Multicenter bonds and respective MO index

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Abstract

The tensor character of the first-order density matrix leads to the definition of an MO multicenter bond index for closed-shell systems. Using Grassmann algebra, a straightforward meaning is attached to this multicenter bond index within the Hartree-Fock approximation. Three-center bond indices clearly distinguish between strong and normal hydrogen bonds; peptide bonds are predicted to be of the same order of magnitude than strong hydrogen bonds. In the same way that the valence of an atoms issues from the definition of bond index, we show that the three-center bond index lends itself to the definition of a bond valence. Within the charge of a bond, we show that its self-charge (i.e. the amount of electrons kept by the atoms involved in the bond) is partitioned in such a way that the more eletronegative atom tends to allocate more electronic charge than the other atom. We also show some results of four-center indices and report six-center indices for hexagonal rings.

Key-words: Multicenter bond index; Hydrogen and peptide bonds; Bond valence; Bond charge apportion.

1. Introduction

In a recent work, it has been assserted that "it is at least arguable that, from the point of view of quantum chemistry as usually practiced, the supercomputer has dissolved the bond" [1]. This polemical work, together with its references, traces the development of the concept of a chemical bond since the middle of the last century. If the most usual chemical bond may be still such a controversial subject, multicenter bonds are expected to be exposed to much more bitter criticism. In Ref. [2] it is remembered that Hückel already recognized that "the allyl cation $(C_3H_5)^+$ contains a three-center, two-electron (3c-2e)π bond". Pimentel [3] mentions a three-center four-electrons (3c-4e) bond for HF_2^-.

Now, the Lewis model, the octet rule and connected concepts are, as is clearly depicted by Sutcliffe [1], independent and even in conflict with Mulliken's formulation of molecular orbital (MO) theory [4]. Needless to say, the bond charge and overlap population conceptions [5] disagree with the Lewis electron-pair model for a bond. This must be kept in mind when molecular orbital (MO) descriptions of (3c-2e) or (3c-4e) bonds are formulated. For example, Coulson [6] puts, in trihalide ions, the four bonding electrons into 3c MO's, inferring net charges on the atoms. The valence bond (VB) approach is instead consistent with Lewis-type models and has been applied for many years to multicenter bonds. Harcourt [7–13] has used both VB and MO methods for these problems.

Of course, anyone dealing with the chemical bond cannot omit Pauling's capital book [14], as well as the deep, elegantly written work of Ruedenberg about the physical nature of the chemical bond [15].

Let us mention two worthwhile contributions to the quantum viewpoint of the chemical bond. Del Re [16] points out that "only from an open-minded and thorough analysis of the various interpretations it should be possible to make real progress" $\cdots$ in this "borderline between chemistry and physics". One of the troubles met with is that chemists "consider a double bond as a superposition of two nonequivalent bonds, one of them being quite different from the typical C-C bond of a saturated compound" [17]. Berthier [18] remembers that "single and double bonds are not true stationary states, but rather molecular valence states, to be defined in the frame of an *ad hoc* model postulating the existence of bonds themselves" [19].

With these cautions in mind, we shall develop here a MO viewpoint for closed-shell cases in the Hartree-Fock approximation.

2. Bond indices for usual bonds

Let us now briefly remind the bond order-bond index historical sequence for usual bonds between atoms A and B. The first π definition of Coulson bond order [20] was intended for hydrocarbons in the Hückel MO approximation. The introduction of overlap **S** lead to two different generalizations by Chirgwin and Coulson [21] and by Löwdin [22].

If the ψ_i MO is related to the ϕ_a atomic orbital through the linear combination of atomic orbitals (LCAO), we have

$$\psi_i = \sum_a x^{ia}\phi_a \ , \tag{1}$$

for the basis is covariant (subindex) and the coefficients x^{ia} contravariant (superindex); the i labelling has no variance [23]. The overlap matrix elements S_{ab} are the integrals

over the whole space

$$S_{ab} = (\phi_a, \phi_b) = \int \phi_a \phi_b dV \tag{2}$$

and $\mathbf{S}$ represents the metric tensor of the system [21].

The charge-bond-order matrix $\mathbf{P}^C$ (charges are its diagonal terms) is defined by Chirgwin and Coulson [21] as

$$P_{ab}^C = \frac{1}{2} \sum_{i,c} (x_{ia} S_{bc} x_{ic} + S_{ac} x_{ic} x_{ib}) \tag{3}$$

We do not specify here the indices variance for reasons which we shall give later. Let us define a matrix $\mathbf{P}$ through

$$P^{ab} = \sum_i x^{ia} x^{ib} \tag{4}$$

The Löwdin definition of the charge-bond order matrix $\mathbf{P}^L$ uses symmetrically orthogonalized orbitals:

$$\mathbf{P}^L = \mathbf{S}^{1/2} \mathbf{P} \mathbf{S}^{1/2} \tag{5}$$

The electronic charge and bond overlap population concepts [5] are usually related to the X-ray evidence of an accumulation of charge along the bonds, even if a warning has been given that electron-rich atoms may exhibit a deficit in bond density [24]. On the other hand, it has been also mentioned [25] that, in order to obtain a suitable picture of a chemical bond, spherically symmetric internal atomic shells should be subtracted from the total electron density. The authors of Ref. [25] remember that the bond concept appeared in chemistry before the discovery of the electronic-nuclear structure of atoms and molecules; they choose to give an approach relying on a force density method, adequate both for covalent and ionic bonds.

When all-valence-electrons calculations were introduced, Hoffmann's EHT (Extended Hückel Theory) [26] and the iterated IEHT version used Mulliken's population analysis, contracting the orbital-orbital charge-bond order matrix to an atom-atom matrix. This orbital-orbital matrix is *not* the first order density matrix $2\mathbf{\Pi}$ which is

$$2\mathbf{\Pi} = 2\mathbf{PS} \quad ; \quad \Pi_c^d = \sum_e P^{de} S_{ec} \tag{6}$$

The matrix $\mathbf{\Pi}$ may be separated into submatrices, $\mathbf{\Pi}_{AA}$, $\mathbf{\Pi}_{AB}$ and so on.

If q_A is the electronic charge of atom A, the total number of electrons N in the system may be written as

$$N = \sum_A q_A = \sum_{a \in A} q_a^a = 2 \sum_{a \in A} \Pi_a^a \tag{7}$$

This definition is not unique. Since $Tr(\mathbf{AB}) = Tr(\mathbf{BA}$, it may be written that

$$N = 2 \sum_{a \in A} (\mathbf{S}^\alpha \mathbf{P} \mathbf{S}^{1-\alpha})_a^a = 2 \sum_{a \in A} P_a'^a = \sum_A q_A \tag{8}$$

for any α [27, p. 152], $2\mathbf{P}'$ being the density matrix. For $\alpha = 0$, q_A are the Mulliken gross atomic charges. For $\alpha = 1/2$, q_A are the Löwdin charges [22, 27].

As $\mathbf{S}$ represents the covariant metric tensor of order two, the density matrix for $\alpha = 0$ is a mixed tensor [23]. The contraction of matrices is thus a contraction in the tensor sense. It is usually not remembered that the atomic orbital charge q_a^a is not an invariant, for a scalar is obtained only by contraction to the atomic charge q_A [28].

Similarly, the atom-atom Mulliken submatrix $\mathbf{M}_{AB}$ has elements

$$(\mathbf{M}_{AB})_{ab} = 2P^{ab}S_{ab} \tag{9}$$

which are also invariant

For orthogonal bases, $\mathbf{S}=\mathbf{I}$, the unit matrix; $2\mathbf{P}$ becomes the density matrix and the distinction between covariant and contravariant components becomes inmaterial. In this case the overlap population vanishes. Wiberg [29] aimed to compare CNDO (Complete Neglect of Differential Overlap) [30] and EHT quantitites for a series of strained system. He devised then a CNDO index W_{AB} obtained through

$$W_{AB} = 4 \sum_{\substack{a \in A \\ b \in B}} P_{ab}^2 \tag{10}$$

We generalized this index for non-orthogonal bases, I_{AB}, as [23, 31]

$$I_{AB} = 2 \sum_{\substack{a \in A \\ b \in B}} \Pi_a^b \Pi_b^a \tag{11}$$

Despite the fact that in Refs. [31, 32] we used it for all-valence-electrons calculations, nothing prevented taking into account the core electrons or enlarging the basis.

Let us now explain briefly the model in mind when defining I_{AB} and how it differs from Mulliken's population analysis.We have just mentioned that overlap population vanishes for orthogonal bases, this is the most evident difference. Another one is that distinction between bonding and antibonding contributions is lost in I_{AB} (see [33]).

Trindle [34] introduced the terms self-charge and active charge for the charge partition involving Wiberg indices, with an evident meaning:

$$q_A = \frac{1}{2} \left(I_{AA} + \sum_{B \neq A} I_{AB} \right) \tag{12}$$

On the other hand, the valence V_A of atom A within a molecule is [35, 36]

$$V_A = \sum_{B \neq A} I_{AB} \tag{13}$$

so that

$$q_A = \frac{1}{2}(I_{AA} + V_A) \tag{14}$$

In a non-orthogonal basis, q_A is the same as Mulliken's, while our partition [27] is different. Both our definition and Mulliken's are more appropriate for covalent bonds

than for ionic bonds [37]. Sannigrahi [38] has covered *ab initio* SCF (self-consistent field) calculations of bond indices and valences using diferent basis sets.

Now, in the hydrogen molecule our model assigns half an electron, both for self-charge and active charge, to each of the hydrogen atoms: I_{AB} is thus equal to one. We have seen in Ref. [31] that in hydrocarbons the hydrogen active charge is still very close to 0.5, its net charge varying thus at the expense of self-charge. The overlap population for H_2 is of course different from 1, just as for most homonuclear and other typical molecules is appreciably different from the integer values expected for single, double and triple bonds. The integer values are self-consistent *a priori*, in the terms of Ref. [39].

