The Three-Center, χ-Electron Chemical Bond

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A definition is proposed for the number of electrons χ involved in a three-center bond, based upon the corresponding two-center bond indices. The number of electrons is fractionary, ranging from about 1 to somewhat more than 4 in the systems considered here. It is seen that the sign of the three-center index does not depend on χ.

Key words: Three-center bond; Multicenter bond indices; Active charge.

1. Introduction

The concept of three-center bond is almost contemporary of the Lewis two-center electron pair bond [1]. A distinction is made between two-electron (2e) and four-electron (4e) three-center (3c) bonds. H_3^+ or diborane are taken as paradigms of 3c–2e bonds and $(FHF)^-$ of 3c–4e bonds [1].

We have introduced a three-center bond index [2] in satisfactory agreement with certain experimental data. The values obtained have negative sign. Sannigrahi and Kar [3] affirm that 3c bond indices have no chemical significance unless they are positive. In [4], it is asserted that negative values could be associated to (3c–2e) bonds, while positive values should indicate (3c–4e) bonds. We show elsewhere that the sign has a straightforward meaning [5] and here that in MO theory the number of electrons taking part in such a bond may be seen from a different viewpoint.

The original Coulson bond order [6] has been devised for the π electrons of alternant hydrocarbons; π systems including heteroatoms led to bond orders which are not comparable with C–C bond orders [7]. Almost universal consent assigns for example a bond order of 2 for the C=C bond in ethylene [8]. Very few examples may be found in early literature which throw π population wholly on the bonds [9, 10]. More recently, a theory considering fluctuations in orbital domains [11, 12] describes these domains along a classical bond with population close to 2 with a small fluctuation from this value. The overwhelming majority of population analysis, of which Mulliken's [13] is by far the most popular, assigns a bond value of 1, 2, and 3 for single, double and triple bonds, respectively.

When all-valence-electrons calculations were introduced, Hoffmann's EHT (extended Hückel theory) [14] used Mulliken's population analysis, which has the drawback of becoming zero for orthogonal bases. The other approximation dealing with all-valence-electrons at that time was CNDO (complete neglect of differential overlap) with its alternative INDO (incomplete neglect of differential overlap) and, in particular, the CNDO/2 variation [15]. Mulliken's orbital-orbital population lends itself to be contracted to an atom-atom population; CNDO orbital-orbital population does not. In order to compare EH and CNDO/2 results, Wiberg [16] was obliged to devise a new bond index for CNDO, by the way in a very humble footnote. Trindle [17] proposed for it a subdivision into self-charge and active charge analogous to Mulliken's atomic and overlap populations. MINDO/3 [18] and MNDO [19] came later.

A few years after the work of Wiberg, which did not receive the full deserved attention, we proposed a bond index which generalized Wiberg's when non-orthogonal bases were used. Although we used it in all-valence electrons calculations [7, 20], nothing prevented taking into account the core electrons or enlarging the basis.

Coming back to our three-center index, we are led to seek an answer to the question: how many electrons are there in a three-center bond?

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2. The Three-Center Bond Index

We restrict ourselves to the ground state of closed-shell systems, which can be described through a single-determinant wave function. The first-order density matrix is a mixed tensor [21]

$$2\Pi_a^b = 2\sum_i x_{ia} x^{ib}, \tag{1}$$

where x_{ia} (x^{ib}) are the covariant (contravariant) coefficients of the i-th occupied MO. This tensor is represented by a matrix. We may build an orbital-orbital tensor [21]

$$I_{ba}^{ab} = 4\Pi_a^b \Pi_b^a, \tag{2}$$

which may also be represented by a matrix; this one is symmetric (otherwise, the tensor could not be represented by a matrix), while the matrix in (1) is asymmetric for non-orthogonal bases. In these cases, there exists a convention stating that the covariant index indicates rows and the contravariant index columns of the corresponding matrix. Contracting the tensor in (2) we obtain the bond index I_{AB} for the bond (formal or not) linking atoms A and B [7, 21]

$$I_{AB} = 4\sum_{\substack{a\in A\\ b\in B}} \Pi_a^b \Pi_b^a. \tag{3}$$

This may be related with the correlation between the fluctuations of the charges q_A and q_B from their average values [22, 23]:

$$\langle(\hat{q}_A - \langle\hat{q}_A\rangle)(\hat{q}_B - \langle\hat{q}_B\rangle)\rangle = -I_{AB}/2, \tag{4}$$

