

## Multicentre Bond Indices from the Generalized Population Analysis of Higher Order Densities

*Robert Ponec and Filip Uhlík*

*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Prague 6, Suchbátka 2, 165 02, Czech Republic*

Received May 6, 1995; revised June 27, 1995; accepted July 27, 1995

Based on the generalized population analysis of appropriate functionals derived from higher order densities, the multicentre bond indices were introduced at both SCF and post-SCF levels. The corresponding indices were applied to the visualization of bonding in several simple molecules both without and with three-centre bonds. The ability of these indices to detect and to localize the presence of three-centre bonds was tested on the analysis of bonding in several simple boranes  $B_2H_6$ ,  $B_4H_{10}$ ,  $B_5H_9$ . The three centre bonds were always detected in complete agreement with expectations. The approach is quite general and can be applied to the visualization of bonding in other cases of molecules with complex bonding patterns.

### INTRODUCTION

The quantum chemical calculations are rapidly becoming a routine tool for obtaining the energies and the structures of both stable and transient molecular species. Unfortunately, the increased sophistication required to reach the desired accuracy inevitably results in a loss of transparency of the corresponding wave functions. For this reason, introduction of sophisticated computational procedures is also accompanied by a parallel design of new methods allowing interpretation and visualization of the structural information hidden in the wave functions.<sup>1-6</sup> Among various techniques of this type, the idea of the so-called population analysis has found the most extensive use.<sup>7-15</sup> This analysis in the form of the so-called Mulliken population analysis<sup>8</sup> has found the widest use but the same idea of partitioning the electron density into contributions that can be directly related to intuitive

but highly appealing concepts of charge density, valence or bond order<sup>16-20</sup> has been used rather frequently and various generalizations of the population analysis have been proposed so far. An example of such a generalization can be, *e.g.*, the recently proposed pair population analysis,<sup>21</sup> in which we demonstrated that the properly chosen pair populations can be used as a new simple means of visualization of the classical structural formula. In its original form, however, the method was straightforwardly applicable only to molecules well described by the Lewis model of localized two-centre two electron (2c-2e) bonds but, for electron deficient molecules with three centre bonds, the resulting picture of molecular structure was not so clear and simple.<sup>22</sup> The question thus naturally appeared whether it would not be possible to design some new indices that would be able to detect the possible presence of three- or multicentre bonding.

The first attempt in this respect is the so-called three-centre bond index independently proposed by Giambiagi<sup>23</sup> and by Sannigrahi and Kar.<sup>24</sup> The similar idea of detecting the possible presence of multicentre bonding was recently used also by us and the resulting methodology of the so-called nonlinear population analysis of the pair densities<sup>25</sup> was successfully applied to the visualization of bonding in various electron deficient molecules.<sup>26</sup> In spite of the promising results of that study, the original formalism had, however, one important conceptual limitation. This limitation is that the formalism of this nonlinear analysis is applicable only to SCF wave functions and the extension to correlated post-SCF wave functions is impossible.

Our aim in this study is to remedy this partial limitation and to propose a new generalized population analysis allowing the multicentre bonds of any order  $k$  to be detected via the so-called multicentre bond indices. Although in this study the approach is practically tested only at the SCF level of theory (for both semiempirical and *ab initio* methods), the formalism itself is completely general and can easily be extended to the level of post-SCF wave functions. Such an extension is at present limited by the restricted availability of correlated higher order densities but we believe that the information hidden in these densities is attractive enough to reward the effort devoted to their future systematic exploration.