The tensor notation permits a much easier visualization of the invariance properties which are usually required from bond indices. Thus, the reduction of an orbital-orbital matrix to an atom-atom matrix (when using non-orthogonal bases) must be carried out according to the definition of tensor contraction. If we explicit the variance of the indices in the Chirgwin and Coulson definition of eq. (3):

$$P_{ab}^C = \frac{1}{2} \sum_{i,c} \left(x^{ia} S_{bc} x^{ic} + S_{ac} x^{ic} x^{ib} \right)$$

$$= \frac{1}{2} \sum_i \left(x^{ia} x'_{ib} + x'_{ia} x^{ib} \right) \qquad (15)$$

It is immediately seen that the Chirgwin and Coulson summation over the orbitals of two atoms is not a tensor contraction, therefore it is not invariant under a unit transformation of the basis [23].

Let us underline that if the basis is orthogonal and such that each atom has only one orbital centered in it (e.g. the π approximation), Chirgwin and Coulson's bond order, Löwdin's and the Mulliken overlap population, all reduce to the original Coulson bond order. The Wiberg index is in this case its square.

An interesting alternative bond order has been proposed by Cohen [40], who makes a thorough discussion of merits and handicaps in the Mulliken formulation. Dick and Freund [41] re-examine some concepts involved in Cohen's bond order. To demonstrate the applicability of Cohen's analysis to excited-state multiconfiguration wavefuntions, they present results for the typical molecules ethane, ethylene and acetylene. They obtain similar results for CNDO and *ab initio* STO-3G expecting a small basis set dependence. Roby, in his pioneering works [42], explores the relevance of electron density projection operators to the definition and use of chemical valence concepts. Guerillot el al. [43] suggest another bond population analysis p_{AB} in the EHT framework and obtain a relation between p_{AB} and the bond length r_{AB}. Elliot and Richards [44] propose a method for obtaining charge densities in defined regions of space from *ab initio* molecular wave funtions: the concept of bond order (1,2 and 3 respectively for ethane, ethylene and ecetylene) is thus placed on a sounder theoretical footing. Julg [45] has put forward a quite different theory considering fluctuations in orbital domains; these domains are described along a classical bond with population close to 2, with a small fluctuation from this value.

Similar to Ref. [44], Bader's topological theory of atoms-in-molecules [46] is a recognized landmark in the theory of the chemical bond. Within its framework, covalent bond orders have been defined [47] and compared with Wiberg indices, stating (incorrectly) that both give zero for so-called noninteracting pairs of atoms. Sharing indices [48] asign

values of 2 and 3 to prototype double and triple bonds. Expressions analogous to eq. (11) have been used in the compelling works of Nalejawski et al. [49].

Mayer [50] has applied definition (11) in *ab initio* calculations and Medrano et al. [51] have applied it to restricted Hartree-Fock (RHF), unrestricted Hartree-Fock (UHF), generalized valence bond (GVB) and configuration interaction (CI) cases.

Fischer and Kollmar [52] have partitioned the energy issued from CNDO calculations; as pointed out by Mayer [50], the exchange part of the diatomic energy components is proportional to the Wiberg index. Thus, the indices in expressions (10) and (11) could be seen as typical quantum quantities, as the exchange concept is. This would elude the objection frequently raised against quantum chemical calculations (see for example [18] and [25]), that the very notion of chemical bond does not occur in quantum mechanics.

3. Hilbert-Grassmann formulation of bond index in the Hartree-Fock approximation

Grassmann algebra is a powerful alternative formulation of the wave function antisymmetry description [53, 54]. Let us briefly summarize this approach, which we shall use further on.

State vectors are defined from the generators of a multilinear space $\mathcal{G}$, which is introduced as an N-linear alternating map of the Hilbert space $\mathcal{H}$. Spin orbitals may be written as outer products between generator elements ξ_μ of the $\mathcal{G}$ space. An N-linear alternating map Δ in the space $\mathcal{H}$ is then [53, 55].

$$\Delta \; : \; \mathcal{H} \times \mathcal{H} \times \cdots \times \mathcal{H} \to \mathcal{G} \tag{16}$$

This means that the mapping Δ involves a unique correspondence between the N-linear alternating map of $\mathcal{H}$ and $\mathcal{G}$. $\mathcal{G}$ is called a Hilbert-Grassmann vector space. The space vector of an N-electron system takes the form

$$|12 \cdots N\rangle = \xi_1 \wedge \xi_2 \wedge \cdots \xi_N \tag{17}$$

If any two ξ_μ are equal, this vanishes as it should. Multilinear alternating maps can be understood as generalizations of determinants [53]. In (17), the products $\wedge$ are tensor products (also called "outer products" or "direct products" [56]).

If we denote by $\mathcal{G}^\dagger$ the conjugated space of $\mathcal{G}$, the generators $\xi_\mu \in \mathcal{G}$ and $\xi^\mu \in \mathcal{G}^\dagger$ have the same properties as the conventional creation and annihilation operators respectively (for instance, they obey the same commutation relations). As the Hilbert space is provided with an inner product $(\xi_\mu \bullet \xi^\nu)$ (generalized scalar product), it is suitable for defining N-order density functionals or, somewhat less general, density matrices [53]. The first-order density matrix (Π_μ^ν) is [53, 54]

$$(\xi_\mu \bullet \xi^\nu) = \Pi_\mu^\nu \delta_{\sigma_\mu \sigma_\nu} \tag{18}$$

where σ_μ is the spin of electron μ. Hence, the $2N$-linear form $\Gamma : \mathcal{H} \times \mathcal{H} \times \cdots \times \mathcal{H} \to R$ (the field of all real numbers) may be defined, in the Hartree-Fock approximation, as

$$\Gamma(\xi_1, \xi_2, \cdots, \xi_N; \xi^1, \xi^2, \cdots, \xi^N) =$$
$$(\xi_1 \wedge \xi_2 \wedge \cdots \wedge \xi_N) \bullet (\xi^1 \wedge \xi^2 \wedge \cdots \wedge \xi^N)$$

$$\tag{19}$$

This in turn is [53, 54]

$$\det\left((\xi_\mu \bullet \xi^\mu)\right) = \det \mathcal{D}_N = d_{12\cdots N}^{12\cdots N} \;\; ;$$
$$\mu = 1, 2, \cdots N \tag{20}$$

For monoelectronic spin orbitals ξ_μ, $\mathcal{D}_N$ takes the form

$$\mathcal{D}_N = \begin{pmatrix} (\xi_1 \bullet \xi^1) & (\xi_1 \bullet \xi^2) \cdots (\xi_1 \bullet \xi^N) \\ (\xi_2 \bullet \xi^1) & (\xi_2 \bullet \xi^2) \cdots (\xi_2 \bullet \xi^N) \\ \vdots & \vdots \\ (\xi_N \bullet \xi^1) & (\xi_N \bullet \xi^2) \cdots (\xi_N \bullet \xi^N) \end{pmatrix}$$

$$\tag{21}$$

Each of the "elements" of $\mathcal{D}_N$ is in turn a matrix. This expression is general; we present here a simple application of it.

For $N = 2$, we have [53, 54]

$$\det(\mathcal{D}_2) = \begin{vmatrix} (\xi_\mu \bullet \xi^\mu) & (\xi_\mu \bullet \xi^\nu) \\ (\xi_\nu \bullet \xi^\mu) & (\xi_\nu \bullet \xi^\nu) \end{vmatrix} =$$

$$= (\xi_\mu \bullet \xi^\mu)(\xi_\nu \bullet \xi^\nu) - (\xi_\nu \bullet \xi^\mu)(\xi_\mu \bullet \xi^\nu)$$
$$= \Pi_\mu^\mu \Pi_\nu^\nu - \Pi_\mu^\nu \Pi_\nu^\mu \delta_{\sigma_\mu \sigma_\nu} \tag{22}$$

Summation over all orbitals $\mu \in A$, $\nu \in B$ and over all spins $\sigma_\mu \sigma_\nu$ yields [53, 54]

$$\sum_{\substack{\mu \in A \\ \nu \in B}} \sum_{\sigma_\nu \sigma_\mu} \det(\mathcal{D}_2) = \sum_{\substack{\mu \in A \\ \nu \in B}} (4\Pi_\mu^\mu \Pi_\nu^\nu - 2\Pi_\mu^\nu \Pi_\nu^\mu) \tag{23}$$

Denoting by $\hat{q}_A$ an operator such that its mean value $\langle \hat{q}_A \rangle$ is the scalar q_A, the left expression is $\langle \hat{q}_A \hat{q}_B \rangle$ [53, 54], which in turn becomes

$$\langle \hat{q}_A \hat{q}_B \rangle = \langle \hat{q}_A \rangle \langle \hat{q}_B \rangle - \frac{1}{2} I_{AB} \tag{24}$$

Or also [28, 53, 57]

$$-I_{AB}/2 = \langle \hat{q}_A \hat{q}_B \rangle - \langle \hat{q}_A \rangle \langle \hat{q}_B \rangle = \langle (\hat{q}_A - \langle \hat{q}_A \rangle)(\hat{q}_B - \langle \hat{q}_B \rangle) \rangle \tag{25}$$

That is, *the bond index I_{AB} means the correlation between the fluctuation in the atomic charges in A and B around their mean values* $\langle \hat{q}_A \rangle$ *and* $\langle \hat{q}_B \rangle$ [28, 57]. Also, due to eq. (13), V_A is the sum of the correlations between the fluctuations in A and these of all other atoms [57].

