

Graphical linking of a MO multicenter bond index to VB structures

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The multicenter bond index proposed within the MO framework depends on the order of the centers for which it is calculated, outside from the 3-c case. For the 6-c case, the eventually different values are 60. A graphical approach links the MO values to VB structures. Benzene, chosen as our paradigm for the 6-c case, illustrates our proposition.

KEY WORDS: multicenter bond index, VB structures, benzene

1. Introduction

Some years ago, we proposed the definition of a multicenter bond index I within the framework of molecular orbital (MO) theory [1]. In the 3-c (three-center) case, this index proved to be particularly suitable for describing different systems [1–3]; 3-c populations have also been remarked and treated within the generalized population analysis framework [4,5]. Thus, for example, I_{ABC} makes apparent the distinction between strong and normal H-bonds, in excellent agreement with H-bond energies obtained from *ab initio* calculations with very extended basis [1]. It predicts that the peptide bond should be of the same order of magnitude as strong H-bonds [1]. I_{ABC} substantiates the importance of secondary bonds in systems containing groups such as CO₂, NO₂ [2] or SC₂ [3]. The 3-c populations have enlightened the bonding in boranes [4,5]. The value for 3-c indices I_{ABC} is independent of the ABC order.

The results for higher order multicenter indices [2] prompted us to propose it as a measure of aromaticity, with promising results [6].

Sannigrahi [7] called our attention to the fact that the multicenter bond index depends on the AB . . . L order. While in the 3-c case it is actually unequivocal, for higher order different values arise. This problem is the subject of the present study.

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The different possible indices for the 4-c case appear in the definition of correlation coefficients between bonds, used to discuss the reactivity of molecular systems in multibond exchange reactions [8]. Nonlinear population analysis using the geminal expansion of pair densities has been used to detect multicenter bonding; the tetraatomic contributions involve all possible ABCD terms [9].

On using I as a measure of aromaticity, we always followed the obvious sense of the rings [6]. Now, if a different path is taken different values may arise and pose the question of their meaning. We show here that the different values for the MO multicenter index may be graphically linked to VBS in a quite appealing way. The relation between the MO and VB viewpoints is an old problem which is being revisited now and then [10]; it certainly deserves a fresh look.

2. MO multicenter bond index

The first-order density matrix for closed-shell systems, allowing to be described through a single-determinant wavefunction, is a mixed tensor [1]:

$$\Pi_a^b = \sum_i x_{ia} x^{ib}, \quad N = 2 \text{Tr}(\Pi), \quad (1)$$

where x_{ia} (x^{ib}) are covariant (contravariant) coefficients of the i th occupied MO and N is the number of electrons in the molecule. Equation (1) is valid for any orthogonal or non-orthogonal atomic basis. The idempotency of the Π matrix has led us to the definition of an index I_{AB} for the bond between atoms A and B [11,12]

$$I_{AB} = 4 \sum_{a \in A, b \in B} \Pi_a^b \Pi_b^a, \quad (2)$$

which is the generalization of the Wiberg index [13] to non-orthogonal basis.

Similarly, as the idempotency of Π holds for any power, a multicenter bond index may be defined as [1]

$$I_{ABC\dots L} = 2^L \sum_{a \in A, b \in B, \dots, l \in L} \Pi_a^b \Pi_b^c \dots \Pi_l^a. \quad (3)$$

As the Π matrix may be divided in sub-matrices of the type Π_{AB} for pairs of atoms, $I_{ABC\dots L}$ in equation (3) may be also written in the form

$$I_{ABC\dots L} = 2^L \text{Tr}(\Pi_{AB} \Pi_{BC} \dots \Pi_{LA}). \quad (4)$$

When there is σ - π separation, each Π_{AB} being block-diagonal in σ and π , the product is also block-diagonal. Hence,

$$I = I^\sigma + I^\pi. \quad (5)$$

Let us represent an L -center bond drawing the L centers on a circle. (Does this recall Rumer diagrams [14]? Yes, of course.) If a bond is represented by an arrow and