$\hat{q}_A$ being the charge operator and [22, 23]

$$\langle\hat{q}_A\rangle = q_A = 2\sum_{a\in A} \Pi_a^a; \quad N = 2\,\mathrm{Tr}\,\Pi. \tag{5}$$

The idempotency of the Π matrix allows us to write [7, 21]

$$N = \left(\frac{1}{2}\right)\sum_{A,B} I_{AB}; \quad q_A = \left(\frac{1}{2}\right)\left(I_{AA} + \sum_{B\neq A} I_{AB}\right). \tag{6}$$

The charge q_A *is* Mulliken's gross population with a quite different partition into self-charge and active charge [17].

Similarly [2]

$$N = \left(\frac{1}{4}\right)\sum_{A,B,C} I_{ABC}; \quad I_{ABC} = 8\sum_{\substack{a\in A\\ b\in B\\ c\in C}} \Pi_a^b \Pi_b^c \Pi_c^a. \tag{7}$$

Sannigrahi and Kar [3] have made an interesting observation, namely that a higher-order bond index cannot generally be determined from a knowledge of lower-order bonds. The summation in (7) includes the possibility of equal subindices (A, B or C); i.e., terms in one, two and three centers appear in N. I_{ABC} is *invariant for any permutation of A, B, C, cyclic [3] or not*. This is easily seen when writing the tensor equivalent to (2):

$$I_{abc}^{bca} = I_{cab}^{abc} = I_{acb}^{bac}. \tag{8}$$

For the contraction to be carried out, the order of the indices is immaterial, as long as it involves a covariant with a contravariant index; however, it cannot involve the covariant and contravariant index of the same Π matrix, for in this case the three-center ABC index splits into one-center and two-center indices.

If we write the expression for I_{ABC} equivalent to (4) for I_{AB}, we obtain [5]

$$\langle(\hat{q}_A - \langle\hat{q}_A\rangle)(\hat{q}_B - \langle\hat{q}_B\rangle)(\hat{q}_C - \langle\hat{q}_C\rangle)\rangle = I_{ABC}/2. \tag{9}$$

I_{AB} uses to be positive (although it is not positive definite in non-orthogonal bases). Thus, (4) means that if q_A fluctuates in one sense from its average value, q_B fluctuates in the opposite sense. As to I_{ABC}, the three fluctuations in (9) are not likely to be all in the same sense; if two are in one sense and one in the opposite sense, either positive or negative values are to be found, *with no evident connection at all with two or four electrons in the three-center bond.*

Recently, covalent bond orders have been proposed [24] within the framework of Bader's topological theory of atoms in molecules [25]; they are compared with Wiberg indices, stating (incorrectly) that both give zero for so-called noninteracting pairs of atoms [24]. On the contrary, Wiberg indices and their generalization emphasize the role of "long bonds" or "secondary bonds" [7, 21, 26, 27]; they are most important in three-center bonds [2, 3, 4, 28, 29]. A sharing index has also been developed [8] and has been compared with covalent bond orders [30], sharing indices being half of covalent bond orders in some cases and quite close in value in most of therm. We think that some of the values reported [8, 24, 30] are too low when compared with those one could expect from chemical intuition. We find, for example, that the indices for LiH should be closer to 1 [29].

Mayer [31] has proposed a model for three-center bonds, where a single atomic orbital is assigned to each of the three centers. This model is used in [4, 32, 33]. Reference [32] deals with I_{ABC} as being a (3c−2e) index for the examples chosen. In [4], Kar states that $q_A + q_B + q_C = 2$ for a (3c−2e) bond. It is curious that neither of them takes into account the partition into active and self-charge.

How many electrons there are in a three-center bond, depends obviously on the model. As the self-charge is confined within the atoms, we would say that in a three-center bond ABC there are χ electrons:

$$\chi = I_{AB} + I_{BC} + I_{AC}. \qquad (10)$$

We shall see in the next section that χ is frequently neither 2 or 4.