4. Multicenter bond index

The $\mathbf{\Pi}$ matrix in eq. (6) is not a symmetric matrix, $\mathbf{\Pi}^{\dagger}$ could be used also as density matrix. The idempotency in $\mathbf{\Pi}$ or $\mathbf{\Pi}^{\dagger}$ [58]

$$\mathbf{\Pi}^2 = \mathbf{\Pi} \tag{26}$$

allows to write

$$N = 2Tr(\mathbf{\Pi}) = 2Tr(\mathbf{\Pi}^2) = 2Tr(\mathbf{\Pi}^3) \tag{27}$$

and so on, for any desired power of $\mathbf{\Pi}$. Up to here, we have taken advantage of the second power [23, 31]; now we extend the definitions for q_A [59]

$$q_A = \frac{1}{2}\sum_B I_{AB} = \frac{1}{4}\sum_{BC} I_{ABC} \tag{28}$$

In expressions (28), B and C must be allowed to be equal to A. [60]. We have

$$I_{ABC} = 8\sum_{\substack{a \in A \\ b \in B \\ c \in C}} \Pi_a^b \Pi_b^c \Pi_c^a \tag{29}$$

where the summations are again tensor contractions.

We could separate the $\mathbf{\Pi}$ matrix in intraatomic and interatomic blocks, with an obvious notation for an L-atomic molecule

$$\mathbf{\Pi} = \begin{bmatrix} \mathbf{\Pi}_{AA} & \mathbf{\Pi}_{AB} & \cdots & \mathbf{\Pi}_{AL} \\ \mathbf{\Pi}_{BA} & \mathbf{\Pi}_{BB} & \cdots & \mathbf{\Pi}_{BL} \\ \vdots & \vdots & & \vdots \\ \mathbf{\Pi}_{LA} & \mathbf{\Pi}_{LB} & \cdots & \mathbf{\Pi}_{LL} \end{bmatrix} \tag{30}$$

Of course, the variance of the indices is ignored by the computer programs. There exists however a convention that the covariant index designs rows and the contravariant one columns. The bond indices I_{AB} may be also obtained through

$$I_{AB} = 4Tr(\mathbf{\Pi}_{AB}\mathbf{\Pi}_{BA}) \tag{31}$$

and similarly [59]

$$I_{ABC} = 8Tr(\mathbf{\Pi}_{AB}\mathbf{\Pi}_{BC}\mathbf{\Pi}_{CA}) = Tr(\mathbf{I}_{ABC}) \tag{32}$$

Although the $\mathbf{\Pi}$ submatrices may be rectangular, the matrix product in (32) yields a square matrix $\mathbf{I}_{ABC}$, allowing for a trace. It may be easily seen that

$$\mathbf{I}_{ABC}^{\dagger} = \mathbf{I}_{ACB} \tag{33}$$

having therefore the same trace. Let us suppose that the basis of atom A has dimensions a, that of atom B dimensions b and so on. The $\mathbf{I}_{ABC}$ matrix is an $a \times a$ square matrix, while $\mathbf{I}_{BAC}$ is a $b \times b$ matrix. The tensor form (29) ensures that any of these matrices has

the same trace, i.e., leads to the same scalar I_{ABC}, which is thus independent of the order of the ABC indices.

We may similarly define

$$I_{ABC\cdots L} = 2^{L-1} \sum_{\substack{a \in A \\ b \in B \\ \vdots \\ \ell \in L}} \Pi_a^b \Pi_b^c \cdots \Pi_\ell^a \tag{34}$$

In Ref. [59] we centered our attention on 3c-bonds. Sannigrahi and Kar [61] have remarked that L-center indices can be calculated from M-center indices ($L < M$) but not vice versa.

5. Three-center bonds and I_{ABC}

It is well known that for typical chemical bonds the index I_{AB} gives integer values close to the chemical intuition [29, 31]. There is no equivalent chemical expectation for I_{ABC}. A look at eqs. (12-14) and (27), however, makes us conjecture that $|I_{ABC}| < 1$ [59].

We have stressed [23, 31] that our definition for I_{AB} held both for bonded and non-bonded atoms. The so-called "long bonds" or "secondary bonds" [7-13,62] are most important in three-center bonds (see Table 1). We have seldom met significant multicenter indices in the absence of secondary bonds. We have repeatedly linked bond orders involving formally non-bonded atoms with VB structures [63–65]. Standard VB and increased valence (IV) calculations [9] show *with complete certainty* that IV structures (i.e., involving long bonds) *always* generate a lower energy than do the standard VB structures.

We report in Table 1 the I_{ABC} values for a sample of systems. We shall discuss in the next section the question of the I_{ABC} sign. Sannigrahi and Kar [61] state that a negative I_{ABC} value means that there is no three-center bond. In Ref. [66] it is hinted that (3c-4e) bonds would be associated with negative I_{ABC} values, although the reverse is not true. Instead, I_{ABC} for "true" (3c-2e) bonds would be positive and greater than 0.1. Positive values are shown in the table for C_3 and B_2H_6. It is also seen that there is a qualitative agreement between semiempirical and *ab initio* results. Within each calculation method the I_{ABC} values for the NO_2 groups are reasonably similar.

Mayer [67] has proposed a model for 3c-bonds, where a single atomic orbital is assigned to each of the three centers; it has been used in Refs. [66, 68, 69].

Ref. [66] takes into account a hypothetical symmetric molecule in Mayer's model. The secondary bond index I_{AC} is

$$I_{AC} = \frac{1}{2} \sum_B I_{ABC} = \frac{1}{2}(I_{ABC} + I_{AAC} + I_{ACC}) \tag{35}$$

For the symmetric molecule ($I_{AAC} = I_{ACC}$), one would more adequately write

$$\begin{aligned} I_{AA'} &= \frac{1}{2}(I_{ABA'} + I_{AAA'} + I_{A'A'A}) \\ &= \frac{1}{2}(I_{ABA'} + 2I_{AAA'}) \end{aligned} \tag{36}$$

so that

$$I_{ABA'} = 2(I_{AA'} - I_{AAA'}) \tag{37}$$

With only an atomic orbital in each center $(I_{AAA'} = q_A I_{AA'})$, it reduces to

$$I_{ABA'} = I_{AA'}(1 - q_A) \tag{38}$$

Thus, for this simplified model for a symmetrical molecule, the sign of the 3c-bond index would be determined by the net charge of the terminal atoms. Ref. [66] discusses also whether a system may be classified as hypervalent, a question much debated in chemical literature.

6. Multicenter bond index and Hilbert-Grassmann formulation

The expansion of $\mathcal{D}_3$ and $\mathcal{D}_4$ starting from eq. (21) is similar to that carried out for $\mathcal{D}_2$ in section 3, although more lengthy [71]. We may write

$$\sum_{\substack{a \in A \\ b \in B \\ c \in C}} \sum_{\sigma_a \sigma_b \sigma_c} = det(\mathcal{D}_3) = \langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle$$

$$= \langle \hat{q}_A \rangle \langle \hat{q}_B \rangle \langle \hat{q}_C \rangle + I_{ABC}/2 - \langle \hat{q}_A \rangle I_{BC}/2 - \langle \hat{q}_B \rangle I_{AC}/2 - \langle \hat{q}_C \rangle I_{AB}/2 \tag{39}$$

The three-center bond index I_{ABC} corresponds to the correlations between the fluctuations of $\hat{q}_A, \hat{q}_B$ and $\hat{q}_C$ from their average values:

$$\frac{1}{2} I_{ABC} = \langle (\hat{q}_A - \langle \hat{q}_A \rangle)$$
$$(\hat{q}_B - \langle \hat{q}_B \rangle)(\hat{q}_C - \langle \hat{q}_C \rangle) \rangle \tag{40}$$

Expression (25) for I_{AB} means that when I_{AB} is positive (for orthogonal bases it is so by definition; for non-orthogonal bases it usually is too, although not necessarily), if q_A fluctuates in one sense from its average value, q_B fluctuates in the opposite sense. From eq. (40) we can infer that as the three fluctuations in the q's 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 *a priori* distinction [71] and *no evident connection at all with the involvement of two or four electrons in the ABC bond*:

Some more algebra starting from $\mathcal{D}_4$ leads to

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \hat{q}_D \rangle = \langle \hat{q}_A \rangle \langle \hat{q}_B \rangle \langle \hat{q}_C \rangle \langle \hat{q}_D \rangle + (\langle \hat{q}_A \rangle I_{BCD} + \langle \hat{q}_B \rangle I_{ACD} + \langle \hat{q}_C \rangle I_{ABD} + \langle \hat{q}_D \rangle I_{ABC})/2 -$$
$$(\langle \hat{q}_A \rangle \langle \hat{q}_B \rangle I_{CD} + \langle \hat{q}_A \rangle \langle \hat{q}_C \rangle I_{BD} + \langle \hat{q}_A \rangle \langle \hat{q}_D \rangle I_{BC} + \langle \hat{q}_B \rangle \langle \hat{q}_C \rangle I_{AD} + \langle \hat{q}_B \rangle \langle \hat{q}_D \rangle I_{AC} +$$
$$\langle \hat{q}_C \rangle \langle \hat{q}_D \rangle I_{AB})/2 + (I_{AB} I_{CD} + I_{AC} I_{BD} + I_{AD} I_{BC})/2 - 3 I_{ABCD}/4 \tag{41}$$

So that [71]

$$-3 I_{ABCD}/4 = \langle (\hat{q}_A - \langle \hat{q}_A \rangle)(\hat{q}_B - \langle \hat{q}_B \rangle)(\hat{q}_C - \langle \hat{q}_C \rangle)(\hat{q}_D - \langle \hat{q}_D \rangle) \rangle \tag{42}$$

The sign of I_{ABCD} can be equally positive or negative. Let us remind that these conclusions are valid within the limits of closed-shell systems in the single-determinant Hartree-Fock approximation.

7. The hydrogen bond, the peptidic bond and their I_{ABC}

Typical 3c bonds are hydrogen bonds; it is well known that strong hydrogen bonding shows a variety of experimental properties clearly different from those of normal hydrogen bonding [72]. It is therefore a challenge for the definition of a 3c-bond index to explore whether it is or not sensitive to this distinction.

