5H_7}^{(\mathrm{eff})} + \Delta_{B_1B_2}^{(\mathrm{eff})} + 4\Delta_{B_1B_5}^{(\mathrm{eff})} + 4\Delta_{B_1H_{12}B_5}^{(\mathrm{eff})} + 2\Delta_{B_1B_2B_5}^{(\mathrm{eff})} = 14.12$$

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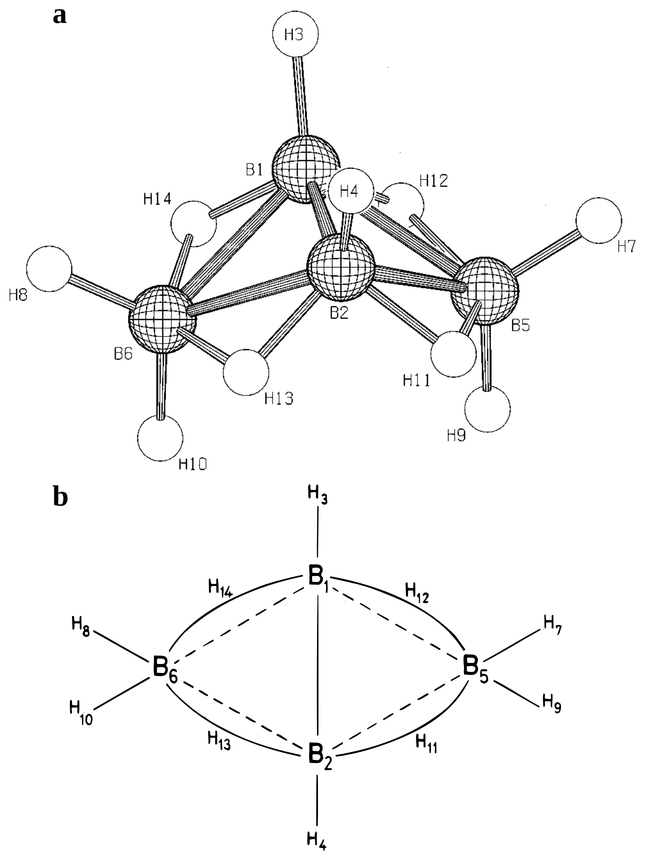

Figure 2. (a) B_4H_{10} tetraborane geometrical conformation. (b) B_4H_{10} tetraborane bonding structure (see text).

Table 2. Three-Center Bonds (3-bond) Population in B_4H_{10}

atom	Δ_A	3-bond	Δ_{ABC}	bond	Δ_{AB}
B(1)	1.120	B(1)H(12)B(5)	0.347	B(1)H(12)	0.278
H(3)	0.041	B(1)B(2)B(5)	0.168	B(5)H(12)	0.131
H(12)	0.021			B(1)B(2)	0.379
B(5)	1.149			B(1)B(5)	0.191
H(7)	0.044			B(1)H(3)	0.768
				B(5)H(7)	0.800

In this connection it is interesting that this kind of additional BBB interaction was observed already by Lipscomb,[22] who proposed to interpret it as being due to donation from a single BB bond to terminal BH_2 groups. We can thus see that the proposed population scheme is able to detect even such a subtle structural effect.

The picture of bonding could be, of course, more precise, but this would require the inclusion of a large number of individually very small populations, so that the transparency of the above simple picture of bonding would be lost. Note, however, that if three-center BHB bonds were not included, the sum would be only 12.43. We can thus see that these three-center bonds expected on the basis of styx number are indeed a crucially important structural factor of this molecule.

