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

Short title: Multicenter bond

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 3c (three-center) case, this index proved to be particularly suitable for describing hydrogen bonds, making apparent the distinction between strong and normal H-bonds. The value for 3c-indices I_{ABC} is independent from the ABC order.

The results for higher order multicenter indices [2] prompted us to propose it as a measure of aromaticity, with promising results [3].

Sannigrahi [4] called our attention to the fact that the multicenter bond index depends on the ABC $\cdots$ order. While in the 3c- case it is actually unequivocal, for higher order different values arise. This problem is the subject of the present study. We show here that the different values for the MO multicenter index may be graphically linked to VB (valence bond) structures in a quite appealing way.

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]:

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

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. Eq. (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 [5]

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

which is the generalization of the Wiberg index [6] to non- orthogonal basis.

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

$$I_{ABC \cdots L} = 2^L \sum_{a \in A, b \in B, \cdots, \ell \in L} \Pi_a^b \Pi_b^c \cdots \Pi_\ell^a \qquad (3)$$

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

$$I_{ABC \cdots L} = 2^L Tr\left(\Pi_{AB} \Pi_{BC} \cdots \Pi_{LA}\right) \qquad (4)$$

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

$$I = I^{\sigma} + I^{\pi} \qquad (5)$$

Let us represent an L-center bond drawing the L centers on a circle (Does this recall Rumer diagrams? [7]; 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 $I_{12\cdots L}$ which corresponds to a closed broken line joining the points $1, 2, \cdots, L, 1$. As the index may be calculated through the trace of a matrix product (Eq. (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 [2]. The MOPAC-PM3 value [8] is 0.08831 and the CNDO and IEHT ones 0.08876 and 0.08941 respectively. Such a striking agreement must be due to the peculiarity of the benzene molecule. We report here the MOPAC-PM3 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 $|I_{ring}|$ values $\sim 10^{-5}$ or less (124356)
(4) -0.01111 (125634)

$$(6)$$

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 [9-10]. Thus, the first value must correspond to a Kekulé (K) structure (Fig. 1 a, the notation is self-explanatory). Similarly, the second value depicts Dewar (D) structures, while the fourth may correspond to K-type or C-type structures. As to group (3) values, they may refer either to K, C, L or M [10]. As in the usual convention,

in Fig. 1 and the following ones, the head of an arrow denotes α spin and its tail β spin (or vice versa).

Of course, K and D represent Rumer diagrams for 6 electrons and $S = 0$ [7]. 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 [10], this enables us to link the different I_{ring} values in a very attractive way.

In Fig. 2, we have associated the 60 *a priori* different possible values with 60 graphical configurations obtained through the broken line mentioned in the previous section. The VB corresponding 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 Fig. 1 we have reported different examples; Fig. 2 reports all the 60 possibilities starting by the atom labelled with number 1, all the atoms in the ring being equivalent.

Configuration No. 1 is unique, involving only 6 *o*. 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 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 Fig. 1 our five basic structures. We are aware that all of them are not independent from one another; nevertheless Wheland [10] states that he had to take them explicitly into account in the treatment of benzene. We use, hence, both the canonical and non-canonical structures of Fig. 1. On the other hand, K, D and C allow spin alternation $(\alpha\beta\alpha\beta\alpha\beta)$, while L and M do not, showing only spin structures of the type $(\alpha\alpha\beta\beta\alpha\beta)$.

Each of the 60 configurations of Fig. 2 may be drawn as a superposition of two basic structures of Fig. 1. Let us take as an example configuration 2 of Fig.2, from family b), i.e. (123465). As we have drawn, this may be read as 12.34.65, a K structure. Nevertheless, the permutation chosen is equivalent to (234651); this yields in turn 23.46.51, which is an M structure. Actually, the complete description is given by joining both

as 12.23.34.46.65.51, which is $K + M$. Any one of the 60 diagrams may be seen in this fashion. Thus, the twelve different polygons of Fig. 2, corresponding to the twelve types of configurations, may be built from two of the basic structures as it is shown in Fig. 3 (see Table 1).

Returning to Fig. 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 f) 29-30 $(K + C)$ show spin alternation, while the others do not.