a matrix, the inverted arrow is the transposed matrix. An L -center index is a number $I_{12\dots L}$ which corresponds to a closed broken line joining the points $1, 2, \dots, L, 1$. As the index may be calculated through the trace of a matrix product (equation (4)), any cyclic permutation yields the same value. As, moreover, a matrix and its transposed have the same trace, any inversion from cyclic to anticyclic order shall also yield the same value. In the drawing, this corresponds to following the broken line starting from any of the L points, in cyclic or anticyclic order. Thus, it is not necessary to calculate the $L!$ permutations but only $L!/(2L) = (L - 1)!/2$. From what precedes, for $L = 3$ there is an unique value. See appendix for $L = 4$.

We shall now analyse the case $L = 6$, using benzene as our paradigm.

3. Benzene

3.1. The graphical approach

Elsewhere, we have calculated the 6-c bond index following the cyclic order using different semiempirical approximations, both with orthogonal and non-orthogonal bases; the MOPAC-PM3 value is 0.08831 and the CNDO and IEHT ones are 0.08876 and 0.08941, respectively [2]. Such a striking agreement must be due to the peculiarity of the benzene molecule. We report here the MOPAC-PM3 [15] values. As we have mentioned in the previous section, the possible permutations are $6!$, i.e., 720, the eventually different values being actually $6!/12 = 60$. Due to the high symmetry of benzene, the values obtained are the following ones, with an ABCDEF order between parentheses:

- (1) 0.08831 (123456),
 - (2) 0.02197 (123654),
 - (3) groups of $|I_{\text{ring}}|$ values $\sim 10^{-5}$ or less (123564),
 - (4) -0.01111 (145236).
- (6)

Although the above values refer to all-valence-electron calculations, let us try to “translate” the ABCDEF order of a given permutation into a VB symbolism, namely a classical π VB approach [16,17]. Thus, the first value must correspond to a Kekulé (K) structure (figure 1(a), the notation is self-explanatory). Similarly, the second value depicts Dewar (D) structures, while the fourth may correspond, as we shall see, to K-type or C-type structures. As to group (3) values, they may refer either to K, C, L or M [17]. As in the usual convention, in figure 1 and the following ones, the tail of an arrow denotes α spin and its head β spin (or vice versa).

Of course, K and D represent Rumer diagrams for 6 electrons and $S = 0$ [14]. It is known that diagrams with crossed arrows may be decomposed into sums of diagrams with uncrossed arrows and that the canonical structures can be only K and D. However, if we include the noncanonical ones C, L and M, as it has been claimed by Wheland [17], this enables us to link the different I_{ring} values in a very attractive way.

In figure 2, we have associated the 60 *a priori* different possible values with 60 graphical configurations obtained through the broken line mentioned in the previous

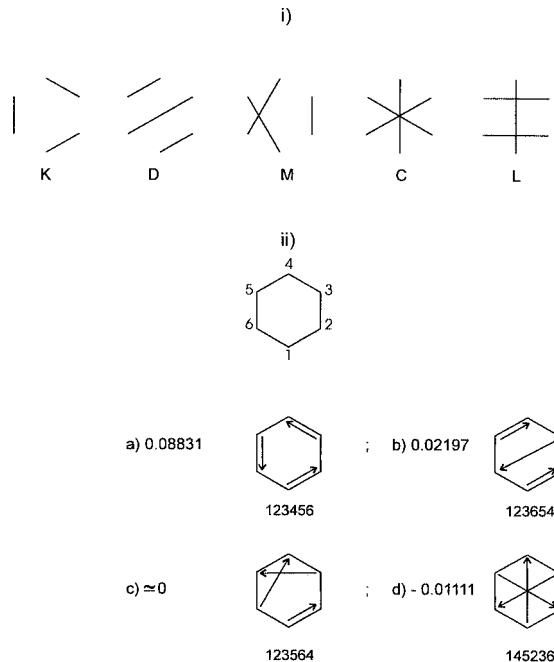


Figure 1. (i) Canonical and noncanonical structures for benzene. K stands for Kekulé; D, Dewar; M, modified; C, Claus; L, Ladenburg. (ii) Examples of VB structures for I_{ring} .

section. The corresponding VB structures are also drawn. We order the configurations according to the number of first-neighbour linked atoms (o , or *ortho*), second-neighbours (m or *meta*) and third-neighbours (p , or *para*). That is, the first configuration has only first-neighbouring atoms and so on. In figure 1 we have reported different examples; figure 2 reports all the 60 possibilities starting by the atom labelled with number 1, all the atoms in the ring being equivalent.