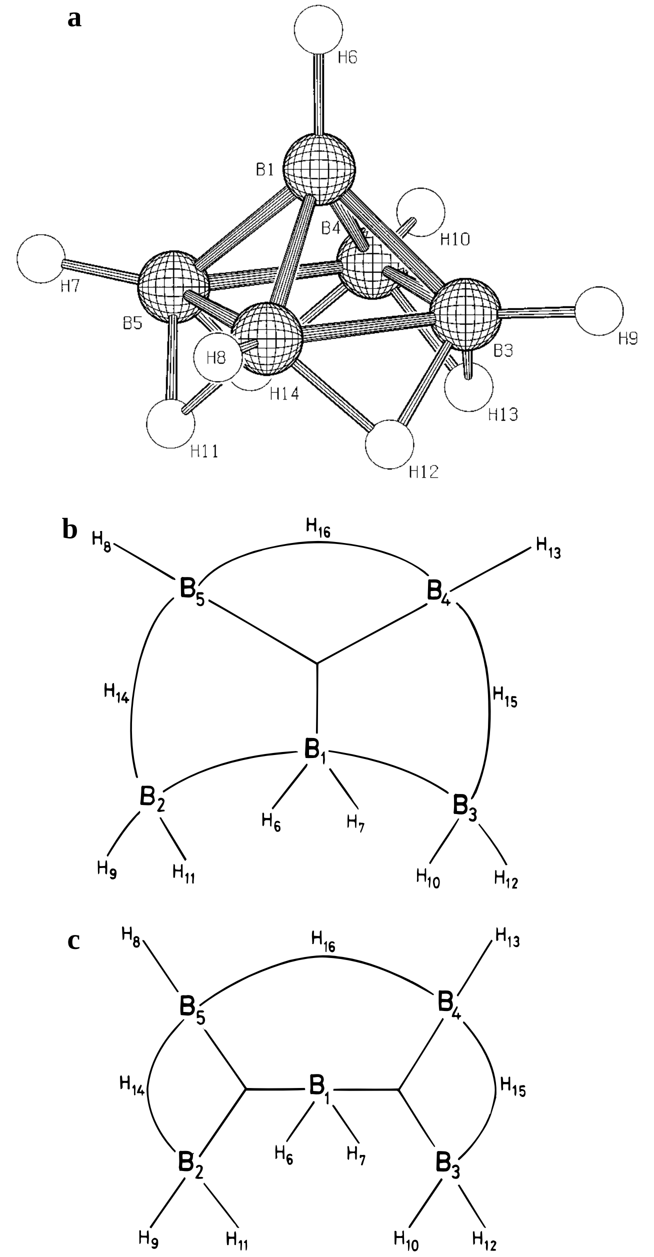

Figure 3. (a) B_5H_{11} geometrical conformation. (b) B_5H_{11} bonding structure **a**. (c) B_5H_{11} bonding structure **b**.

Table 3. Three-Center Bonds (3-Bond) Population in B_5H_{11}

atom	Δ_A	3-bond	Δ_{ABC}	bond	Δ_{AB}
B(1)	1.112	B(1)B(2)B(5)	0.270	B(1)B(2)	0.199
H(6)	0.020	B(1)B(4)B(5)	0.163	B(1)B(5)	0.268
B(5)	1.108	B(2)B(5)H(14)	0.357	B(2)B(5)	0.256
B(2)	1.148	B(4)B(5)H(16)	0.365	B(4)B(5)	0.189
H(7)	0.043	B(1)B(2)H(6)	0.167	B(2)H(6)	0.046
H(8)	0.041	B(1)B(2)B(3)	0.024	B(5)H(14)	0.286
H(9)	0.043			B(5)H(16)	0.195
H(11)	0.045			B(1)H(6)	0.337
H(14)	0.021			B(1)H(7)	0.766
H(16)	0.022			B(2)H(9)	0.792
				B(2)H(11)	0.790
				B(2)H(14)	0.122
				B(5)H(8)	0.768

Pentaborane B_5H_{11}. This molecule (see Figure 3a) has the styx number 3203, which is consistent with two structures denoted as **a** and **b** (see Figure 3, parts b and c, respectively) and which differ in the location of the three-center BBB bonds. As discussed by Lipscomb,[23] the ambiguity in deciding between these two alternatives can be resolved using the localization techniques, which slightly favor structure **b**, with central three-center BBB bonds, over structure **a**, with open BBB bond. Let us now look at how this ambiguity is resolved within our population scheme. Thus, e.g., a brief look at Table 3 shows that, in addition to clearly visible BHB three-center bonds, there are two symmetry equivalent contributions from the $B_1B_2B_5$ bond and one contribution corresponding to the $B_1B_3B_4$ bond. There is not, however, a contribution corresponding to a $B_1B_2B_3$

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open three-center bond. This can be regarded as a first indication of the preference of structure **b** over structure **a**. Another independent support in favor of structure **b** comes from a comparison of approximate normalization sums corresponding to structures **a** and **b**. These two normalizations give, for structure **a**,

$$\sum_{A}\Delta_{A}^{(\mathrm{eff})} +2\Delta_{B_1B_2}^{(\mathrm{eff})} + 2\Delta_{B_1B_5}^{(\mathrm{eff})} + +2\Delta_{B_5H_{14}}^{(\mathrm{eff})} + 2\Delta_{B_5H_{16}}^{(\mathrm{eff})} + \Delta_{B_1H_6}^{(\mathrm{eff})} + \Delta_{B_1H_7}^{(\mathrm{eff})} + 2\Delta_{B_2H_9}^{(\mathrm{eff})} + 2\Delta_{B_2H_{11}}^{(\mathrm{eff})} + 2\Delta_{B_5H_8}^{(\mathrm{eff})} + 2\Delta_{B_2H_{14}}^{(\mathrm{eff})} + \Delta_{B_1B_4B_5}^{(\mathrm{eff})} + 2\Delta_{B_2H_{14}H_5}^{(\mathrm{eff})} + \Delta_{B_4H_{16}B_5}^{(\mathrm{eff})} = 15.19$$