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 [9]. The value for configurations 29-30 is the lowest in the series and the third one in absolute value. The other configurations correspond to diagram superpositions without spin alternation.

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 Figs. 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 MO's, aside from normalization, i.e. whether or not overlap is introduced. If Ψ denotes MO's and φ atomic orbitals, we may write [11]

$$
\begin{aligned}
\Psi_1 &= 6^{-1/2}\left(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4 + \varphi_5 + \varphi_6\right) \\
\Psi_2 &= 12^{-1/2}\left(2\varphi_1 + \varphi_2 - \varphi_3 - 2\varphi_4 - \varphi_5 + \varphi_6\right) \\
\Psi_3 &= (1/2)\left(\varphi_2 + \varphi_3 - \varphi_5 - \varphi_6\right) \\
\psi_4 &= 12^{-1/2}\left(2\varphi_1 - \varphi_2 - \varphi_3 + 2\varphi_4 - \varphi_5 - \varphi_6\right) \quad (7) \\
\Psi_5 &= (1/2)\left(\varphi_- \varphi_3 + \varphi_5 - \varphi_6\right) \\
\Psi_6 &= 6^{-1/2}\left(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4 + \varphi_5 - \varphi_6\right)
\end{aligned}
$$

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 Eq.(3) as a product of Coulson bond orders P_{AB}, being

$$
P_{AB} = 2\sum_i c_{iA} c_{iB} \qquad (8)
$$

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

In the case of benzene, where σ-π separation may be safely assumed, we have mentioned that, as each Π_{AB} in eq.(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 Fig. 1 a) would have

$$
I^\pi_{123456} = P_{12}P_{23}P_{34}P_{45}P_{56}P_{61} = (2/3)^6 = 0.087791
$$

Similarly, for the structure in Fig. 1b):

$$
I^\pi_{165234} = P_{16}P_{65}P_{52}P_{23}P_{34}P_{41} = (2/3)^4(-1/3)^2 = 0.021947
$$

As to Fig. 1d) we have

$$
I^\pi_{145236} = P_{14}P_{45}P_{52}P_{23}P_{36}P_{61} = (2/3)^3(-1/3)^3 = -0.010974
$$

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^π_{ring}, so that e.g. $I^\pi_{123564} = 0$. The σ values for I between two atoms in *meta* position are not zero, but very low any-way.

Now, if we compare the previous π values with those in (6), taking into account Eq. (5), we are led to the conclusion that, in benzene, the ring index is mainly

Figure 1

i)

K   D   M   C   L

ii)
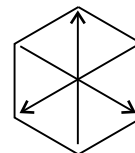

a) 0.08831   ;   b) 0.02197

123456   165234

c) $\simeq 0$;   d) - 0.01111

123564   145236

Figure 1. i) Canonical and non-canonical structures for benzene. K stands for Kekulé; D, Dewar; M. modified; C, Claus; L, Ladenburg. ii) Examples of VB structures for I_{ring}.
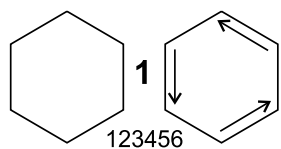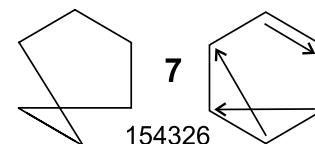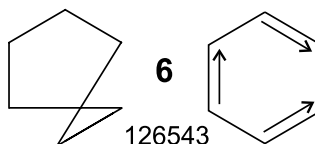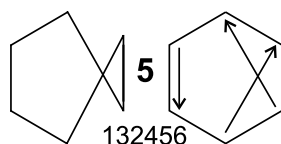
Figure 2

a) Only *o* i.e. 6 *o*

1
123456

b) 4*o* + 2*m*

2
123465

3
123546

4
124356

5
132456

6
126543

7
154326

c) 4*o* + 2 *p*

8
125436

9
143256

10
123654

d) 3*o* + 2*m* +1*p*

*)