The ABCDEF order has been given according to the following convention. The polygon starts from 1; atom 1 is linked to two other atoms in the polygon, the second atom is the one having the lowest label in counterclockwise direction. A cyclic permutation, say FABCDE, leads to another VBS, both being complementary; in the sense that the polygon is obtained by superposition of two VBS, as explained further on and may be seen in figure 3. It may happen that a certain VBS appears twice in the 60 configurations; this would mean that it contributes to the I value in both cases.

Configuration No. 1 is unique, involving only $6o$. From 2 to 7 we have a family ($4o + 2m$) and from 8 to 10 the family ($4o + 2p$). From 11 to 28, we have the largest family, with 18 members ($3o + 2m + 1p$). Actually two “sub-families” arise here, one from 11 to 22 and another one from 23 to 28. The difference between them consists in that the first one involves one atom which is not bonded to any other in o position; hence, two different values could arise. Configurations 29 and 30 belong to the family ($3o + 3p$). Then come the ($2o + 4m$) configurations 31–39, which in turn may be

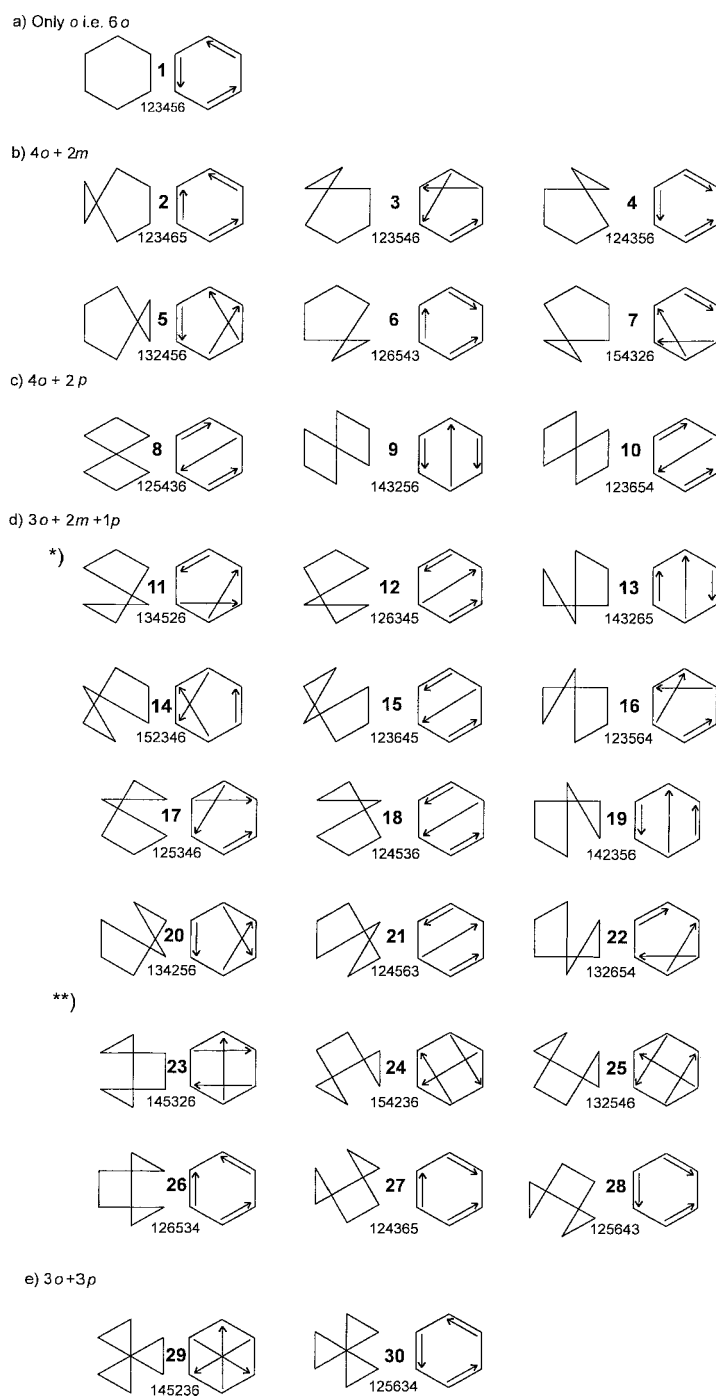
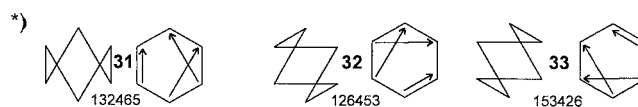