## THEORETICAL

### *SCF level of theory*

Introduction of the multicentre bond indices can be best demonstrated by starting with the simple case of the standard Mulliken population analysis. Within this analysis, the monoatomic populations (charge densities) can be straightforwardly introduced from the partitioning of the normalization

relation Eq. (1) according to Eq. (2), where  $\mathbf{P}$  represents the usual charge density bond order matrix and  $\mathbf{S}$  the overlap matrix.

$$N = \int \rho(1) d\tau_1 \quad (1)$$

$$N = \sum_A \sum_{\alpha} (PS)_{\alpha\alpha} = \sum_A \Pi_A^{(1)} \quad (2)$$

The first order density  $\rho(1)$  is not, however, the only quantity normalized to the total number of electrons  $N$ . The same normalization is satisfied also for some other quantities derived from higher order densities. The simplest example of such a quantity is the so-called exchange part of the pair density which is given by Eq. (3) and where  $\rho_1(1,2)$  is defined as Eq. (4).

$$\gamma^{\text{exch}}(1,2) = \frac{1}{4} \rho_1^2(1,2) \quad (3)$$

$$\rho_1(1,2) = 2 \sum_i^{\text{occ}} \phi_i(1)\phi_i(2) \quad (4)$$

This exchange part of pair density satisfies normalization (5).

$$N = 2 \int \gamma^{\text{exch}}(1,2) d\tau_1 d\tau_2 \quad (5)$$

Like normalization Eq. (2), also Eq. (5) can be decomposed into various contributions. The only difference in comparison with partitioning Eq. (2) is that not only mono- but also biatomic contributions can be introduced in this case.

$$N = \frac{1}{2} \sum_{\alpha} \sum_{\beta} (PS)_{\alpha\beta} (PS)_{\beta\alpha} = \sum_A \Pi_A^{(2)} + \sum_{A < B} \Pi_{AB}^{(2)} \quad (6)$$

This type of analysis is closely related to the previously introduced pair population analysis<sup>21</sup> and the populations  $\Pi_A^{(2)}, \Pi_{AB}^{(2)}$  are in fact identical with the effective pair populations of that analysis.

The practical use of partitioning Eq. (6) is based on the empirical observation that the exact normalization sum Eq. (7) can be frequently simplified to the form Eq. (8)

$$N = \sum_A \Pi_A^{(2)} + \sum_{A < B} \Pi_{AB}^{(2)} \quad (7)$$

$$N \approx \sum_A \Pi_A^{(2)} + \sum_{A < B}^{\text{bonded}} \Pi_{AB}^{(2)} \quad (8)$$

in which the summation is restricted only to the pairs of atoms that are classically bonded in the structural formula. In another words, populations  $\Pi_{AB}^{(2)}$  attain nonnegligible values only between classically bonded atoms while for the nonbonded atoms their values are small.

Because of this ability to detect and to localize the two-centre bonds, populations  $\Pi_{AB}^{(2)}$  can be regarded as two-centre bond indices.

The approximate normalization Eq. (8) was, however, found to hold with reasonable accuracy only for molecules well described by the Lewis model of 2c-2e bonds. If such is not the case, as it is, *e.g.*, with electron deficient molecules, Eq. (8) fails to hold and the contributions between nonbonded pairs of atoms start to appear. This can be regarded as an indirect indicator of the presence of multicentre bonding.<sup>25</sup>

In this study, we want to demonstrate that it is possible to formulate a criterion in terms of which the presence of multicenter bonding can be detected directly. In addition to the formalism of nonlinear pair population analysis, where such a possibility was introduced recently<sup>25</sup>, there is yet another possibility which is based on the concept of the so-called multicenter bond indices.<sup>23,24,27</sup> This possibility arises from the useful normalization relations analogous to Eqs. (2) and (5), which hold for the appropriate functionals derived from the higher order densities. Thus, *e.g.*, in the case of third order density  $\Gamma(1,2,3)$  which in the case of SCF closed shell approximation is given by

$$\begin{aligned} \Gamma(1,2,3) = & \frac{1}{6} \rho(1)\rho(2)\rho(3) - \frac{1}{12} \rho(1)\rho_1^2(2,3) - \frac{1}{12} \rho(2)\rho_1^2(1,3) - \\ & - \frac{1}{12} \rho(3)\rho_1^2(1,2) + \frac{1}{12} \rho_1(1,2)\rho_1(2,3)\rho_1(3,1) \end{aligned} \quad (9)$$