3. Results and Discussion

Table 1 shows a trend in I_{HOH} and $I_{\mathrm{HH'}}$ which we have found also in other XH_n-type compounds (NH_3, NH_4^+ and CH_4). Even if the fifth decimal is obviously not significant, we have reported the figures in order to evidence that I_{XH} is maximum and $I_{\mathrm{HH'}} \cong I_{\mathrm{HXH'}} \cong 0$ at the equilibrium position. As a consequence, due to (4), the fluctuations of the q_{H}'s around their average values are either zero or not correlated to each other. We have found this feature only for this type of compounds, being thus, it seems, specific of the HH′ correlation.

Table 1. Bond indices I_{12}, I_{23} and I_{123} as functions of the HOH′ angle for the water molecule, number 1 labelling oxygen.

Angle (°)	I_{12}	I_{23}	I_{123}
70	0.94156	0.03586	0.01078
75	0.95500	0.02386	0.00865
80	0.96461	0.01525	0.00433
85	0.97131	0.00916	0.00256
90	0.97575	0.00498	0.00138
95	0.97842	0.00227	0.00063
100	0.97965	0.00070	0.00020
105	**0.97969**	**0.00005**	**0.00001**
110	0.97869	0.00015	0.00004
115	0.97673	0.00091	0.00027
120	0.97385	0.00228	0.00070
125	0.97006	0.00423	0.00136
130	0.96529	0.00680	0.00227
135	0.95947	0.01002	0.00350
140	0.95255	0.01391	0.00509
145	0.94455	0.01847	0.00710
150	0.93540	0.02376	0.00960

We give in Table 2 the values of χ and I_{ABC} for CO_2 and C_3. We have seen [2, 21] that these molecules have significant secondary bonds. It is quite striking that, although χ is somewhat higher than four in both of them, their three-center bond indices differ in sign.

One of the paradigms of (3c−2e) bonds, H_3^+ [1], has the most peculiar characteristic of being self-consistent "a priori", in the terms of [34]. That is, any quantity calculated is independent from the basis used. Thus, $\chi = 1.333$ and $I_{ABC} = 0.296$. Only for a model where atoms retain no charge and give up all to the bonds, the χ value can be 2.

The other usual model for a (3c−2e) bond is B_2H_6 [1]. Pauling [35] assigns to diborane bond numbers adding to roughly 1.5 for the BHB bond. We have $\chi = 1.540$ (1.683) and I_{BHB} 0.241 (0.276) for IEH (CNDO). In [3] I_{BHB} is 0.234 (STO-3G), 0.215 (4-31G) and 0.238 (6-31G*); from the values of [36] we may get $\chi = 1.370$ (4-31G). It is thus seen that all values of I_{ABC} are in fair agreement, and the available values for χ may be placed in the range 1.4−1.7 (not 2).

We have reported in Table 3 χ and I_{ABC} for a sample of systems. Let us examine, first of all, the paradigm for (3c−4e) bonds, i.e. $(FHF)^-$. Once again, supposing that fluorine furnishes to the system only one electron, this is a (3c−4e) bond if and only if all the charge involved is active charge. Actually, χ for all hydrogen bonds (including other ones not reported here) is approximately 1, but I_{ABC} suffers larger variations. Even if we have found that the I_{ABC} values for the peptide bond NCO are of the same order or magnitude than those of strong hydrogen bonds [2], χ gives around 3 electrons for it.

For nitrous oxide N_2O, the values obtained for χ are consistent with the previously obtained bond indices [21] which, in turn, agree with recent studies discarding the classical hypothesis of a pentavalent

	IEH		CNDO		STO-3G		4-31G[a]	6-31G*[a]
	χ	I_{ABC}	χ	I_{ABC}	χ	I_{ABC}	I_{ABC}	I_{ABC}
CO_2	4.459	−0.546	4.134	−0.352	4.326	−0.444		
C_3	4.474	0.497	4.421	0.456	4.315	0.407	0.359	0.315

Table 2. χ and I_{ABC} for CO_2 and C_3, calculated following different approximations. Geometries as in [2] and [21].

[a] [3].

Table 3. χ and I_{ABC} for a sample of systems, calculated following different approximations. Geometrics as in [2] and [21].