Figure 2. Geometrical configurations and Rumer-type structures; o means *ortho*, m *meta* and p *para* types of neighbours. The first position is always 1.

f) $2o + 4m$ 

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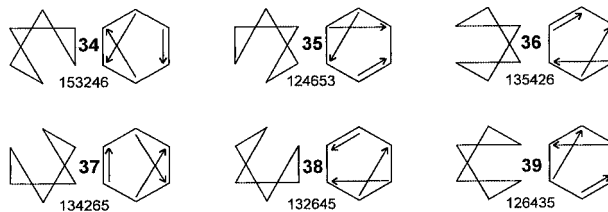
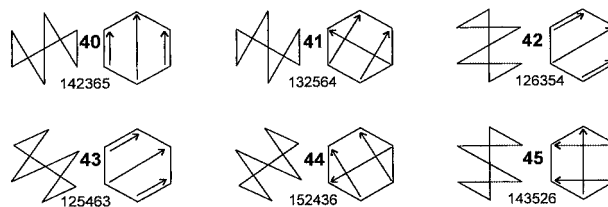
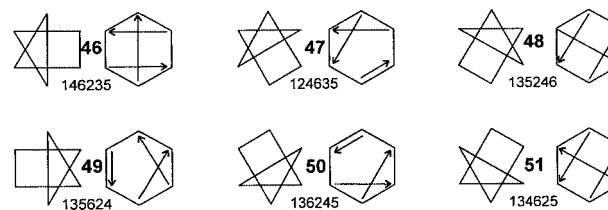
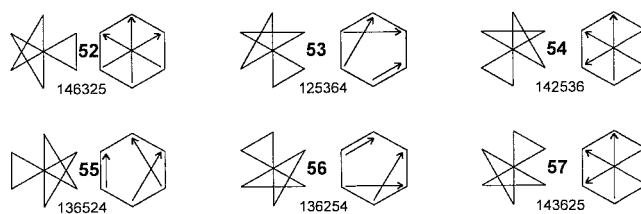
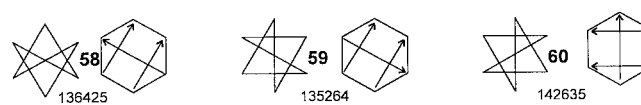
g) $2o + 2m + 2p$ h) $1o + 4m + 1p$ i) $1o + 2m + 3p$ j) $4m + 2p$ 

Figure 2. (Continued.)