it is possible to introduce the functional  $D(1,2,3)$

$$\begin{aligned} D(1,2,3) = & \Gamma(1,2,3) - \frac{1}{6} \rho(1)\rho(2)\rho(3) + \frac{1}{12} \rho(1)\rho_1^2(2,3) + \frac{1}{12} \rho(2)\rho_1^2(1,3) + \\ & + \frac{1}{12} \rho(3)\rho_1^2(1,2) = \frac{1}{12} \rho_1(1,2)\rho_1(2,3)\rho_1(3,1) \end{aligned} \quad (10)$$

which satisfies the normalization condition (11)

$$N = 3 \int D(1,2,3) d\tau_1 d\tau_2 d\tau_3 . \quad (11)$$

In keeping with the philosophy of population analysis, expression Eq. (11) can be partitioned into mono-, bi- and triatomic contributions according to Eq. (12).

$$N = \frac{1}{4} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} (PS)_{\alpha\beta} (PS)_{\beta\gamma} (PS)_{\gamma\alpha} = \sum_A \Pi_A^{(3)} + \sum_{A < B} \Pi_{AB}^{(3)} + \sum_{A < B < C} \Pi_{ABC}^{(3)} \quad (12)$$

The importance of this equation is again that, for molecules well described by the Lewis model of 2c-2e bonds, the above normalization is satisfactorily fulfilled with pair contributions involving only the pairs of directly bonded atoms.

$$N \approx \sum_A \overset{\text{bonded}}{\Pi_A^{(3)}} + \sum_A \overset{\text{bonded}}{\Pi_{AB}^{(3)}} \quad (13)$$

If this is not the case so that multicentre bonding can be expected to play the role, the triatomic contributions are likely to contribute. Here it is, however, interesting that these triatomic contributions are not distributed evenly between all possible triads but are strongly localized to only certain groups of atoms, namely to those where the three centre bonds are expected. In this case the approximate Eq. (12) can be rewritten as

$$N \approx \sum_A \overset{\text{bonded}}{\Pi_A^{(3)}} + \sum_{A < B} \overset{\text{bonded}}{\Pi_{AB}^{(3)}} + \sum_{A < B < C} \overset{3c}{\Pi_{ABC}^{(3)}} . \quad (14)$$

This interesting ability of three centre populations  $\Pi_{ABC}^{(3)}$  to detect and to localize the presence of three-centre bonds was first recognized by Giambiagi<sup>23</sup> and by Sannigrahi and Kar<sup>24</sup> who heuristically proposed the quantity  $I_{ABC}$  as the so-called three-centre bond index and discussed its properties.

$$I_{ABC} = \sum_{\alpha}^A \sum_{\beta}^B \sum_{\gamma}^C (PS)_{\alpha\beta} (PS)_{\beta\gamma} (PS)_{\gamma\alpha} \quad (15)$$

The above procedure for introduction of the three centre bond index can be straightforwardly extended to higher order densities of arbitrary order k.

Using the same procedure as described above for  $k = 3$ , it is possible to introduce the functional  $D(1,2,\dots,k)$ .

$$D(1,2,\dots,k) = \frac{\rho_1(1,2)\rho_1(2,3)\dots\rho_1(k-1,k)\rho_1(k,1)}{2^{k-1}} \quad (16)$$

which satisfies the normalization condition.

$$N \approx k \int D(1,2,\dots,k) d\tau_1 d\tau_2 \dots d\tau_k \quad (17)$$

This normalization can be again partitioned as

$$\begin{aligned} N &= \frac{1}{2^{k-1}} \sum_{\alpha} \sum_{\beta} \dots \sum_{\kappa} (PS)_{\alpha\beta} (PS)_{\beta\gamma} \dots (PS)_{\lambda\kappa} (PS)_{\kappa\alpha} = \\ &= \sum_A \Pi_A^{(k)} + \sum_{A < B} \Pi_{AB}^{(k)} + \sum_{A < B < \dots < K} \Pi_{AB\dots K}^{(k)}. \end{aligned} \quad (18)$$