The hydrogen bond energy, ΔE, 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. The values reported in Refs. [73] and [74] are estimated from experimental measurements; different sources of error are thoroughly discussed in Ref. [74], where the value reported is the hydrogen bond enthalpy of formation, averaged over simple systems in the gas phase. The rest of the ΔE values arise from *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.

As our aim is merely to verify whether hydrogen bond indices split into two groups, the few examples reported for normal hydrogen bonds are sufficient for our purpose. Table 2 shows actually a clear-cut qualitative separation between strong and normal hydrogen bonds. We certainly would not expect a linear correlation between I_{XHY} and ΔE. Although it has been questioned whether the strongest hydrogen bond known in the literature shoud be really ascribed to $(FHF)^-$, it is very satisfactory that $(FHF)^-$ shows the highest *ab initio* I_{XHY} value in the table. Semiempirical and *ab initio* indices show qualitatively similar features, STO-3G and STO-6G being almost equal.

Normal hydrogen bonds are undoubtedly 3c-bonds. We would not hence be so incisive as Sannigrahi and Kar [61] in establishing a limit of $I_{ABC} > 0.1$ in order that a 3c-bond would taken as such.

For table 3 we have selected a few examples in order to estimate the peptide bond index I_{OCN}. Formamide is always adopted as the simplest possible model for this linkage and the importance of the corresponding secondary bond has been pointed out [86]. N-methyl acetamide has been also proposed as a pattern [87]. Similarly, we have chosen the glycine dipeptide as the simplest peptide bond obtained starting from amino acids. Again, STO-3G and STO-6G give the same indices. The fluoride ion seems to reinforce the peptide bond of formamide.

It is not at all simple to find an energy quantity that can be associated with this kind of intramolecular bonding, even on a relative scale [88]. As we have seen above, the intermolecular bond energy is simply taken as the energy difference between the dimer and the separate monomers. Other kinds of energy decomposition devised for hydrogen bonds [80] are not applicable to the peptide bond. Within this small sample, the strikingly consistent values obtained for I_{OCN} suggest that the peptide bond is of the same order of magnitude that of strong hydrogen bonds.

8. Other assorted calculations

A thorough study of multicenter bonding in 30 electron-deficient systems (molecules and small clusters) is carried out in Ref. [89]. Most of the systems have significant 3c-indices and for a few of them also 4c-indices are given, of which the only appreciable value

is that for the B_4 cluster, with a 4c-index of 0.12. Localized MO's are represented for systems of $4 - 10$ and $12 - 22$ valence electrons, giving a graphical sense to the discussion. The calculated I_{ABC} values show qualitative correlation with the energy of the interaction between the species into which a molecule is likely to dissociate. Particular striking are the 3c-bonds involving Be, in view of its closed-shell electronic configuration.

Ab initio (SCF and post-SCF) calculations have been performed in order to ascertain the stability and bonding of MXY^- ions ($M = H, Li, Na; X, Y = F, C\ell$) [90]. The authors expected to verify a previously given criterion for 3c-4e bonds [66]; actually, this criterion turns out not to be satisfied for nearly all the systems studied. They show instead high binding energy.

Kar [69] has examined the role of the central atom in 3c bonding for systems of the type $(ABA)^+$; using Mayer's model [67] for a symmetric 3c-bond with one orbital per atom, he obtains $I_{ABA'}$ as a function of the polarity p of the central atom ($p = q_B - 1$). The results for some systems of this kind apparently verify this trend. Within the limits $p = -1$ and $p = 1$, $I_{ABA'}$ increases up to 0.3 and then decreases.

Three series of dimers, $(LiXH_n)_2$, $(HBeXH_n)_2$ and $(H_2BXH_n)_2$ (where $X = H, Li, Be, C, N, O$ or F) have been calculated using *ab initio* methods [68]; electronegativity increases for X along each series. Three-center bonds $LiXLi$ and $BeXBe$ are found in the dimers of $LiXH_n$ and $HBXH_n$ ($X = H, Li, Be, B$ or C); BXB 3c-bonds are found in the dimers of H_2BXH_n ($X = H, Li, Be$ or B).

In another work about the structure and stability of $LiBH_2$ and $HBeBH_2$ dimers [91], it is concluded that the structure of these systems is due to 3c bonding; in particular, the planarity of the $LiBH_2$ dimer is essentially related with $HBLi$ 3c bonding ($I_{ABC} = 0.15$).

Another kind of 3c-bond which has deserved attention in the literature is the bridge in [1,1,1] propellane (C_5H_6) and other analogous systems [25,92-94]. In Ref. [94] an unusual 3c-2e CBC bond is postulated for $(1,5\text{-}C_2B_3H_5)$ and $(1,5\text{-}C_2B_3H_3)$. In Ref. [95] this bond is not found, there would be instead a weak BCB 3c-bond in $1,5\text{-}C_2B_2H_5$. The authors recommend the use of localized MO's and discuss this question.

As early as 1969, Harcourt [7] compared MO, IV and VB calculations for 3c bonds, arriving to the near-equivalence of MO and IV wavefunctions. To our knowledge, [11] is the first reference in literature to four-center bonding; more, the 4c-6e bond is introduced. We shall see in section 10 that we have found 4c bonds having betwen 5 and 7 electrons. It has also been supposed [12] that 4c-5e bonding units can be involved in the conduction mechanism of n-type semiconductors.

9. How many electrons are there in a three-center bond?

Of course, the answer depends of the model. Very few examples may be found in early MO literature which suppose that the π population is wholly on the bonds [96]. In the series of Ruedenberg et al. about the free-electron network model for conjugated systems [97, 98], tails appear when electrons are forced into the bonds, forbidding atoms to keep part of them. Now, if the self-charge is confined within the atoms, we would say that in a three-center bond ABC there are χ electrons [70]:

$$\chi = I_{AB} + I_{BC} + I_{AC} \tag{43}$$

and in a four-center bond $ABCD$

$$\chi = I_{AB} + I_{BC} + I_{CD} + I_{AC} + I_{AD} + I_{BD} \qquad (44)$$

Let us now examine χ for 3c-bonds; we find that χ is frequently neither 2 or 4.

We give in Table 4 the values of I_{ABC} and χ for a sample of systems. First of all, let us look at the results for $(FHF)^-$, the paradigm of (3c-4e) bonds. Supposing that fluorine furnishes one electron to the system, this is a (3c-4e) bond if an only if all the charge involved is active charge. Actually, χ for all hydrogen bonds, strong or not (including other ones not reported in the table) is approximately 1, while I_{ABC} is subject to large variations. Although we have found that the peptide bond NCO has I_{NCO} values of the same order of magnitude than those of strong hydrogen bonds [59], the corresponding χs give around 3 electrons.

Ozone too has $\chi \simeq 3$, although the predominant resonance structures would ascribe six electrons to it [99, p. 365]. From this and other results one might be tempted to double all χ values, obtaining numbers more in agreement with the Lewis model. A single but very important instance prevents this possibility. One of the paradigms of (3c-2e) bonds is H_3^+ [2], which has the most peculiar characteristic of being self-consistent $a\ priori$, in the terms of Ref. [39]; that is, any quantity calculated is independent from the basis used. Thus, $\chi = 1.333$ and $I_{ABC} = 0.296$ (only for a model retaining no charge on the atoms χ shall be 2). If χ is doubled, it yields and unacceptable results of 2.666.

The other usual pattern for a (3c-2e) bond is B_2H_6 [2]. Pauling [14, chap. 10, particularly 10.7] 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 Ref.[61], $I_{BHB'}$ is 0.234 (STO-3G), 0.215 4-31G) and 0.238 (6-31G*); from the values in Ref. [89] 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 are within the range 1.4-1.7, not reaching the predicted value 2.

The values obtained for χ in nitrous oxide N_2O are consistent with the previously obtained bond indices [23] which, in turn, agree with recent studies discarding the classical hypothesis of a pentavalent nitrogen [100]. The long $N-N'$ bond in N_2O_4 [101] is certainly related to the low value of $I_{NN'O}$, 5 to 6 times less than that of $I_{ONO'}$ reported in the table. As to χ, it is $\simeq 2$ for $(NN'O)$; accordingly, the "very long bond" NO index is almost zero.

We have seen that CO_2 and C_3 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.

We have chosen to include $(LiH)_2$ in Table 5, instead of putting it in Table 4, because its hydrogen bond is different from those of Table 4; it has a positive I_{ABC} value and χ is higher. The table shows also χ and I_{ABC} for $C\ell F_3$ and SF_4, where different 3c 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 entirely 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* basis, chemical intuition looses any reference frame with the introduction of diffuse functions; the very notion of an atom in a molecule is affected.

We may infer from Tables 4 and 5 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.

10. Bond valence and bond charge apportion

Both our model and Mulliken's suffer from the disadvantage of charge equipartition of the bond population between the two atoms involved [106, 107]; therefore, as we have already mentioned, they are more appropriate for covalent bonds than for ionic bonds. Different definitions have been proposed in order to overcome this problem; the best known at present is undoubtedly Bader's topological theory [46]. Refs. [107, 111] are worthwhile mentioning. In Extended Hückel approach [26] a weight is introduced in the off-diagonal terms of the Hamiltonian [112], in order to improve Mulliken population analysis. We ourselves have considered the problem twice [28, 113]. In the appendix of Ref. [23] we have returned to the definition proposed in [113], containing a weight factor involving the differences between the electronegativities of A and B. Anyway, we left it aside, for our results in other kinds of molecules were not satisfactory enough.

