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DEFINITION OF A MULTICENTRAL BOND INDEX

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ABSTRACT

The tensor character of the first-order density matrix leads to the definition of an MO multicentral bond index for closed-shell systems. It is here applied to three-center bonds. Satisfactory results are obtained for compounds involving"secondary" bonds, strong and normal hydrogen bonds; the index for the peptide bond is found to be similar to that of strong hydrogen bonds.

Key-words: Bond index; Multicentral bond index.

1. Introduction

The very notion of chemical bond is a permanent subject of argumentation[1-5]. As soon as one departs from the most classical patterns, the dispute is unavoidable[6]. Multicentral bonds may hence seem more difficult to face. We shall show here a prescription which permits to define an MO multicentral bond index.

The tensor properties of the first-order density matrix have been shown to indicate a route towards the construction of appealing molecular invariants[7]. Among them, the bond index[7,8,9] and its derived quantity valence[6,10,11] are the best known in chemical literature.

The tensor character of certain widespread matrices was first recognized in the Chirgwin and Coulson classical pioneer work[12]. The variance of the tensor indices becomes explicit only in non-orthogonal bases; the molecular invariants arising from tensor contraction may hence slip by when orthogonal (or orthogonalized) bases are employed. Their chemical significance is of course the same, for this meaning cannot depend upon the particular basis being or not orthogonal[13].

The word "invariant", such as we use it here, must be intended strictly in the tensor sense, i.e. a scalar[14]. The corresponding quantities shall remain unchanged under a unitary transformation of the basis. They may instead display other kinds of basis variation; for instance, they are certainly not

invariant regarding an extension of the basis.

In this note, we shall focus our attention on three-center bonds and discuss some illustrative examples.

2. Building multicentral bond indices

We shall restrict ourselves to the ground state of closed-shell systems, susceptible hence of being described through s single-determinant wavefunction. Nevertheless, several of the formulae used in this section are more general.

For non-orthogonal bases, the first-order density matrix is a mixed tensor[7]

$$2\Pi_{\underline{a}}^{\underline{b}} = 2 \sum_{\underline{i}} x_{\underline{ia}} x^{\underline{ib}} \qquad (1)$$

where $x_{\underline{ia}}$ ($x^{\underline{ib}}$) are covariant (contravariant) coefficients of the $\underline{i}$-th occupied MO. This tensor is represented by a matrix and N, the number of electrons in the molecule, is

$$N = 2 \, \mathrm{Tr} \, \Pi \qquad (2)$$

If we separate the Π matrix in intra-atomic and inter-atomic blocks, it may be written, with an obvious notation for an L-atoms molecule, as

$$\Pi = \begin{pmatrix} \Pi_{AA} & \Pi_{AB} & \cdots\cdots & \Pi_{AL} \\ \Pi_{BA} & \Pi_{BB} & \cdots\cdots & \Pi_{BL} \\ \vdots & & & \\ \Pi_{LA} & \Pi_{LB} & \cdots\cdots & \Pi_{LL} \end{pmatrix} \qquad (3)$$

where $\Pi_{BA} = \Pi_{AB}^{\dagger}$. The submatrices have the dimensions corresponding to the basis chosen for each atom (i.e. Π_{AA} has dimensions $\underline{a}\times\underline{a}$ and the non-diagonal ones are often rectangular[7]).

The Mulliken atomic charge q_A is

$$q_A = 2\ \mathrm{Tr}\ \Pi_{AA} \tag{4}$$

Now, the fact that Π is an idempotent matrix has been exploited in order to propose a partition of q_A into self-charge and active charge as follows[7,9,15]:

$$q_A = (1/2) \sum_B I_{AB} = (1/2)(I_{AA} + \sum_{B\neq A} I_{AB}) = (1/2)(I_{AA}+V_A) \tag{5}$$

where V_A is the valence of atom A[10,11] and the bond index between atoms A and B is[8,9]

$$I_{AB} = 4 \sum_{\substack{a\in A \\ b\in B}} \Pi_{\underline{a}\underline{b}}\Pi_{\underline{b}\underline{a}} \tag{6}$$

Eq.(6) underlines the importance of the tensor character of Π, for it represents a tensor contraction leading to a scalar, i.e. an invariant in the tensor sense. In practice, of course, the variance of the indices is ignored by the computer programs; the bond indices I_{AB} may be also obtained through

$$I_{AB} = 4\ \mathrm{Tr}(\Pi_{AB}\Pi_{BA}) \tag{7}$$

Just as we have profited of the alternative expression to (2):

$$N = 2\ \mathrm{Tr}(\Pi^2) \tag{8}$$

we may equally well write

$$N = 2\ \mathrm{Tr}(\Pi^3) \tag{9}$$

and so on, for any desired power of Π.