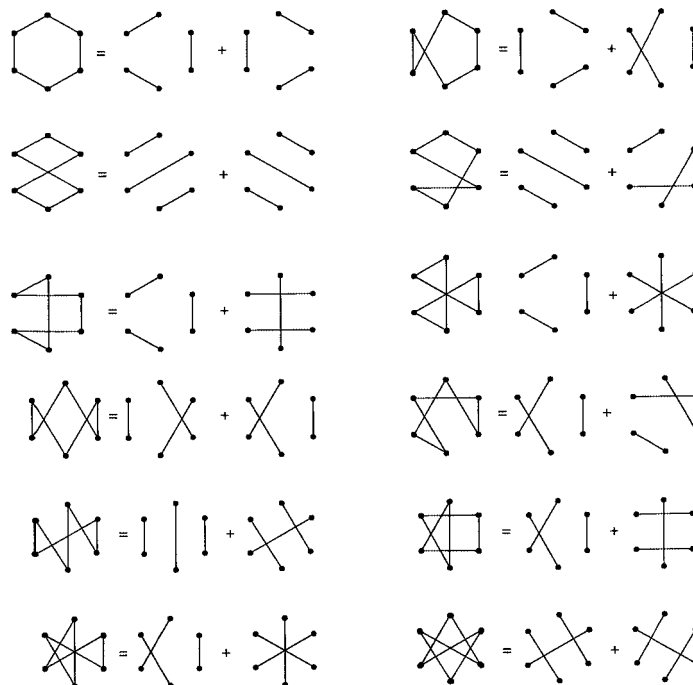


Figure 3. The superposition of two basic structures of figure 1 yields the twelve polygons in figure 2.

divided into the groups 31–33, where the bonds between first neighbours are mutually parallel, and 34–39, where they are oblique; similarly, two values could be found. The $(2o + 2m + 2p)$ configurations 40–45 come next, then the $(1o + 4m + 1p)$ family 46–51. From 52 to 57 the configurations are $(1o + 2m + 3p)$ and finally the family 58–60 $(4m + 2p)$.

We have drawn in figure 1 our five basic structures. We are aware that all of them are not independent from one another; nevertheless Wheland [17] states that he had to take them explicitly into account in the treatment of benzene. We use, hence, both the canonical and noncanonical structures of figure 1. On the other hand, K, D and C allow spin alternation $(\alpha\beta\alpha\beta)$, while L and M do not, showing only spin structures of the type $(\alpha\alpha\beta\beta)$.

Each of the 60 configurations of figure 2 may be drawn as a superposition of two basic structures of figure 1. Let us take as an example configuration 30 of figure 2, from family (e), i.e., (125634). According to the adopted convention, this is read as 12.56.34, a K structure. Nevertheless, the permutation chosen is equivalent to (256341); this yields in turn 25.63.41, which is a C structure. Actually, the complete description is given by joining both as 12.25.56.63.34.41, which is K + C. Any one of the 60 diagrams may be seen in this fashion. Thus, the twelve different polygons of figure 2, corresponding to the twelve types of configurations, may be built from two of the basic structures as it is shown in figure 3 (see table 1).

Table 1
The twelve I_{ring} values for the configurations represented in figure 2.
The superposition of basic structures is shown in figure 3.

Type	Configurations	Superposition	I_{ring}
a	1	K + K	0.08831
b	2–7	K + M	1.3×10^{-5}
c	8–10	D + D	0.02197
d*	11–22	D + M	1.4×10^{-6}
d**	23–28	K + L	-1.2×10^{-5}
e	29–30	K + C	-0.01111
f*	31–33	M + M	3.6×10^{-7}
f**	34–39	M + M	1.3×10^{-7}
g	40–45	D + L	-2.9×10^{-7}
h	46–51	M + L	-1.1×10^{-8}
i	52–57	M + C	-3.7×10^{-8}
j	58–60	L + L	7×10^{-10}

Returning to figure 2 and looking at the VB superposition in the twelve cases, it is seen that the diagrams corresponding to (a) 1 (K, K); (c) 8–10 (D, D) and (e) 29–30 (K, C) show spin alternation, while the others do not; K, D and C in these ones correspond to different branching diagrams [14].

The I_{ring} values for (a) and (c) are the highest ones; accordingly, the corresponding VB structures (K and D, respectively) are those contributing most heavily to the benzene ground state wavefunction [16]. The value for configurations 29–30 is the lowest in the series and the third one in absolute value.