The last term of this expansion is closely related to the multicentre bond index  $I_{(ABC\dots K)}$  of Giambiagi<sup>23,27</sup> and Sannigrahi and Kar,<sup>24</sup>

$$I_{ABC\dots K} = \sum_{\alpha} \sum_{\beta} \dots \sum_{\kappa} (PS)_{\alpha\beta} (PS)_{\beta\gamma} \dots (PS)_{\kappa\alpha} \quad (19)$$

and, parallel to what was found for  $k = 2$  and 3, the nonvanishing values of this index can be expected to indicate the presence of  $k$ -th centre bonding.

#### *Post-SCF level of theory*

Introduction of multicentre bond indices at correlated level is quite analogous to the previous case of SCF. The crucial role is played by the functionals  $\Delta(1,2,\dots,k)$  derived from higher order densities so as to satisfy the normalization to the total number of electrons  $N$ . The simplest situation that is for  $k = 2$  where the functional  $\Delta(1,2)$  is defined as a difference between the true (correlated) pair density and the product of first order densities.

$$\Delta(1,2) = \frac{1}{2} \rho(1)\rho(2) - \Gamma(1,2) \quad (20)$$

This quantity satisfies the correct normalization

$$N = 2 \int \Delta(1,2) d\tau_1 d\tau_2 \quad (21)$$

so that the two-centre bond indices can be straightforwardly introduced as biatomic contributions of the partitioning.

$$N = \sum_A \Pi_A^{(2)} + \sum_{A < B} \Pi_{AB}^{(2)} \quad (22)$$

Similarly, introduction of the (correlated) three centre bond index is based on the functional  $\Delta(1,2,3)$  related to the total three- particle density  $\Gamma(1,2,3)$ .

$$\begin{aligned} \Delta(1,2,3) = & \Gamma(1,2,3) - \frac{1}{6} \rho(1)\rho(2)\rho(3) + \frac{1}{3} \rho(1)\Delta(2,3) + \\ & + \frac{1}{3} \rho(2)\Delta(1,3) + \frac{1}{3} \rho(3)\Delta(1,2) \end{aligned} \quad (23)$$

and satisfying the required normalization

$$N = 3 \int \Delta(1,2,3) d\tau_1 d\tau_2 d\tau_3 \quad (24)$$

In a similar way, it would be possible to introduce also the multicentre bond indices of any order  $k$  but, due to the restricted availability of correlated higher order densities, the practical testing of post-SCF bond indices still has to wait for its systematic exploration. For this reason, we were also forced to confine ourselves in testing the applicability of multicentre bond indices to only the simplest case of SCF approximation. In the following part, the results of our calculations (at both semiempirical and *ab initio* levels) will be reported. Before reporting the results of these calculations it is of interest to mention a general problem common to all kinds of population analyses. This problem is the basis set dependence of the resulting populations. In the case of the pair population analysis, this problem was addressed in a recent study<sup>22</sup> and we found that this analysis is much less sensitive to the quality of the basis than the normal Mulliken population analysis of the first order density  $\rho(1)$ . Since the pair population analysis is a special case of the generalized population analysis proposed here, we believe that the similar little sensitivity to the quality of the basis will hold in this case as well. Moreover, the basis set dependence can be expected to break down in the limits of complete basis.<sup>28</sup>

## RESULTS AND DISCUSSION

In order to demonstrate the ability of multicentre bond indices to detect the presence of multicentre bonds, it is first necessary to show that, for molecules well represented by the Lewis model of 2c-2e bonds, the values of three- and higher-centre bond indices are negligible. For this purpose, the above approach was applied to a series of simple molecules like CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub> and, according to our previous experience that higher than 3-centre bonding is apparently very rare, we confined ourselves only to the analysis of the functional  $D(1,2,3)$  allowing detection of 3-centre bonds maximally. The calculations were performed at both semiempirical and *ab initio* levels.