Let us return to eq. (28):

$$I_{AB} = \frac{1}{2} \sum_C I_{ABC} \tag{45}$$

where, as we have said, C must be allowed to be equal to A and B. It is curious that, although Sannigrahi and Kar, in Ref. [61], have written that for a triatomic molecule

$$I_{ABC} = 2I_{AC} - (I_{ACA} + I_{ACC}) , \tag{46}$$

in the following works they clearly drop out the quantities within parenthesis. Hence, actually, for any molecule (45) means

$$I_{AB} = \frac{1}{2}(I_{AAB} + I_{ABB}) + \frac{1}{2} \sum_{C \neq A,B} I_{ABC} \tag{47}$$

Similarly to expression (12), the first terms may be thought of as the self-charge of the bond, while the *bond AB valence V_{AB}* would be the active charge of the bond

$$V_{AB} = \sum_{C \neq A,B} I_{ABC} \tag{48}$$

We could even generalize

$$V_{ABC} = \sum_{D \neq A,B,C} I_{ABCD} \tag{49}$$

and so on, but here we shall restrict ourselves to use V_{AB} [1].

---

[1] In Ref. [114], what is called V_{AB}, valence of the AB bond, is actually I_{AB} and it is used for a study of reactions

Our expression (48) is different from that obtained if in our group valence V_G [115]

$$V_G = \sum_{\substack{A \in G \\ B \notin G}} I_{AB} \qquad (50)$$

the group is reduced to a bond AB:

$$V_{AB} = \sum_{C \neq A, B} (I_{AC} + I_{BC}) \qquad (51)$$

This last quantity corresponds to chemical intuition for a group valence and is always positive. Expression (48) gives us instead information about a bond's inclination to be involved in three-center bonding.

We cannot infer a meaning for the sign of V_{AB}, it remains still for us an open question. Thus, we can make no *a priori* distinction between positive and negative vaues of V_{AB}.

From eq. (48), in a triatomic molecule $V_{AB} = I_{ABC}$. It follows that $V_{AB} = V_{BC} = V_{AC}$; although this does not sound as entirely satisfactory, it is equivalent to charge equipartition in the usual 2c case.

What does I_{ABC} mean if C is equal to A or B? Let us postulate that in eq. (47) I_{AAB} and I_{ABB} are, respectively, the contributions of atoms A and B to the bond AB (remembering that I_{ABC} is invariant for any permutation of indices [59]). Thus, we offer a way out to the 2c-equipartition problem, for the self-charge *of a bond* is hence made of the *different* contributions of the two atoms involved.

We could, similarly, split I_{ABC} in 4c-indices and thus avoid the equipartition involved in V_{AB}; we choose to stop here.

We have shown that, despite the unquestionable success of *ab initio* methods, semiempirical MO calculations of the magnitudes that we study in this work are equally competitive. The results of the remaining tables have been obtained using CNDO/2 [30]. IEH [116] and MOPAC-PM3 [117].

Table 6 reports the main results for a few systems involving the CO_2 3c-bond. Once more, we verify that "long bonds" are most important. A significant I_{ABC} value is always parallel to an expressive I_{AC} index. For example, the IEH approximation gives a range of 0.52-0.57 for I_{23} between the corresponding oxygens for the systems in the table. The long-bond structures have been found to make a considerable contribution in advanced VB calculations [119]. It is well known that MO and VB calculations are equivalent at the same sophistication level [120, 121]. It is therefore satisfactory that both approaches predict an equally important role for "long bonds". Within each calculation method for the charged species there is a close agreement between the values of I_{123}, the bond self-charge and the CO bond valence. The difference between the results of charged and neutral systems may be partly due to the difference in geometry. However, it could be expected that the charges -1 and -2 would lead to a larger range of values than the one shown in the table. As expected oxygen, being more electronegative, allocates more bond self-charge than carbon. IEH seems to enhance I_{ABC} values and MOPAC exaggerates the differences between I_{AAB} and I_{ABB}.

The geometry for the isoelectronic NO and SN dimers is drawn in Fig. 4. Two different structures have been proposed for the NO dimer; the $cis-(C_{2v})$ structure (a)

and the rectangular C_{2h} one (b) [118, p.513]. The literature reports arguments favouring one or the other. The small $I_{NN'}$ value in (a) (~ 0.24) is due to the long NN' bond that, as in N_2O_4, has been underlined and partly ascribed to the repulsion between the nitrogen lone-pair electrons [101, 123]. In Table 7, the I_{123} index corresponds to an $NN'O$ 3c-bond for structure (a) and to an NON' 3c-bond for structure (b). Despite the fact that the geometry of both molecule is appreciably different, there is a remarkable agreement between the I_{123} values predicted by the three calculation methods for both structures. The 4c-indices are also quite close to each other and significant, of the same order of magnitude than several 3c-indices. The valence of nitrogen coincides in this case with χ_{123}. Although somewhat lower than usual values it remains, as expected, higher than V_0, which in turn keeps within the range $2.37 - 2.54$.

Table 8 shows results for the SN dimer, isoelectronic with the NO dimer. For this system only, we have included two other calculation options, both of them Extended Hückel without iteration: the first one with the same parameters than IEH, the second one with different parameters including d orbitals for sulfur [124]. It is seen that the inclusion or not of these orbitals makes most of the difference, for CNDO includes them for second-row atoms. Thus, CNDO results are qualitatively similar to those labelled EH2, except for the sign of I_{1234}. Instead, $I_{SNS'}$, and the 4c-index issuing from the other methods are much closer, respectively, to I_{123} and I_{1234} of Table 7. In this molecule, V_S coincides with $\chi_{SNS'}$, and V_N with $\chi_{NSN'}$. Of course, the inclusion of d orbitals increases sulfur's valence.

Not shown in the Table, there is also a high value for the secondary NN' bond, predicted in IEH (0.66) and MOPAC (0.42) results. For the EH1 calculation, the secondary SS' bond is more important than the secondary NN' one; the same thing happens when $3d$ orbitals are included in the sulfur basis. An STO-6G VB study [124] concludes that structures including $3d$ sulfur orbitals do not contribute substantially, while the structure involving the NN' long bond is dominant in the ground state.

Hydrazoic acid HN_3 is the subject of several works dealing with the problem of the central nitrogen's hypervalence (for example [100] and [126]). Ref.[100] makes an appealing distinction between geometric and electronic hypervalence, concluding that HN_3 can be considered geometrically but not electronically hypervalent, while Ref. [126] mentions $N_1N_2N_3$ as a (4e-3c) bond, meaning the four π electrons from the three nitrogens. We show our results in Table 9. We obtain a somewhat-more-than-four-electrons-3c bond, our electrons being $(\sigma + \pi)$, for part of them are kept by the atoms as self-charge. As [100], we predict for the central nitrogen a valence near to 4, while N_1 and N_3 have a valence around 3. The "long bond" N_1N_3 is of course responsible for this last result. The values for bond valences are noteworthy, for the three calculation methods bonds N_1N_2 and N_2N_3 have very close valences, while the bond self-charges are fairly different.

In Ref. [126], VB hybridization values are assigned to the atomic hybrid orbitals h of each nitrogen, through the formula $h = s + \lambda p$:

for N_1, in the N_1N_2 bond $h = s + 2.8p$

for N_2, in both bonds $h = s + p$

for N_3, in the N_2N_3 bond $h = s + 1.41p$

As the electronegativity increases with increasing s character, this would yield $I_{122} > I_{112}$ and $I_{223} > I_{233}$, in agreement with CNDO and IEH results in Table 9. The MOPAC results invert the first relation and predict equipartition in the second one. The 4c index is higher than other 3c-ones not shown in the Table and the methods show a qualitative agreement.

Cyanopolyynes (HC_nN) form an appealing family of compounds, from which a recent study has picked HC_6N [127]; we have in turn chosen from this study the three most probable structures, shown in Fig. 5, and reported our most significant results for indices and bond valences in Table 10.

The most striking of them is I_{ABC} for the C_3 ring in (a) and (b). Despite the difference in the groups at each side of the double bond, its bond self-charge roughly obeys equipartition; for the single bond, instead, the carbon with an electron lone pair contributes clearly less than the other one to the bond self-charge.

For the sake of comparison, we have calculated $|I_{ABC}|$ for the strained 3c rings of cyclopropene and $(CH_2)_2X(X = CH_2, NH, O, S, SO$ and $SO_2)$. It is generally lower than 0.06 in CNDO, than 0.03 in IEH and lower than 0.01 in MOPAC. CNDO gives $\chi \simeq 3$ for all but cyclopropene. Cyclopropene's value for χ is ~ 4 in the three approximations as expected, due to the π electrons. It is known that the S series (ethylene sulfide, episulfoxide and episulfone) is anomalous in the $C - S, S - O$ an $C - C$ distances [128, 129]. The structural anomalies are reflected in our I_{ABC} values. CNDO results for χ are not monotonous, while IEH's and MOPAC's decrease along the series.

For structure (c), the C_5C_6 and C_6C_7 bonds are both double bonds at first sight; actually, however, C_5C_6 is a somewhat-less-than-double bond (1.357Å) and C_6C_7 a somewhat-more-than-double one (1.301Å), the former having a bond valence lower than the last one. The partition of charge is different for both bonds, more emphasized by MOPAC.

The absolute values of I_{1234} for (a) and (c) are very high and correspond to a bond sequence triple-single-triple. The values of I_{123} and I_{234} for (a) and (c) are low; this is due to the lack of the corresponding "secondary bonds" 1-3 and 2-4. Let us underline that the I_{1234} values for (a) and (c) are similar to significant three-center indices such as those of strong hydrogen bonds and peptide bonds of Tables 2 and 3. $|I_{1234}|$ for (b) and other $|I_{ABCD}|s$ for the three molecules that do not appear in the table, have values within the range 0.05-0.10, including different kinds of multiplicity in the bond sequences.

The (1234)-bond would be for (a) and (c) *a priori*, according to our model, a (4c-7e) bond; the corresponding χs are somewhat less than 7. Ref. [11] introduces (4c-6e) systems. In (b) the bond would be a (4c-6e) one; actually, χ is ~ 5.5.