Similarly, we may write

$$q_A = (1/4) \sum_{BC}' I_{ABC} \tag{10}$$

where

$$I_{ABC} = 8 \sum_{\underline{abc}}' \Pi_{\underline{a}}^{\underline{b}} \Pi_{\underline{b}}^{\underline{c}} \Pi_{\underline{c}}^{\underline{a}} \tag{11}$$

Eq.(11), as Eq.(6), emphasizes the tensor contraction which is not evident in the operational expression

$$I_{ABC} = 8\ \mathrm{Tr}(\Pi_{AB}\Pi_{BC}\Pi_{CA}) = \mathrm{Tr}\ I_{ABC} \tag{12}$$

Although the Π submatrices may be rectangular, the matrix product in (12) yields an $\underline{a}\times\underline{a}$ square matrix I_{ABC}, allowing for a trace. It may be easily seen that the matrices I_{ABC} obey

$$I_{ABC}^{\dagger} = I_{ACB} \tag{13}$$

having therefore the same trace.

The I_{BAC} matrix has dimensions $\underline{b}\times\underline{b}$, which could then be different from the dimensions of I_{ABC}. However, Eq.(11) ensures us that any of these matrices yields the same trace, i.e. leads to the same scalar I_{ABC}, which is thus independent of the order of the ABC indices.

We dispose accordingly of an index which lends itself to describe three-center bonds, and as such we shall test it in the following section.

3. Results and discussion

Although the idempotency of the Π matrix may be used *a priori* in order to build any multicentral bond index, we shall show in this section examples of three-center bonds. When I_{AB} is calculated for usual chemical bonds it gives, as is well known, values close to chemical intuition, i.e. around 1, 2 or 3 for single, double or triple bonds[8,9]. There is no equivalent chemical expectation for I_{ABC}. However, looking at formulae (5) and (10), we would guess that $|I_{ABC}| < 1$.

We have chosen three kind of examples for I_{ABC} calculations. In the first one, we explore the influence of "secondary" bonds, i.e. the formally non-bonded atoms. In the second one we study strong and normal hydrogen bonding. Finally, we attempt to give a quantitative estimate for the peptide bond.

In the three Tables, we have reported values for I_{ABC} calculated with the CNDO/2 method, and with *ab initio* STO-3G, STO-6G basis sets.

Table I

Table I shows I_{ABC} for a sample of molecules and I_{AC} for the "secondary" bonds. All geometries are taken from ref.[16] Formula (11) gives a hint that I_{ABC} shall exhibit a significant value if there is a "secondary" bond AC. In ref.[7] we have reported IEH results for a series of compounds where "non-bonded" atoms have high I_{AC} values; some of these compounds appear in Table I. The term "long bond" has also been used for describ-

ing this situation[17,18]. Here we are concerned with these bonds only in connection with I_{ABC}. The Table confirms that an expressive value for I_{ABC} correlates to the presence of a "secondary" bond. The STO-3G and STO-6G values are seen to be very similar, except for ozone. This is the only case, among the many ones we have calculated, where STO-3G and STO-6G give also appreciably different results for I_{AB} and I_{AC}; the detection of lone pairs in each oxygen of ozone gives instead quite consistent results between different approximations[19].

Figure 1

Table II reports the I_{XHY} index for the hydrogen-bonded systems drawn in Figure 1. As it is by now established, strong hydrogen bonding shows a variety of experimental properties clearly distinguishable from normal hydrogen bonding[21]. It seems hence worthwhile to see whether or not I_{XHY} evidences this distinction.

ΔE, the hydrogen bond energy, means the binding energy of the system relative to two separated monomers. It is not always clear which are the appropriate monomers in each case. It has even been questioned if the strongest bond known in literature should be really ascribed to the hydrogen difluoride anion; This kind of problems are discussed in refs.[31,32,33]. The values reported from [29] and [30] are estimated from experimental measurements; different sources of error are thoroughly discussed in [30], where the number reported is the hydrogen bond

enthalpy of formation, averaged over simple systems in the gaseous phase. The rest of the ΔE values arise from different ab initio calculations, most of them for very extended basis sets. Ever more extended basis sets do not ensure ever better ΔE predictions; we do not report them as the best possible values, but only in order to correlate them with our I_{XHY} indices.

Table II

The Table shows a clearcut qualitative separation between strong and normal hydrogen bonds. As a linear correlation between I_{XHY} and ΔE would be rather unexpected, it is quite satisfactory that hydrogen difluoride anion has the highest ab initio I_{XHY} value in the Table. Semiempirical and ab initio indices show qualitative similar features, STO-3G and STO-6G being almost equal.