TABLE I

Comparison of MNDO and STO-3G calculated values of multicentre populations for a series of several simple molecules

Molecule	Population	MNDO	STO-3G
CH <sub>4</sub>	C	1.01	3.23
	H	0.26	0.20
	CH	1.47	1.49
	H...H	0.01	0.01
	CHH	0.00	0.00
	HHH	0.00	0.00
NH <sub>3</sub>	N	2.95	5.18
	H	0.20	0.15
	NH	1.48	1.44
	H...H	0.00	0.01
	NHH	0.00	0.00
	HHH	0.00	0.00
H <sub>2</sub> O	O	4.79	6.81
	H	0.15	0.15
	OH	1.45	1.44
	H...H	0.00	0.01
	HOH	0.00	0.00
C <sub>2</sub> H <sub>4</sub>	C	1.11	3.34
	H	0.22	0.16
	CH	1.44	1.48
	CC	2.97	3.02
	H...H	0.00	0.00
	HCH	0.00	0.00
	CCH	0.00	0.00
	HHH	0.00	0.00

Semiempirical calculations were performed by the standard MNDO method included in the MOPAC 6 package,<sup>29</sup> for *ab initio* calculations, the Gaussian 92 series of programs was used<sup>30</sup> with the minimal STO-3G basis. In all cases, the molecules were considered in completely optimized molecular geometries. The resulting values of mono-, bi- and triatomic populations are compared in Table I.

Let us discuss now the conclusions suggested by these values. First of all it is possible to see that, irrespective of the method used and in keeping with the expected absence of three-centre bonding in these simple molecules, the 3-centre populations  $I_{ABC}^{(3)}$  are practically negligible. In addition to this, it is possible to see that all biatomic contributions between the pairs of classically nonbonded atoms are also practically negligible. As a consequence, the approximate normalization Eq. (13) is satisfied extremely well, thus suggesting close adherence of these molecules to the classical structural formula. The only greater differences between semiempirical and *ab initio* methods are observed for monoatomic contributions on heavy atoms but this difference ( $\approx 2$ ) is clearly due to the neglect of 1s core electrons in semiempirical methods.

As a further example, the formalism of the multicenter population analysis was applied to the molecule of  $B_2H_6$ , for which the presence of two 3-center bonds is generally accepted.<sup>31-33</sup> The calculations were again performed at semiempirical (MNDO) and *ab initio* (4-31G) levels and the resulting populations are compared in Table II. Similarly as in previous cases, the resulting picture is practically insensitive to the method used, and greater devia-

TABLE II

Comparison of MNDO and 4-31G calculated values of selected multicentre populations for diborane

Molecule	Population	MNDO	4-31G
$B_2H_6$	B	0.64	2.58
	H <sub>t</sub>	0.27	0.28
	H <sub>b</sub>	0.22	0.29
	BH <sub>t</sub>	1.42	1.51
	BH <sub>b</sub>	0.52	0.54
	B...B	0.46	0.42
	H <sub>t</sub> ...H <sub>t</sub>	0.00	0.00
	H <sub>b</sub> ...H <sub>b</sub>	0.08	0.14
	BH <sub>t</sub> H <sub>t</sub>	0.00	-0.01
	BH <sub>b</sub> H <sub>b</sub>	0.00	-0.03
	BH <sub>b</sub> B	0.35	0.32

tions in the values of monoatomic contributions are again due to neglect of core electrons in the MNDO method. The most important conclusion suggested by this Table is the dominance of mono- and biatomic contributions between the pairs of bonded atoms. However, as it can be seen, the approximate normalization Eq. (13) valid for the case of the strict adherence to the classical model is not satisfied with satisfactory precision, so the presence of nonbonded pair or three-centre contributions to bonding can be expected.