In short, we have found for benzene the four values (6). Actually, in the third group small values appear which amount to the nine eventually different values expected. We have reproduced all of them in table 1, together with the corresponding configurations of figures 2 and 3. Although decidedly unrealistic, it is possible to discriminate between two (and only two) different numbers $\sim 10^{-5}$, one (and only one) $\sim 10^{-6}$, three (and only three) $\sim 10^{-7}$, two (and only two) $\sim 10^{-8}$ and a last one (only one) $\sim 10^{-10}$. We wish to record them because we shall show elsewhere that, for 6-c rings with lower symmetry than that of benzene, these groups of solutions split into more different values.

3.2. About π bond orders

As it is well known, this is the only molecule for which the high symmetry (D_{6h}) determines the π MOs, aside from normalization, i.e., whether or not overlap is introduced. If Ψ denotes MOs and φ atomic orbitals, we may write (see, e.g., [18]):

$$\begin{aligned}
 \Psi_1 &= 6^{-1/2}(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4 + \varphi_5 + \varphi_6), \\
 \Psi_2 &= 12^{-1/2}(2\varphi_1 + \varphi_2 - \varphi_3 - 2\varphi_4 - \varphi_5 + \varphi_6), \\
 \Psi_3 &= \frac{1}{2}(\varphi_2 + \varphi_3 - \varphi_5 - \varphi_6),
 \end{aligned}
 \tag{7a}$$

$$\begin{aligned}
\Psi_4 &= 12^{-1/2}(2\varphi_1 - \varphi_2 - \varphi_3 + 2\varphi_4 - \varphi_5 - \varphi_6), \\
\Psi_5 &= \frac{1}{2}(\varphi_2 - \varphi_3 + \varphi_5 - \varphi_6), \\
\Psi_6 &= 6^{-1/2}(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4 + \varphi_5 - \varphi_6).
\end{aligned}
\tag{7b}$$

For the ground state, the Coulson bond orders are $2/3$ for neighbouring atoms, 0 (zero) for two atoms in *meta* position and $-1/3$ for two atoms in *para* position, respectively.

Now, let us suppose that we could calculate equation (3) as a product of Coulson bond orders P_{AB} , being

$$P_{AB} = 2 \sum_i c_{iA} c_{iB}, \tag{8}$$

where c_{iA} are the coefficients appearing in equations (7).

In the case of benzene, where σ - π separation may be safely assumed, we have mentioned that, as each Π_{AB} in equation (4) is block-diagonal in σ and π , the product is also block-diagonal.

Let us calculate the π part of I_{ring} . For example, the structure in figure 1(a) would have

$$I_{123456}^{\pi} = P_{12} P_{23} P_{34} P_{45} P_{56} P_{61} = \left(\frac{2}{3}\right)^6 = 0.087791.$$

Similarly, for the structure in figure 1(b):

$$I_{123654}^{\pi} = P_{12} P_{23} P_{36} P_{65} P_{54} P_{41} = \left(\frac{2}{3}\right)^4 \left(-\frac{1}{3}\right)^2 = 0.021947.$$

As to figure 1(d), we have

$$I_{145236}^{\pi} = P_{14} P_{45} P_{52} P_{23} P_{36} P_{61} = \left(\frac{2}{3}\right)^3 \left(-\frac{1}{3}\right)^3 = -0.010974.$$

As the P_{AC} 's (Coulson bond orders for two atoms in *meta* position) are identically zero, any structure involving one of them leads to a zero value of I_{ring}^{π} , so that, e.g., $I_{123564}^{\pi} = 0$. The σ values for I between two atoms in *meta* position are not zero, but very low anyway.

Now, if we compare the previous π values with those in (6), taking into account equation (5), we are led to the conclusion that, in benzene, the ring index is mainly due to π delocalization. As I_{ring} involves also the σ skeleton, this is unexpected. The σ contribution is small but not negligible and it is seen at once that it is positive for the structures of the type 1(a), while negative for those of 1(d).