and, for structure **b**,

$$\sum_{A}\Delta_{A}^{(\mathrm{eff})} + 2\Delta_{B_1B_2}^{(\mathrm{eff})} + 2\Delta_{B_1B_5}^{(\mathrm{eff})} + 2\Delta_{B_5H_{14}}^{(\mathrm{eff})} + 2\Delta_{B_5H_{16}}^{(\mathrm{eff})} + \Delta_{B_1H_6}^{(\mathrm{eff})} + \Delta_{B_1H_7}^{(\mathrm{eff})} + 2\Delta_{B_2H_9}^{(\mathrm{eff})} + 2\Delta_{B_2H_{11}}^{(\mathrm{eff})} + 2\Delta_{B_5H_8}^{(\mathrm{eff})} + 2\Delta_{B_2H_{14}}^{(\mathrm{eff})} + 2\Delta_{B_1B_2B_5}^{(\mathrm{eff})} + 2\Delta_{B_2H_{14}H_5}^{(\mathrm{eff})} + \Delta_{B_4H_{16}B_5}^{(\mathrm{eff})} = 15.77$$

As it is possible to see, the normalization sum is slightly higher for structure **b** than for **a**, which indicates that structure **b** describes the distribution of electron pairs in the molecule slightly better than structure **a**.

In addition to providing independent qualitative support for the structural assignment based on localization techniques, the above population scheme has yet another important advantage. This advantage arises again from the existence of approximate normalization relations which allow one to look at the eventual presence of additional structural features whose inclusion is essential for the description of the structure. Thus, e.g., if we look at normalization sums for **a** and **b**, it is possible to see that the resulting values deviate considerably from the ideal limit 18. This again implies that some other bonding interactions, not involved in the classical (styx) structures, are likely to operate. That this is indeed the case can be seen from an inspection of the Table 3, which shows that there are some nonnegligible bonding interactions corresponding to B_2B_5, B_4B_5, and $B_1B_2H_6$ bonds even if these atoms are not directly bonded in either **a** or **b**. If we take all (nonnegligible) bonding interactions into account and include them into the approximate normalization, the result is 16.77. This is already much closer to the ideal limit, so that we can see that the inclusion of classically neglected contributions considerably improves the accuracy of the picture of bonding and gives us a rather good idea of where the electron pairs are localized in the molecule. Here it is useful to stress that the precission of the approximate normalization could still be increased, but this would again require the use of a large number of individually small contributions which would greatly complicate the resulting picture of bonding.

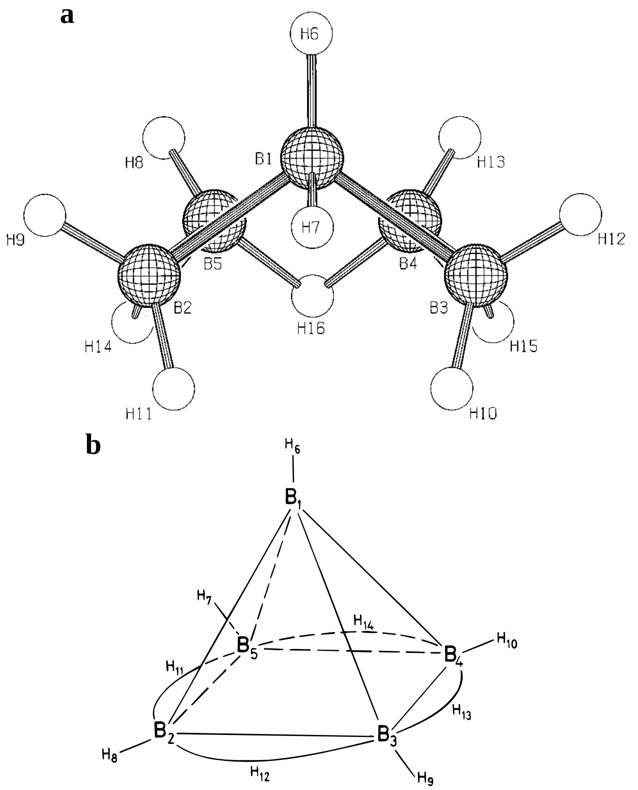

Figure 4. (a) B_5H_9 pentaborane geometrical conformation. (b) B_5H_9 pentaborane bonding structure (see text).