$$\sum_A \Pi_A^{(3)} + 4\Pi_{B-H_t}^{(3)} + 4\Pi_{B-H_b}^{(3)} = 10.56 \quad (25)$$

As it can be seen from the Table, this is indeed the case and the nonbonded B...B pair- and two B...H<sub>bridg</sub>...B three-centre populations are the dominant contributions to correcting the picture of bonding in this case. The picture of bonding suggested by the above analysis thus closely corresponds to the set of 4 B-H bonds between the borons and the terminal hydrogens and two three-centre BHB bonds involving the bridging hydrogens. In order to demonstrate the accuracy of such a generally accepted picture of bonding, it is possible to use normalization Eq. (26), which clearly demonstrates that all important bonding interactions are exhausted by this model.

$$\sum_A \Pi_A^{(3)} + 4\Pi_{B-H_t}^{(3)} + 4\Pi_{B-H_b}^{(3)} + 2\Pi_{BH_bB}^{(3)} + \Pi_{B...B} = 11.49 \approx 12 \quad (26)$$

In view of the success of the above population analysis in detecting the three-centre bonding in B<sub>2</sub>H<sub>6</sub> we decided to apply the same approach to higher boranes (B<sub>4</sub>H<sub>10</sub> and B<sub>5</sub>H<sub>9</sub>) for which the 3-centre bonds are also generally accepted.<sup>31,34,35</sup> In this case, the analysis was performed only for the *ab initio* wave function generated again in 4-31G basis by the GAUSSIAN 92 series of programs.<sup>30</sup> The resulting values of symmetry unique mono-, bi- and triatomic populations greater than 0.03 are summarized in Tables III and IV.

Let us now discuss the conclusions suggested by these values, first for the case of B<sub>4</sub>H<sub>10</sub>. First of all, it is possible to see that, despite the large number of possible combinations, the number of nonnegligible populations is relatively very small. This suggests that the bonding interactions are remarkably localized to only certain well restricted regions. The resulting picture of bonding is, therefore, relatively simple and closely corresponds to what can be expected on the basis of the Lipscomb rules.<sup>34,35</sup> According to these rules, the structure of B<sub>4</sub>H<sub>10</sub> can be represented by the set of six 2c-2e BH bonds between the borons and terminal hydrogens together with two

TABLE III  
4-31G calculated values of selected  
multicentre populations for B<sub>4</sub>H<sub>10</sub>

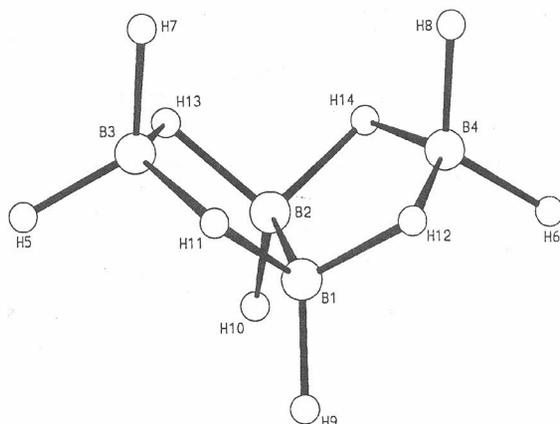
Molecule	Group	Population
B <sub>4</sub> H <sub>10</sub>	B <sub>1</sub>	2.64
	B <sub>3</sub>	2.62
	H <sub>5</sub>	0.25
	H <sub>9</sub>	0.23
	H <sub>11</sub>	0.22
	B <sub>1</sub> B <sub>2</sub>	0.62
	B <sub>1</sub> B <sub>3</sub>	0.36
	B <sub>1</sub> H <sub>9</sub>	0.99
	B <sub>1</sub> H <sub>11</sub>	0.59
	B <sub>3</sub> H <sub>5</sub>	0.98
	B <sub>3</sub> H <sub>11</sub>	0.31
	B <sub>1</sub> B <sub>2</sub> B <sub>3</sub>	0.12
	B <sub>1</sub> B <sub>3</sub> H <sub>11</sub>	0.30