11
134526

12
126345

13
143265

14
152346

15
123645

16
123564
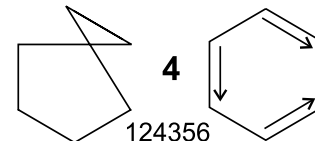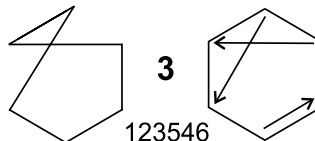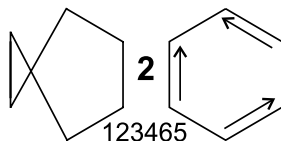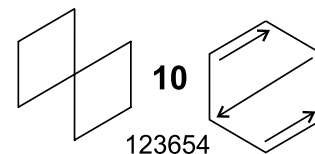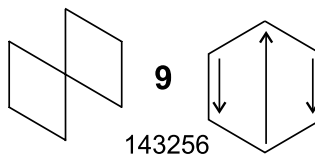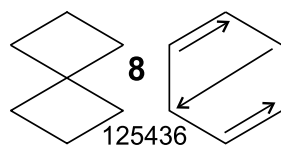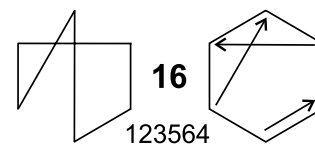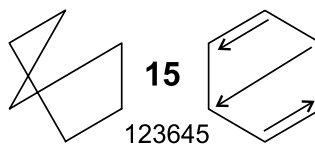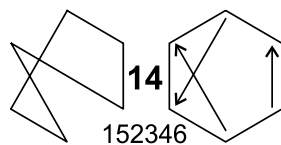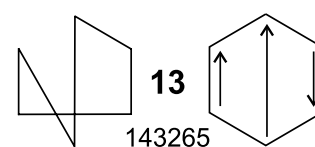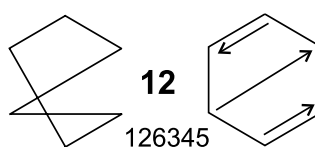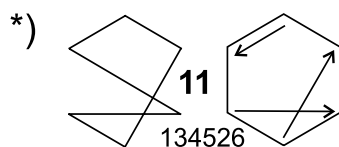
Figure 2. Geometrical configurations and Rumer-type structures; *o* means *ortho*, *m meta* and *p para* types of neighbours. The first position is always 1.

17 125346

18 124536

19 142356

20 134256

**)

21 124563

22 132654

23 145326

24 154236

25 132546

26 126534

27 124365

28 125643

e) $3o+3p$

29 145236

30 125634

f) $2o+4p$

*)