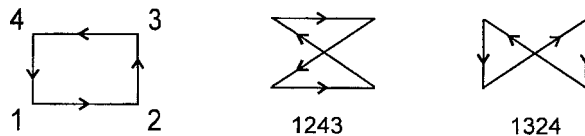


Figure 4. The different configurations for a 4-center ring.

4. Conclusions

- The different possible values for an MO multicenter bond index are studied through the I_{ring} benzene case, taken as a paradigm.
- Graphically, it is possible to “translate” the MO values for I_{ring} into classical VB structures.
- *A priori*, twelve different values are possible; only three of them being numerically significant.
- The highest value and the next one correspond to Kekulé and Dewar structures, respectively.
- In benzene I_{ring} turns to be mainly π in nature.

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Appendix

For $L = 4$, the possible values are three if the atoms of the cycle are of the same nature, as in cyclobutadiene. They are represented in figure 4; for a rectangular cyclobutadiene, as the most stable form is, the second and third configurations are not identical.

References

- [1] M. Giambiagi, M.S. de Giambiagi and K.C. Mundim, Definition of a multicenter bond index, *Struct. Chem.* 1 (1990) 423–427.
- [2] M.S. de Giambiagi, M. Giambiagi and M.S. Fortes, Multicenter bonds, bond valence and charge apportion, *J. Mol. Struct. (Theochem)* 391 (1997) 141–150.
- [3] A.B. Sannigrahi and T. Kar, Three-center bond index, *Chem. Phys. Lett.* 173 (1990) 569–572.
- [4] R. Ponec and F. Uhlik, Multicenter bond indices from the generalized population analysis of higher order densities, *Croat. Chim. Acta* 69 (1996) 941–954.
- [5] R.C. Boichichio, R. Ponec and F. Uhlik, *Ab initio* SCF nonlinear population analysis. A new means of detection and localization of multicenter bonding, *Inorg. Chem.* 36 (1997) 5363–5368.
- [6] M. Giambiagi, M.S. de Giambiagi, C.D. dos Santos Silva and A. Paiva de Figueiredo, Multicenter bond indices as a measure of aromaticity, *Phys. Chem. Chem. Phys.* 2 (2000) 3381–3392.
- [7] A.B. Sannigrahi, private communication.

- [8] T. Yamasaki and W.A. Goddard III, Correlation analysis of chemical bonds, *J. Phys. Chem. A* 102 (1998) 2919–2933.
- [9] R. Ponc and R.C. Bochicchio, Nonlinear population analysis from geminal expansion of pair densities, *Int. J. Quant. Chem.* 54 (1995) 99–105.
- [10] P.C. Hiberty, Thinking and computing valence bond in organic chemistry, *J. Mol. Structure (Theochem)* 451 (1998) 237–261.
- [11] M. Giambiagi, M.S. de Giambiagi, D.R. Grepel and C.D. Heymann, Sur la définition d'un indice de liaison (TEV) pour des bases non orthogonales. Propriétés et applications, *J. Chim. Phys.* 72 (1975) 15–22.
- [12] M.S. de Giambiagi, M. Giambiagi and F.E. Jorge, Some considerations about indices in non-orthogonal bases and the MO calculation of valence and oxidation number, *Z. Naturforsch.* 39a (1984) 1259–1273.
- [13] K. Wiberg, Application of the Pople–Santry–Segal CNDO method to the cyclopropylcarbinyl and cyclobutyl cation and to cyclobutane, *Tetrahedron* 24 (1968) 1083–1096.
- [14] R. Pauncz, *Spin Eigenfunctions* (Plenum, New York, 1979) chapter 5.
- [15] J.J.P. Stewart, MOPAC, a semiempirical molecular orbital program, *J. Comp.-Aided Mol. Design* 4 (special issue) (1990) 1–105.
- [16] G.W. Wheland, *Resonance in Organic Chemistry* (Wiley, New York, 1955) chapter 9.
- [17] G.H. Wheland, Modified valence-bond treatment of unsaturated and aromatic compounds, *J. Chem. Phys.* 23 (1955) 79–83.
- [18] I.N. Levine, *Quantum Chemistry* (Prentice Hall, 1991) chapter 16.