TABLE IV  
4-31G calculated values of selected  
multicentre populations for B<sub>5</sub>H<sub>9</sub>

Molecule	Group	Population
B <sub>5</sub> H <sub>9</sub>	B <sub>1</sub>	2.57
	B <sub>3</sub>	2.60
	H <sub>2</sub>	0.24
	H <sub>7</sub>	0.22
	H <sub>11</sub>	0.24
	B <sub>1</sub> B <sub>3</sub>	0.58
	B <sub>3</sub> B <sub>4</sub>	0.48
	B <sub>1</sub> H <sub>2</sub>	1.00
	B <sub>1</sub> H <sub>11</sub>	0.04
	B <sub>3</sub> H <sub>7</sub>	0.99
	B <sub>3</sub> B <sub>5</sub>	0.05
	B <sub>3</sub> H <sub>11</sub>	0.44
	B <sub>1</sub> B <sub>3</sub> B <sub>4</sub>	0.15
	B <sub>3</sub> B <sub>4</sub> H <sub>11</sub>	0.30

BBB and four BHB three-centre bonds (Scheme I). As it can be seen from Table III, this is exactly the picture suggested by the values of populations.

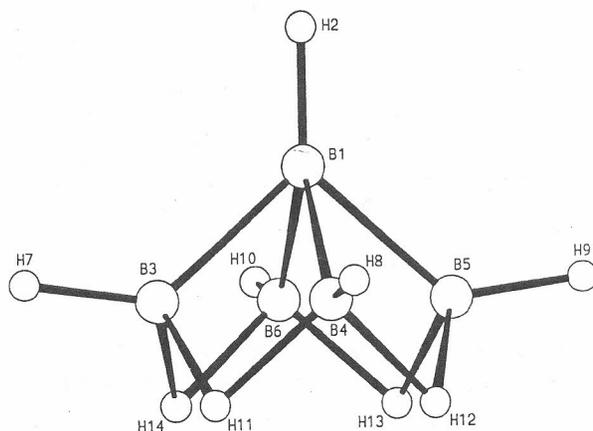
Practically the same close correspondence between the expectations of Lipscomb rules and the values of populations is also observed for B<sub>5</sub>H<sub>9</sub>. Its structure can be described by a schematic structural formula (Scheme II)



Scheme I

and, as it can be seen from Table IV, this formula with its presence of four BBB three-centre bonds and four BHB three-centre bonds closely corresponds to the predictions of the Lipscomb rules as well as the more recent studies of orbital localization.

Summarizing the above results, it is perhaps possible to conclude that the multicentre bond indices represent new, remarkably sensitive, means of detection of multicentre bonding and we believe that their future systematic use may considerably help in the understanding of bonding in molecules like boranes, transition metal complexes *etc.*, for which the presence of three- or multicentre bonding is generally required.