Table 4. Three-Center Bonds (3-Bond) Population in B_5H_9

atom	Δ_A	3-bond	Δ_{ABC}	bond	Δ_{AB}
B(1)	1.099	*B*(1)*B*(2)*B*(3)	0.233	*B*(1)*B*(2)	0.336
B(2)	1.106	*B*(2)*H*(12)*B*(3)	0.351	*B*(2)*B*(5)	0.219
H(6)	0.042	*B*(1)*B*(2)*B*(4)	0.081	*B*(2)*H*(12)	0.202
H(11)	0.023	*B*(1)*B*(2)*H*(6)	0.024	*B*(2)*B*(4)	0.029
H(7)	0.040			*B*(1)*H*(6)	0.745
				B(2)*H*(8)	0.773

B_5H_9. This example is especially interesting since it demonstrates that, when the structure of electron deficient boranes is visualized, the proposed population scheme is frequently able to overcome ambiguities encountered with various localization schemes. Thus, e.g., as discussed by Lipscomb,[23] the pentaborane B_5H_9 (see Figure 4a) is an example of a system where the localization techniques fail to give an unambiguous picture of bonding since the resulting picture strongly depends on the type of orbitals from which one starts. In order to eliminate this problem the use of randomized sets of molecular orbitals was proposed. As we will see below, this type of problem is completely eliminated within the population analysis and the resulting picture of bonding is unique. In addition to eliminating the ambiguity of localization techniques, the population scheme has yet another important advantage, and this is that it automatically eliminates the problem of the resonance of several structures required sometimes to compensate for the inadequacy of the styx numbering. Thus, e.g., the styx number of B_5H_9 is 4120, which means that the molecule should contain four BHB three-center bonds, one three-center BBB bond, and two BB two-center bonds. The existence of one three-center BBB bond is not, however, consistent with the C_{4v} symmetry of the molecule (see Figure 4b), which requires the equivalence of all equatorial boron atoms, so that the resonance of four equivalent structures had to be invoked. Let us now look at how the problem of resonance is dealt with using the population analysis. The corresponding values of pair populations are summarized in Table 4. First of all it is possible to see that there are indeed four symmetry equivalent three-center BHB pair populations, each of which is roughly comparable to the BHB pair population in diborane. This allows us to expect that each of these BHB populations corresponds to one “complete” three-center bond. Let us now similarly look at the three-center BBB bonds. In keeping with the C_{4v} symmetry there are indeed four symmetry equivalent three-center BBB populations, but each of them is now smaller than the contribution from the “complete” three-center bond. This suggests that these three-center BBB bonds have to be regarded as only “fractional”, and the requirements of the styx numbering can still be satisfied if we admit that four “fractional” BBB bonds is equivalent to one “complete” bond. A similar situation with fractional bonds is encountered also for two-center BB bonds, where there are again four symmetry equivalent BB two-center populations, each of which is again lower than would correspond to a "normal" 2c−2e bond. We can thus see that the "resonance/fractional bonds" picture of bonding is immediatly revealed by the population scheme, which really is a nice feature of this analysis.

In order to estimate the accuracy of the bonding picture suggested by the population analysis, the approximate normalization sum can again be used, and such a sum, which takes into account the above mentioned most significant pair populations, equals 16.142.

As this is still not very close to the ideal limit of 17, it is apparent that there are still some other bonding interactions not involved in the classical styx number, but the problem is that they again are dissipated into a large number of individually small contributions so that their inclusion would considerably complicate the picture of bonding.

Final Remarks and Conclusions

The results presented here allow us to conclude that statistical nonlinear population analysis opens new possibilities for the detection and localization of multicenter bonding patterns so that the nature of bonding in electron deficient systems can easily be visualized and understood. On the basis of these as well as other results, we believe that this technique can be useful also in the investigation of other systems with complex bonding patterns such as carboranes, organometallic coordination compounds, and metal clusters as well as systems of a solid state nature like polymers, layers, and crystals. Another class of systems where such a population analysis might be interesting is the metalloids (Si, Ge, As, Sb, Te). For instance, small Si clusters are "metal like" but bulk Si has simple covalent bonds (diamond structure).[14] Actually many systems would benefit from such analysis. In this connection it is, however, fair to say that, like any type of Mulliken-like analysis, also the present analysis is basis set dependent. Being aware of this dependence, we have recently performed a study of basis set sensitivity for closely related linear pair population,[24] and we found that except for very small basis sets this sensitivity is in fact lower than might have been anticipated.

Another point which might be interesting to stress in connection with the existence of three-center bonding can indirectly be detected already from the linear pair population analysis. The condition for a three-center bond to exist between centers ABC is the existence of fractional bond orders (effective pair populations) between all possible pairs of atoms AB, BC, and AC.[9,25]

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