31 132465

32 126453

33 153426

**)

34 153246

35 124653

36 135426

37 134265

38 132645

39 126435

g) $2o + 2m + 2p$

40 142365

41 132564

42 126354

43 125463

44 152436

45 143526

h) $1o + 4m + 1p$

46 146235

47 124635

48 135246

49 135624

50 136245

51 134625

i) $1o + 2m + 3p$

52
146325

53
125364

54
142536

55
136524

56
136254

57
143625

j) $4m + 2p$

58
136425

59
135264
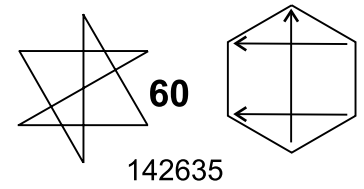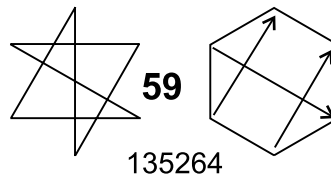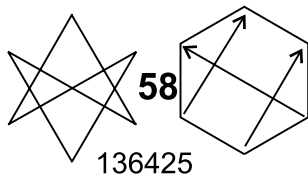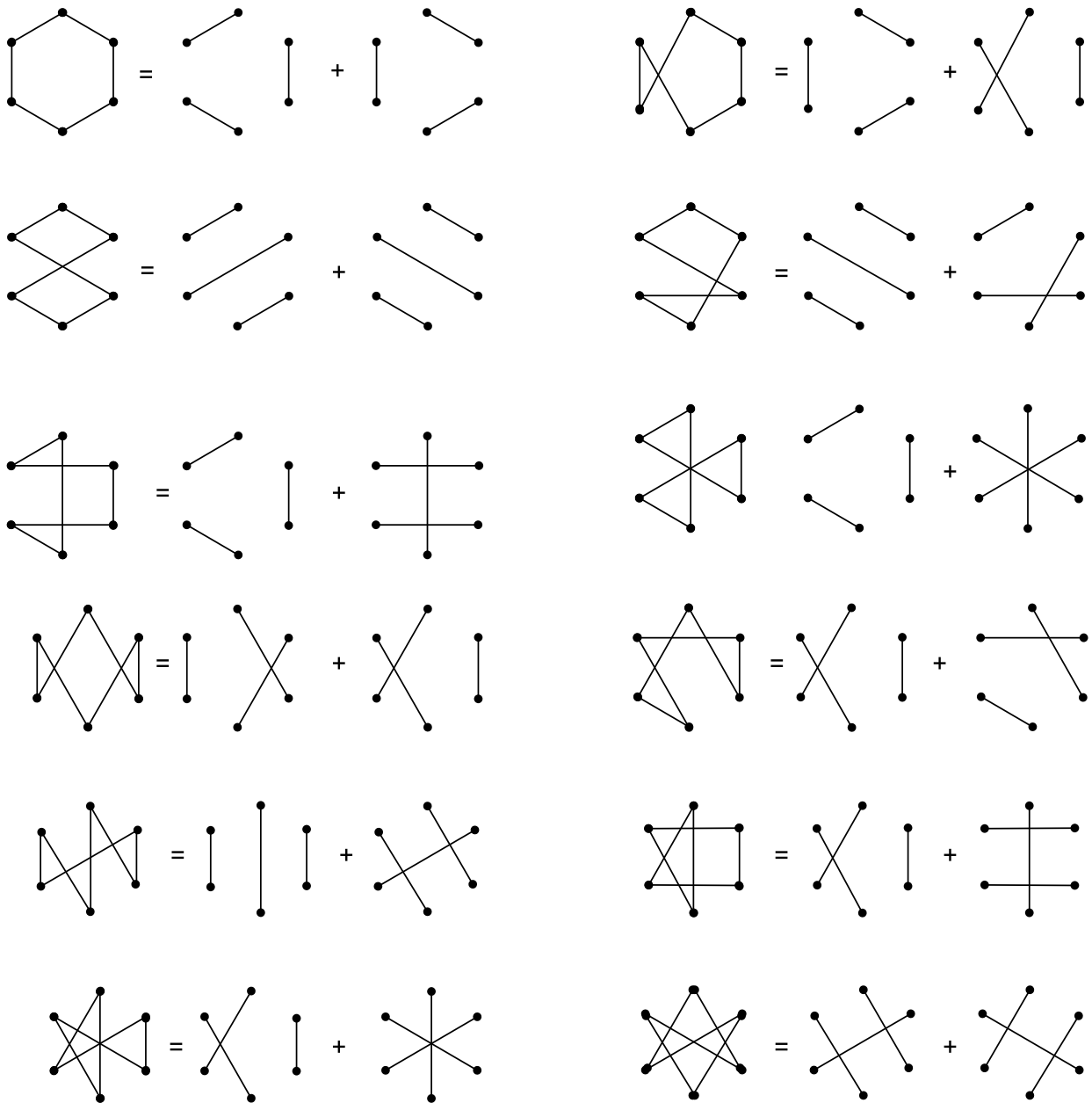

60
142635

Figure 3

Figure 3. The superposition of two basic structures of Fig. 1 yields the twelve polygons in Fig. 2.
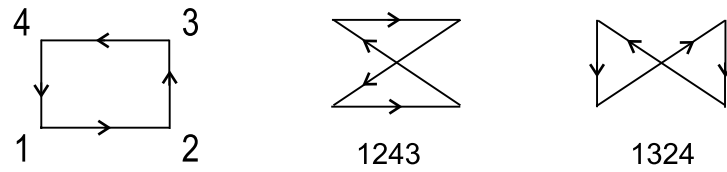
Figure 4

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

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}