Scheme II

## BIBLIOGRAPHY

1. P. C. Hiberty and C. Leforestier, *J. Am. Chem. Soc.* **100** (1978) 2012.
2. P. C. Hiberty and G. Ohanessian, *Int. J. Quant. Chem.* **27** (1985) 245,259.
3. A. Julg and P. Julg, *Int. J. Quant. Chem.* **13** (1978) 483.
4. P. Karafiloglou, *Chem. Phys.* **140** (1990) 373.
5. P. Karafiloglou and G. Ohanessian, *J. Chem. Educ.* **68** (1991) 583.
6. R. F. W. Bader, *Chem. Rev.* **91** (1991) 893.
7. R. McWeeny, *Proc. Roy. Soc.* **A233** (1954) 63.
8. R. S. Mulliken, *J. Chem. Phys.* **23** (1955) 1833.
9. K. Ruedenberg, *Rev. Mod. Phys.* **34** (1962) 326.
10. K. R. Roby, *Mol. Phys.* **27** (1974) 81.
11. R. Ahlrichs and C. Erhardt, *Theor. Chim. Acta* **68** (1985) 231.
12. C. Trindle, *J. Am. Chem. Soc.* **91** (1969) 219.
13. K. B. Wiberg, *Tetrahedron* **24** (1968) 1083.
14. R. Bochicchio, *Theochem* **228** (1991) 209.
15. R. Parrondo, P. Karafiloglou, and E. S. Marcos, *Int. J. Quant. Chem.* **52** (1994) 1127.
16. M. S. Gopinathan and K. Jug, *Theor. Chim. Acta* **63** (1983) 497.
17. K. Jug, *J. Comput. Chem.* **5** (1984) 555.
18. I. Mayer, *Chem. Phys. Lett.* **97** (1983) 270.
19. I. Mayer, *Int. J. Quant. Chem.* **29** (1986) 73.
20. J. Cioslowski and S. T. Mixon, *J. Am. Chem. Soc.* **113** (1991) 4142.
21. R. Ponec and M. Strnad, *Int. J. Quant. Chem.* **50** (1994) 43.
22. D. L. Cooper, R. Ponec, T. Thorsteinsson, and G. Raos, *Int. J. Quant. Chem.* in press.
23. M. Giambiagi, M. S. Giambiagi, and K. C. Mundim, *Struct. Chem.* **1** (1990) 123.
24. A. B. Sannigrahi and T. K. Kar, *Chem. Phys. Lett.* **173** (1990) 569.
25. R. Ponec and R. Bochicchio, *Int. J. Quant. Chem.* **54**, **99** (1995).
26. R. Ponec and K. Jug, *Int. J. Quant. Chem.* submitted.
27. K. C. Mundim, M. Giambiagi, and M. S. Giambiagi, *J. Phys. Chem* **98** (1994) 6118.
28. J. Cioslowski and P. Surjan, *Theochem* **255** (1992) 9.
29. J. J. P. Stewart, MOPAC, QCPE 455, Indiana University, Bloomington IN 1983.
30. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Reploge, R. Gomperts, J. L. Anders, K. Ragvachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox., D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, GAUSSIAN-92 Revision C, Gaussian Inc. Pittsburgh PA 1992.
31. K. Wade, *Electron Deficient Compounds, Studies in Modern Chemistry*, T. Nelson and Sons Ltd. 1971.
32. J. Cioslowski and M. L. McKee, *J. Phys. Chem.* **96** (1992) 9264.
33. M. Sironi, M. Raimondi, D. L. Cooper, and J. Gerratt, *J. Phys. Chem.* **95** (1991) 10617.
34. W. N. Lipscomb in *Boron Hydride Chemistry*, E. L. Muetterties (Ed.), Academic Press, New York 1975.
35. R. E. Dickenson and W. N. Lipscomb, *J. Chem. Phys* **27** (1957) 212.

**SAŽETAK****Indeksi za višecentrične veze dobiveni na osnovi poopćene populacijske analize gustoća višega reda***Robert Ponec i Filip Uhlík*

Na osnovi poopćene populacijske analize prikladnih funkcionala definiranih na gustoćama viših redova, uvedeni su indeksi za višecentrične veze i to na razini SCF-računa ili višoj. Ti su indeksi upotrebljeni za vizualizaciju kemijske veze u nekim jednostavnim molekulama sa ili bez trocentričnih veza. Prikladnost ovih indeksa za uočavanje i lokaliziranje trocentričnih veza je provjerena na nizu jednostavnih borana ( $B_2H_6$ ,  $B_4H_{10}$ ,  $B_5H_9$ ). Uveden je pristup oopćenit i može se primijeniti za vizualizaciju kemijske veze i u drugim molekulama s kompleksnim tipovima kemijske veze.