Table 11 shows results for the most typical monosubstituted benzenes. The apportion of bond self-charge in the CX bond is consistent for CNDO and IEH, while MOPAC predicts inverted behaviour in benzene and toluene and bond self-charge equipartition for aniline. In toluene the bond concerned may be considered to be $C(sp^2) - C'(sp^3)$; as such, due to the difference in electronegativity, an electronic displacement towards the ring is produced. For phenol and fluorobenzene the more electronegative atom again contributes more to I_{CX}. The bond valence V_{CX} is quite small for benzene and toluene; this means that the CX bond is practically not involved in multicenter bonding, while the other compounds evidence some degree of partititon.

For the ring index, agreement between the three calculation methods is very close.

The index value is significant and quite similar for the five molecules. It is tempting to associate this behavior to the similar corresponding values of the conjugation energy (within 8% [130]).

Table 12 reports the ring 6c-index for a few standard pattern rings. Benzene and pyridine, which are known to have similar aromaticity, have equal values of I^2. Borazine has physical properties similar to benzene's, its chemical properties are instead different and they suggest little aromatic character [118, p.238]. Even if MOPAC-PM3 does not provide parameters for boron, the CNDO and IEH values are clearly lower than those of benzene and pyridine.

The last decades have seen an ever growing interest in unsaturated sulfur-nitrogen compounds, of which the $(S_3N_3)^-$ ring system is a prototype [131]. This is a 10 π-electron six-membered ring [132]. It has been recently concluded that this kind of electron-rich systems have weak aromaticity, their bonding strength decreasing with respect to the 6 π-electrons counterparts [133]. It is therefore satisfactory that the $(S_3N_3)^-$ ring indices in the Table are two orders of magnitude lower than benzene's or pyridine's and also much lower than borazine's.

11. Concluding remarks

We give in this work a panoramic view of multicenter bonds and an MO expression of the corresponding indices, for closed-shell systems in the single-determinant Hartree-Fock approximation. We describe first the model dealt with for usual two-center bonds.

The tensor notation is particularly useful in order to manifest the invariant properties required from any quantity intending to have a chemical meaning. Grassmann algebra is shown to be a powerful alternative formulation of the wave function antisymmetry description.

Multicenter bond indices are defined from the first-order density matrix. Bond indices (of two or more atomic centers) mean the correlation between the fluctuations of the atomic charges from their average values. "Secondary bonds" or "long bonds" play a substantial role in multicenter bonds. Three center bond indices clearly distinguish between strong and normal hydrogen bonds; the indices for peptide bonds are of the same order of magnitude as those of strong hydrogen bonds.

The number of electrons involved in three-center bonds is fractionary and ranges from about 1 to somewhat more than 4.

In the same way that the valence of an atom issues from the definition of bond index, the three-center bond index lends itself to the definition of a bond valence, reflecting the inclination of the bond to be involved in three-center bonding.

The bond self-charge apportion corrects the equipartion in the two-center index. The apportion is such that the more electronegative atom tends to keep a greater amount of electrons in the bond than the other atom.

Four-center bond indices are usually lower than three-center ones. However, we show possible structures for a cianopolyyne where an index I_{ABCD} involving two triple bonds is of the same order of magnitude than other significant I_{ABC} values.

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[2]The 6c- I value of pyridine in Ref. [59] is wrong.