Roos, Kraemer and Diercksen[25] have obtained a slightly asymmetric hydrogen bond for system 6, but they expect that this asymmetry disappears in a more refined treatment. For this reason, we have reported symmetric and asymmetric bond indices, both of which exhibit significantly higher relative values than those of the corresponding energies of the systems 2 to 5.

As our aim is merely to verify if hydrogen bond indices split into two groups, the examples reported here for the normal hydrogen bonds are enough for our purposes. The ΔE values for them are of the usual order of magnitude.

Table III

In Table III we have selected a few examples in order to report values for the peptide bond index I_{OCN}. Formamide is always adopted as the simplest possible model for this linkage and very recently the importance of its "secondary" bond has been remarked[34]. Geometry has been taken from ref.[35]. N-methyl acetamide has been also proposed as pattern[36]. Similarly, we have chosen the glycine dipeptide as the simplest peptide bond obtained starting from amino acids. The geometry for the glycine unit is that obtained in ref.[37].

It is seen that, as before, STO-3G and STO-6G give equal I_{ABC} indices. The fluoride ion seems to reinforce the peptide bond in formamide.

It is not at all trivial to find an energy quantity which can be associated with such a kind of intramolecular bonding, even on a relative scale[38]. As we have seen above, the intermolecular hydrogen bond energy is just taken as the difference in energy between the dimer and the separate monomers. Other kinds of energy decomposition devised for hydrogen bonds[26] are not applicable to the peptide bond. Let us remind that other quantities, such as the forces acting within the molecule, could be used in the characterization of chemical bonds[5]. However few, the strikingly consistent values obtained for I_{OCN} suggest that the peptide bond is of the same order of magnitude as strong hydrogen bonds.

Finally, let us mention a multicentral bond index for more than three centers. The benzene ring has a six-center index of 0.088 in the three approximations, while the index for the pyridine ring is $< 10^{-4}$.

4. Conclusions

- Multicentral bonds may be related to a bond index defined from the first-order density matrix for closed-shell systems.

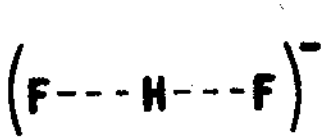
- "Secondary" bonds are shown to have an expressive influence on sample three-center bonds.

- Three-center bond indices clearly distinguish between strong and normal hydrogen bonds, correlating to hydrogen bond energy.

- The obtained indices for the peptide bond are of the same order of magnitude as those for strong hydrogen bonds.

LEGEND TO FIGURE

Figure 1: Systems appearing in Tables II and III. In each one, we have indicated the reference from which geometry is taken. 1[20], hydrogen difluoride ion; 2[21], formamide-fluoride ion; 3[22], protonated H_2O dimer; 4[23], protonated HF dimer; 5[24], bi-formate anion; 6[25], protonated dihydroxyl; 7[26], cyclic formamide dimer; 8[27], HF dimer; 9[28], H_2O dimer; 10[16], N-methyl acetamide; 11[37], glycine dipeptide.



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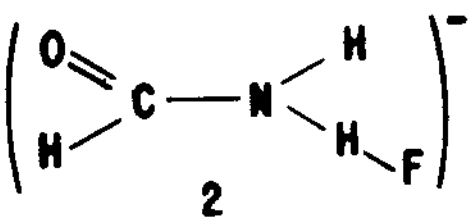

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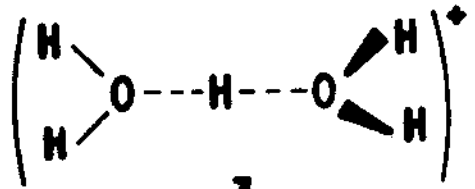

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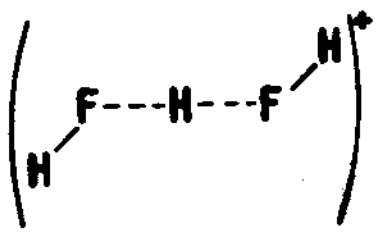

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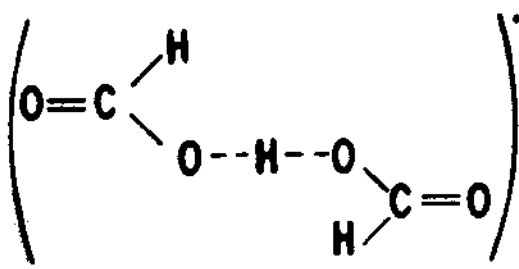