System	ABC	IEH		CNDO		STO-3G		STO-6G	
		χ	I_{ABC}	χ	I_{ABC}	χ	I_{ABC}	χ	I_{ABC}
$(FHF)^-$	FHF	1.210	−0.231	1.065	−0.171	1.201	−0.227	1.194	−0.223
$(HOHOH)^-$	OHO	1.240	−0.248	1.079	−0.175	1.117	−0.191	1.112	−0.189
$(FH)_2$	FHF	1.037	−0.096	0.946	−0.005	0.961	−0.013	0.954	−0.011
$(H_2O)_2$	OHO	1.014	−0.052	0.981	−0.005	0.963	−0.015	0.954	−0.014
Formamide	NCO	3.143	−0.224	3.136	−0.161	3.151	−0.184	3.146	−0.183
Gly.Gly	NCO	3.081	−0.208	3.022	−0.155	3.090	−0.170	3.087	−0.170
O_3	OOO	3.235	−0.278	3.130	−0.286	2.831	−0.346	3.205	−0.326
N_2O	NNO	4.521	−0.532	4.232	−0.344	4.197	−0.455	4.194	−0.454
N_2O_4	ONO	3.382	−0.292	3.319	−0.268	3.524	−0.358	3.523	−0.358

Table 4. χ and I_{ABC} for $(LiH)_2$, ClF_3 and SF_4, calculated following different approximations. The geometry of $(LiH)_2$ is taken from [40], that of ClF_3 from [42] and that of SF_4 from [43].

	IEH		CNDO		STO-3G		6-31G*		STO-3G*		6-31+G*	
	χ	I_{ABC}	χ	I_{ABC}	χ	I_{ABC} [c]	χ	I_{ABC} [c]	χ	I_{ABC} [c]	χ	I_{ABC} [c]
$(LiH)_2/ABC$												
LiHLi	1.292	0.195	1.493	0.245		0.241 [a]	1.23 [b]	0.177 [a]				
ClF_3/ABC												
F_aClF_a	1.408	−0.116	2.153	−0.027	1.406	−0.163	1.254	−0.080	2.145	−0.049	0.9990	−0.068
F_aClF_e	1.453	−0.139	2.256	−0.019	1.465	−0.124	1.457	−0.037	2.201	−0.054	1.340	−0.039
SF_4/ABC												
F_aSF_a	1.467	−0.133	2.236	−0.016	1.422	−0.116	1.371	−0.027	2.227	−0.020	0.870	0.018
F_eSF_e	1.672	−0.044	2.499	−0.023	1.684	−0.049	1.739	−0.026	2.435	−0.040	1.577	−0.034
F_aSF_e	1.580	−0.093	2.373	−0.029	1.561	−0.083	1.553	−0.029	2.348	−0.050	1.195	−0.023

[a] [3], [b] [41], [c] [4].

nitrogen [37]. The long N−N′ bond in N_2O_4 [38] is certainly related to the low value of $I_{NN'O}$, 5 to 6 times less than that of I_{ONO} reported in Table 3. As to χ, it is $\simeq 2$ for (NN′O); accordingly, the "very long bond" NO index is almost zero.

For ozone we find also $\chi \simeq 3$, although the predominant resonance structures would ascribe six electrons to it [39]. One might be tempted to double all χ values, obtaining numbers more in agreement with the Lewis model. This would lead to the definitely unacceptable result of $\chi = 2.666$ for H_3^+.

We have chosen to include $(LiH)_2$ in Table 4, instead of Table 3, because it decidedly has not a hydrogen bond as those of Table 3: it has a positive I_{ABC} value, and χ is significantly higher. The table shows also χ and I_{ABC} for ClF_3 and SF_4, where different three-center associations are possible. The values for χ split into two groups: $\chi > 2$ (CNDO, STO-3G*) and a range 1.2−1.7 (IEH, STO-3G, 6-31G*). The CNDO approximation includes 3d orbitals for the second-row atoms. It is therefore not surprising that CNDO performs almost as STO-3G*; it is however unexpected that the IEH values are so close to the STO-3G ones and not too different from those issuing from a 6-31G* calculation. As to the 6-31+G* approximation, chemical intuition looses a reference frame with the introduction of diffuse functions; the very notion of an atom within a molecule becomes affected.

Inspection of the tables leads to the main conclusion that the I_{ABC}'s order of magnitude and sign are *fairly independent of the bases used in the calculations* and that semiempirical methods are as competitive as "ab initio" ones for this kind of concepts.

In short, the number of electrons in a three-center bond is fractionary and ranges from about 1 to somewhat more than 4.

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