The six-center ring index in benzene, monosubstituted benzenes and other six-center rings may be related to aromaticity.
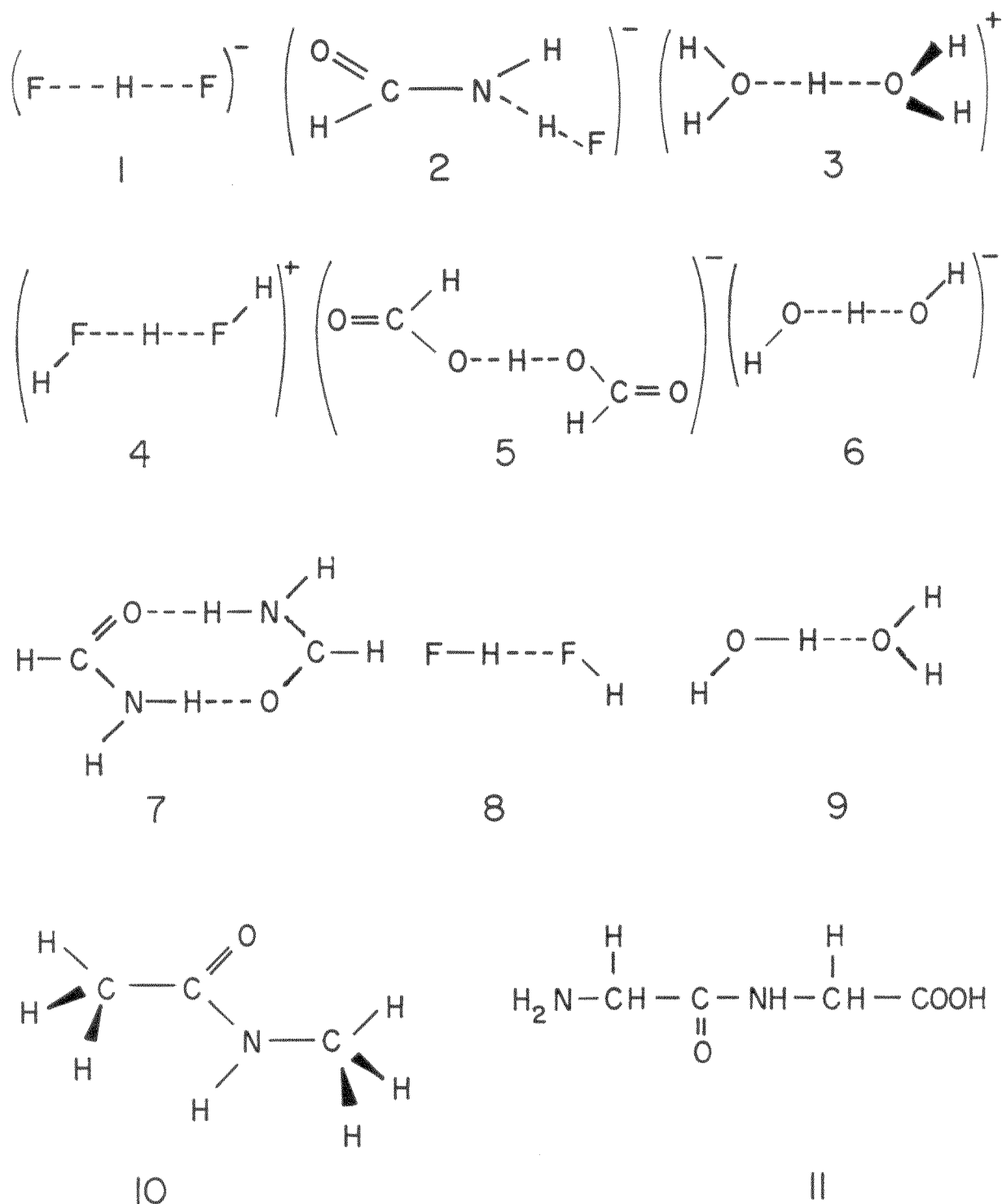
Figure 1. Systems appearing in Table 2 and 3. In each one, we have indicated the reference from which the geometry is taken. 1, hydrogen difluoride ion [75]; 2, formamide-fluoride ion [72]; 3, protonated H_2O dimer [76]; 4, protonated HF dimer [77]; 5, biformate anion [78]; 6, protonated dihydroxyl [79]; 7, cyclic formamide dimer [80]; 8, FH dimer [81]; 9, H_2O dimer [82]; 10, *N*-methyl acetamide [83]; 11, glycine dipeptide [85].
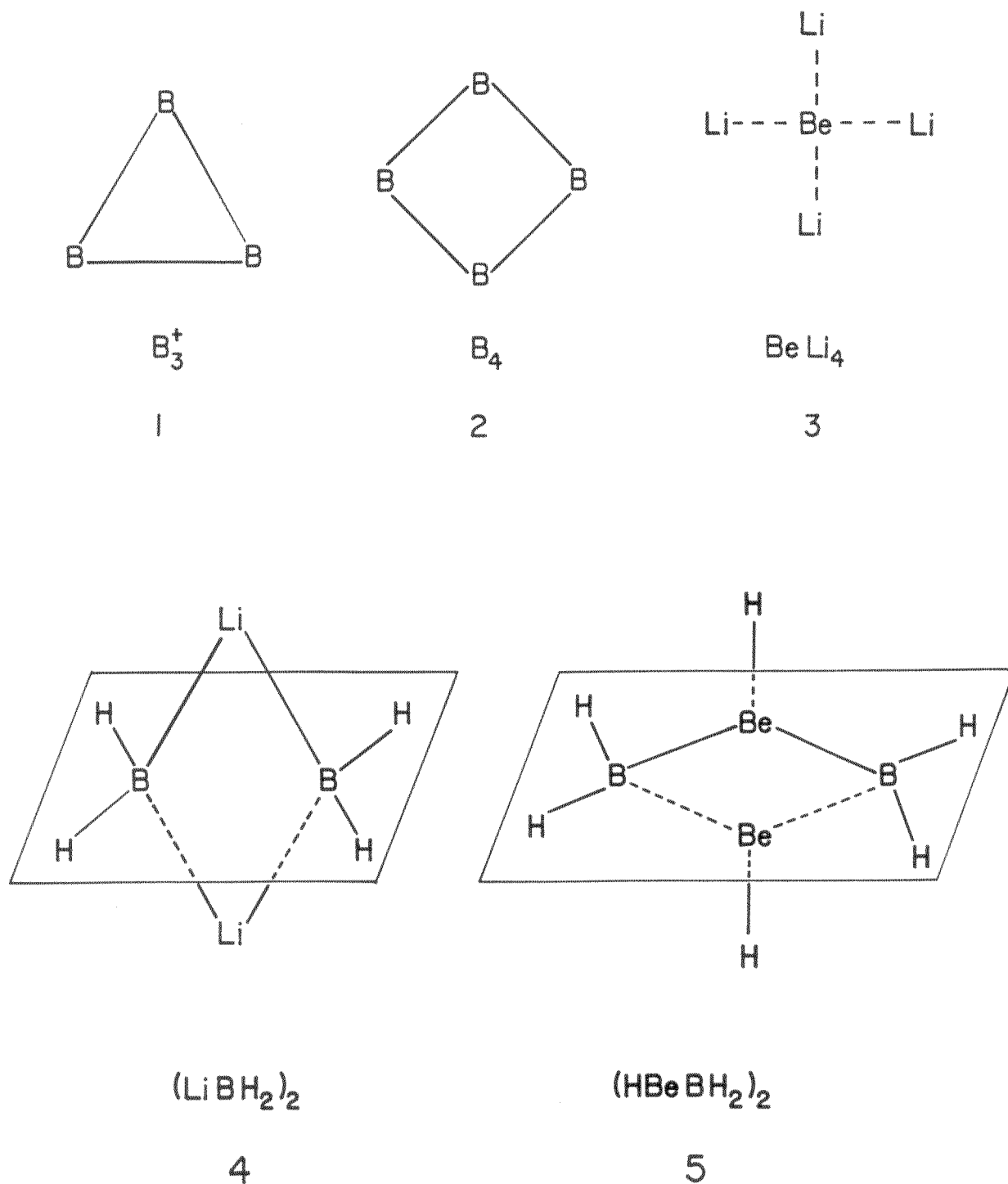
Figure 2. Some of the molecules with significant I_{ABC} or I_{ABCD} mentioned in section 8. See [89] for 1, 2, 3 and [91] for 4, 5.
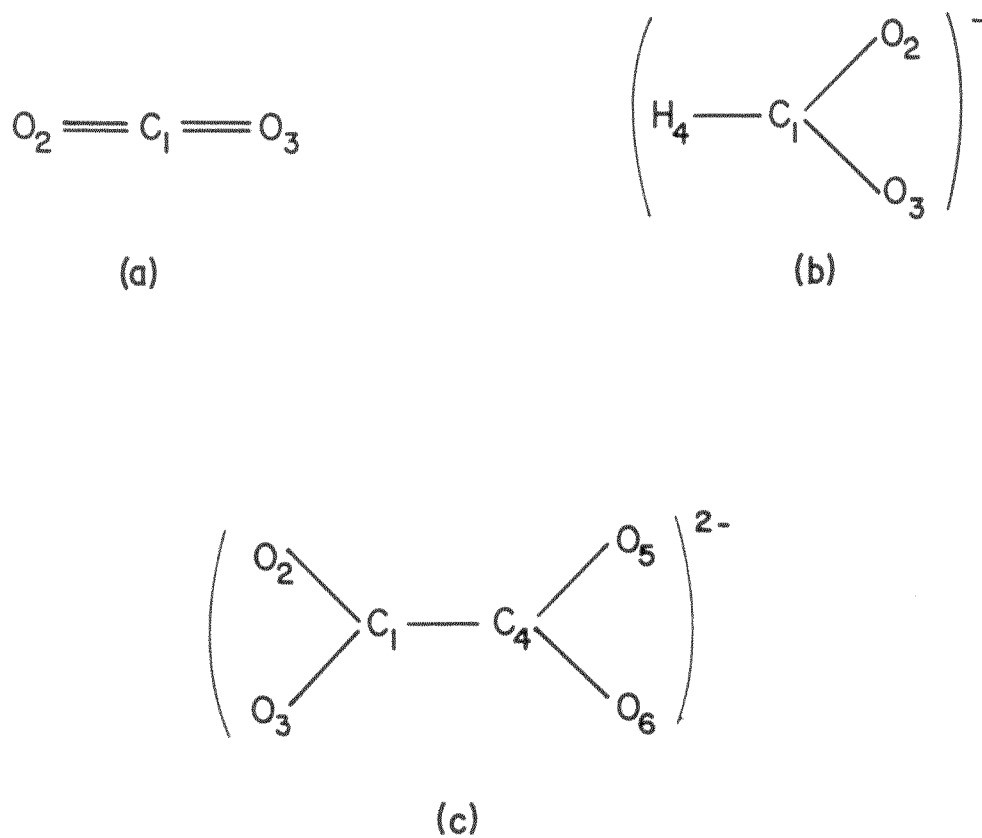
Figure 3. Systems containing the CO_2 3c-bond. Geometries from: (a)[14, p.267]; (b) optimized through MOPAC-PM3; (c)[118, p.523]. All distances in Å.
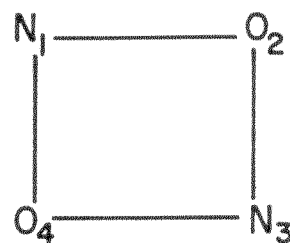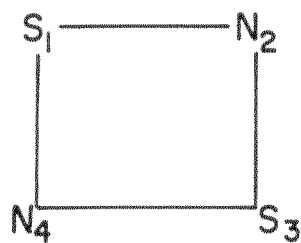
Figure 4. Conformations for the NO and SN dimers.(a) and (b) from [118, p.513]; (c) [122] All distances in Å.
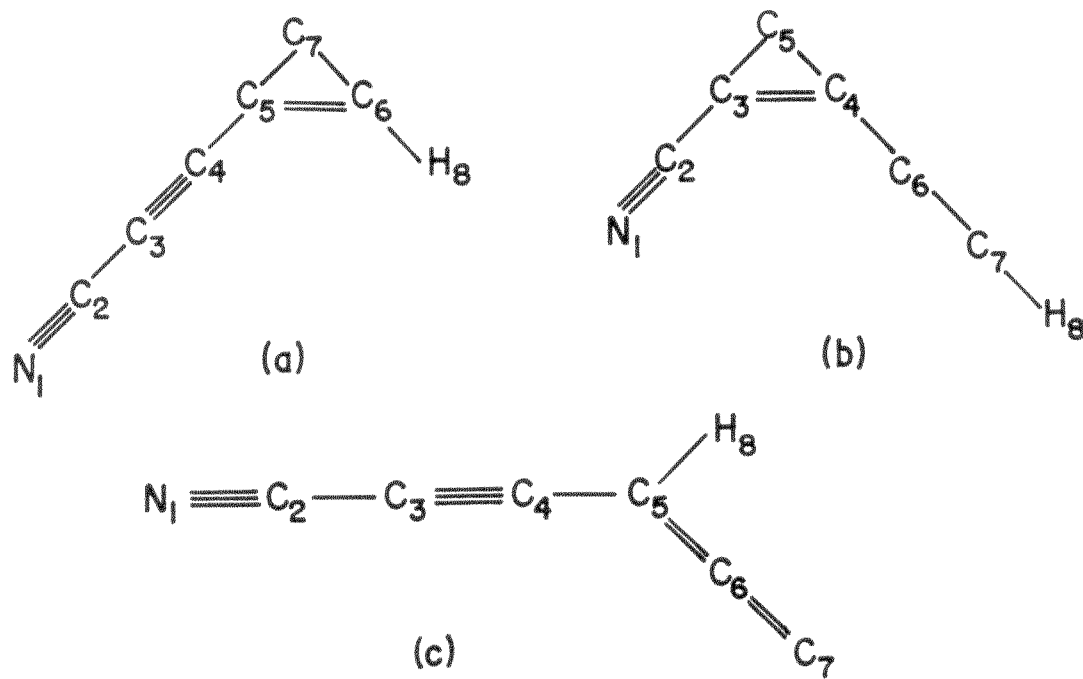
Figure 5. The most probable structures for HC_6N [127].

Table 1: Three-center bond index I_{ABC} and secondary bond-index (I_{AC}) for a sample of systems, calculated following different approximations. See the corresponding references for geometries. [a][59]; [b][61]; [c][66]; [d][70].

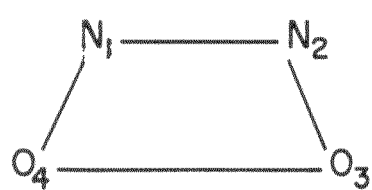| System	ABC	CNDO	IEH	STO-3G	STO-6G	4-31G	6-31G*
H_2O	HOH'	0.000[a]		0.004[a]	0.004(0.011)[a]	-0.006(0.001)[b]	-0.008(0.004)
H_2O_2[a]	$OO'H$	-0.002		0.001	0.001(0.010)		
F_2O[a]	FOF'	-0.019		-0.031	-0.031(0.042)		
O_3	$OO'O''$	-0.286[a]	-0.278[d]	-0.346[d]	-0.326(0.503)[c]		
CO_2	OCO'	-0.352[a]	-0.546[d]	-0.444[a]	-0.444(0.295)[a]		-0.224[c]
C_3	$CC'C''$	0.456[d]	0.497[a]	0.407(0.364)[d]		0.359(0.304)[b]	0.315(0.281)[b]
N_2O	$NN'O$	-0.344[a]	-0.532[d]	-0.455[a]	-0.454(0.581)[a]		
B_2H_6	BHB'	0.276[d]	0.241[d]	0.234(0.520)[b]		0.215(0.482)[b]	0.238(0.515)[b]
$(LiF)_2$[b]	$LiFLi'$ $FLiF'$			0.098(0.109) -0.034(0.041)		0.061(0.025) -0.0077(0.002)	0.012(0.022) -0.004(0.0)
O_2NNO_2	ONO'	-0.268[a]		-0.358[a]	-0.358(0.436)[a]		
O_2NONO_2	ONO'	-0.230[a]		-0.315[a]	-0.314(0.391)[a]		
FNO_2	ONO'	-0.236		-0.318	-0.318(0.414)		

Table 2. Three-center hydrogen bond index I_{XHY}, calculated following different approximations (see Fig. 1) . ΔE, hydrogen bond energy, each one with its reference source.