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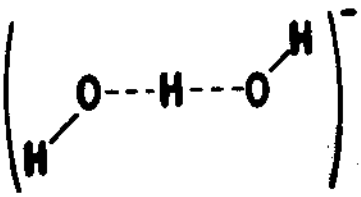

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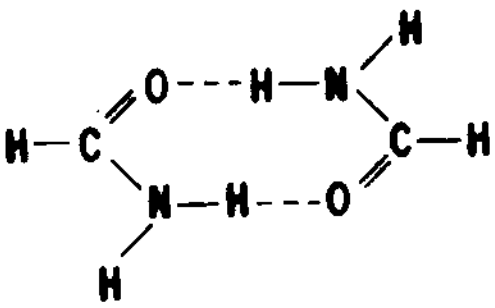

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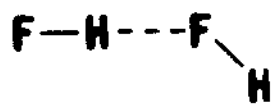

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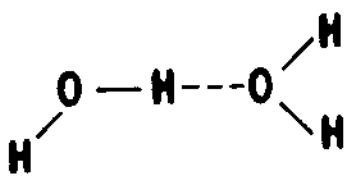

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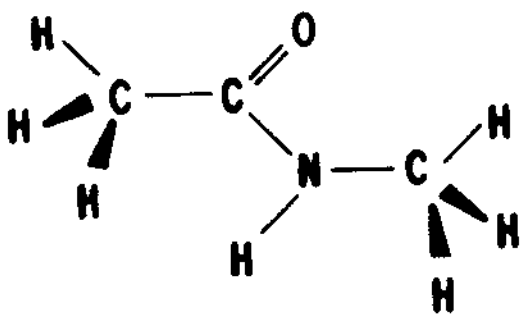

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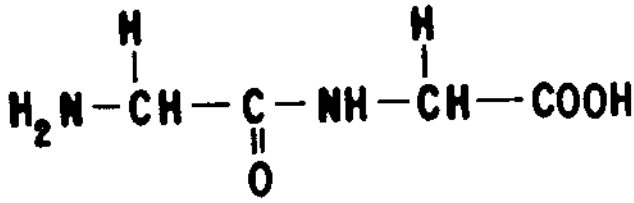

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Table I: Three-center bond index I_{ABC} for a sample of molecules, calculated following different approximations. I_{AC} is the bond index from eq.(6).

Molecule	ABC	I_{ABC}			I_{AC}
		CNDO/2	STO-3G	STO-6G	STO-6G
H_2O	HOH	0.0000	0.0036	0.0038	0.0113
H_2O_2	OOH	-0.0017	0.0008	0.0011	0.0100
F_2O	FOF	-0.0193	-0.0308	-0.0310	0.0422
O_3	OOO	-0.2859	-0.1730	-0.3256	0.5032
CO_2	OCO	-0.3522	-0.4443	-0.4436	0.2948
N_2O	NNO	-0.3438	-0.4554	-0.4538	0.5812
O_2NNO_2	ONO[a]	-0.2676	-0.3579	-0.3580	0.4360
O_2NONO_2	ONO[a]	-0.2297	-0.3147	-0.3143	0.3912
FNO_2	ONO	-0.2357	-0.3178	-0.3179	0.4140

[a] ONO refers to the NO_2 group.

Table II: Three-center hydrogen bond index I_{XHY}, calculated following different approximations. The systems appear in Figure 1. ΔE, hydrogen bond energy, each one with its reference source.

System	$-I_{XHY}$ CNDO/2	STO-3G	STO-6G	ΔE(kJ/mol)
1	0.1710	0.2266	0.2235	214[21]
2	0.0887	0.1098	0.1087	148[21]
3	0.1180	0.1233	0.1213	135[22]
4	0.0941	0.1047	0.1018	128[23]
5	0.1463	0.1474	0.1454	123[24]
6[a]	0.1754	0.1908	0.1890	105[25]
	0.1521	0.1752	0.1734	
7	0.0062	0.0176	0.0162	31.8[26]
8	0.0054	0.0126	0.0113	18.8[27]; 25.1[29]
9	0.0053	0.0149	0.0136	20.2[28]; 20.9[30]

[a] Upper row, symmetric; lower row, asymmetric.

Table III: Three-center bond index I_{OCN} for selected peptide bonds, calculated following different approximations. The systems appear in Figure 1.

System	$-I_{OCN}$ CNDO/2	STO-3G	STO-6G
Formamide	0.1606	0.1838	0.1834
Formamide-fluoride ion	0.1995	0.2672	0.2674
N-methyl acetamide	0.2284	0.1766	0.1769
Glycine dipeptide	0.1546	0.1699	0.1698

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