System	$-I_{XHY}$			$\Delta E(kJmol^{-1})$	Ref.
	CNDO	STO-3G	STO-6G		
1	0.171	0.227	0.224	214	72
2	0.089	0.110	0.110	148	72
3	0.118	0.123	0.123	135	76
4	0.094	0.105	0.102	128	77
5	0.146	0.147	0.145	123	78
6	0.175	0.191	0.189	105	79
7	0.006	0.018	0.016	31.8	80
8	0.005	0.013	0.011	18.8, 25.1	81,73
9	0.005	0.015	0.014	20.2, 20.9	82,74

Table 3: Three-center bond index I_{OCN} for selected peptide bonds calculated following different approximations (see Fig. 1). The geometry of formamide is taken from Ref. [84]; for the glycine unit it is the same than that of Ref. [85].

System	$-I_{OCN}$		
	CNDO	STO-3G	STO-6G
Formamide	0.161	0.184	0.183
Formamide-fluoride ion	0.199	0.267	0.267
N-methyl acetamide	0.228	0.177	0.177
Glycine dipeptide	0.155	0.170	0.170

Table 4: Three-center bond index I_{ABC} and number of electrons χ for a sample of systems, calculated following different approximations. Geometries as in Refs. [59] and [70].

System	ABC	IEH		CNDO		STO-3G		STO-6G	
		I_{ABC}	χ	I_{ABC}	χ	I_{ABC}	χ	I_{ABC}	χ
$(FHF)^-$	FHF'	-0.231	1.210	-0.171	1.065	-0.227	1.201	-0.223	1.194
$HOHOH)^-$	OHO'	-0.248	1.240	-0.175	1.079	-0.191	1.117	-0.189	1.112
$(FH)_2$	FHF'	-0.096	1.037	-0.005	0.946	-0.013	0.961	-0.011	0.954
$(H_2O)_2$	OHO'	-0.052	1.014	-0.005	0.981	-0.015	0.963	-0.014	0.954
Formamide	NCO	-0.224	3.143	-0.161	3.136	-0.184	3.151	-0.183	3.146
Gly.Gly	NCO	-0.208	3.081	-0.155	3.022	-0.170	3.090	-0.170	3.087
O_3	$OO'O''$	-0.278	3.235	-0.286	3.130	-0.346	2.831	-0.326	3.205
N_2O	$NN'O$	-0.532	4.521	-0.344	4.232	-0.455	4.197	-0.454	4.194
N_2O_4	ONO'	-0.292	3.382	-0.268	3.319	-0.358	3.524	-0.358	3.523
CO_2	OCO'	-0.546	4.459	-0.352	4.134	-0.444	4.326		
C_3	$CC'C''$	0.497	4.474	0.456	4.421	0.407	4.315		

Table 5. Number of electrons χ and 3c-bond index I_{ABC} for $(LiH)_2$, ClF_3 and SF_4, calculated following different approximations. The geometry of $(LiH)_2$ is taken from [102], that of ClF_3 from [103], and that of SF_4 from [104]. The subindices a and e stand respectively for axial and equatorial. [a][61]; [b][105]; [c][66].

	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	0.999	-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

Table 6. Systems containing the CO_2 3c-bond. See Fig. 3 for geometries and labelling.

		CNDO	IEH	MOPAC
(a)	I_{123}	-0.352	-0.544	-0.348
	χ_{123}	4.134	4.474	4.106
	I_{112}	1.672	1.854	1.663
	I_{122}	2.525	2.590	2.489
	V_{12}	-0.352	-0.544	-0.348
(b)	I_{123}	-0.211	-0.357	-0.223
	χ_{123}	3.236	3.331	3.148
	I_{112}	1.394	1.408	1.281
	I_{122}	1.931	1.754	1.943
	V_{12}	-0.263	-0.386	-0.261
(c)	I_{123}	-0.211	-0.323	-0.215
	χ_{123}	3.111	3.217	3.095
	I_{112}	1.322	1.344	1.251
	I_{122}	1.842	1.701	1.915
	V_{12}	-0.236	-0.352	-0.250
	V_{14}	-0.069	-0.171	-0.115

Table 7. *NO* dimers (see Fig. 4). For (b), $V_{23} = V_{12}$.

	(a)			(b)		
	CNDO	IEH	MOPAC	CNDO	IEH	MOPAC
I_{123}	-0.138	-0.146	-0.145	-0.142	-0.145	-0.147
χ_{123}	2.890	2.829	2.835	2.706	2.756	2.763
I_{234}	-0.044	-0.070	-0.057	-0.101	-0.093	-0.087
χ_{234}	2.371	2.469	2.397	2.539	2.536	2.504
I_{112}	0.716	0.608	0.662	0.344	0.331	0.320
I_{122}	0.716	0.608	0.662	0.384	0.383	0.380
I_{223}	1.889	1.874	1.834	2.665	2.686	2.639
I_{233}	2.553	2.637	2.599	1.822	1.843	1.860
I_{1234}	0.032	0.046	0.040	0.059	0.057	0.054
V_{12}	-0.277	-0.293	-0.290	-0.243	-0.238	-0.233
V_{23}	-0.182	-0.216	-0.202			

Table 8. *SN* dimer (see Fig. 4). (*) Non-iterated option in Ref. [116]. (**) Non-iterated option. Parameters inclusing $3d$ orbitals for sulfur [124]

	CNDO	IEH	MOPAC	EH1[*]	EH2[**]
$I_{SNS'}$	-0.184	-0.042	-0.110	-0.137	-0.228
$V_S = \chi_{SNS'}$	3.857	2.406	2.653	2.664	4.341
$I_{NSN'}$	-0.028	-0.152	-0.171	-0.111	-0.052
$V_N = \chi_{NSN'}$	3.082	2.959	2.852	2.486	3.135
$I_{SS'N}$	1.144	1.323	1.341	0.984	1.033
$I_{NN'S}$	1.635	1.171	1.372	1.567	1.785
I_{1234}	-0.016	0.033	0.060	0.060	0.020
V_{SN}	0.156	-0.193	-0.280	-0.248	0.176

Table 9. Hydrazoid acid ($N_1=N_2-N_3-H_4$). Geometry from [99], p. 340.

	CNDO	IEH	MOPAC
I_{123}	-0.300	-0.467	-0.327
χ_{123}	4.153	4.386	4.261
I_{1234}	-0.045	-0.026	-0.039
χ_{1234}	5.145	5.382	5.245
V_{12}	-0.312	-0.483	-0.345
V_{23}	-0.288	-0.452	-0.307
V_1	2.813	2.973	2.855
V_2	3.848	3.678	3.925
V_3	2.637	3.116	2.727
I_{112}	2.466	2.217	2.713
I_{122}	2.752	2.680	2.563
I_{223}	1.6562	1.769	1.600
I_{233}	1.416	1.591	1.605

Table 10. Some multicenter indices for the structure of HC_6N shown in Fig. 5. Geometry from Ref. [127]

		CNDO	IEH	MOPAC
(a)	I_{123}	-0.012	-0.043	-0.003
	χ_{123}	3.987	3.948	3.952
	I_{234}	0.014	0.014	0.009
	χ_{234}	3.820	3.699	3.828
	I_{567}	0.279	0.217	0.241
	χ_{567}	3.987	3.829	4.015
	I_{556}	1.336	1.394	1.508
	I_{566}	1.337	1.386	1.429
	I_{557}	1.189	1.101	1.339
	I_{577}	0.889	0.801	0.785
	I_{1234}	-0.154	-0.215	-0.113
	χ_{1234}	6.783	6.601	6.802
	V_{56}	0.257	0.183	0.214
	V_{57}	0.298	0.250	0.247
(b)	I_{123}	-0.017	-0.033	0.005
	χ_{123}	3.978	3.927	3.931
	I_{345}	0.265	0.203	0.231
	χ_{345}	3.868	3.646	3.919
	I_{334}	1.275	1.307	1.467
	I_{344}	1.251	1.291	1.383
	I_{445}	1.239	1.170	1.319
	I_{445}	0.937	0.873	0.792
	I_{1234}	-0.066	-0.095	-0.050
	χ_{1234}	5.444	5.419	5.521
	V_{34}	0.250	0.157	0.181
	V_{45}	0.321	0.231	0.244

Table 10. (cont.)

		CNDO	IEH	MOPAC
(c)	I_{123}	-0.003	-0.022	0.001
	χ_{123}	3.987	3.946	3.953
	I_{234}	0.013	0.019	0.008
	χ_{234}	3.805	3.727	3.828
	I_{567}	0.166	0.131	0.176
	χ_{567}	4.035	3.924	3.914
	I_{556}	1.545	1.585	1.380
	I_{566}	1.561	1.524	1.770
	I_{667}	2.422	2.271	2.564
	I_{677}	1.860	1.843	1.417
	I_{1234}	-0.154	-0.219	-0.114
	χ_{1234}	6.764	6.6392	6.804
	V_{56}	0.156	0.111	0.146
	V_{67}	0.202	0.189	0.208

Table 11. Monosubstituted benzenes. Geometries of 1, 2 and from [85]. Geometries of 3,4 optimized by MOPAC-PM3. X means respectively H', C', N, O and F. I(ring) is the 6c-index.

	I_{CXX}, I_{CCX}			V_{CX}			I(ring)		
	CNDO	IEH	MOPAC	CNDO	IEH	MOPAC	CNDO	IEH	MOPAC
Benzene	0.957	0.963	1.064	-0.0081	-0.0017	0.0015	0.0888	0.0894	0.0883
	0.964	0.986	0.868						
toluene	1.039	1.010	0.932	0.0054	0.0027	-0.0005	0.0850	0.0872	0.0864
	1.020	1.053	1.053						
aniline	1.194	1.314	1.115	-0.0585	-0.1199	-0.0799	0.0825	0.0782	0.0797
	0.951	0.950	1.113						
phenol	1.245	1.359	1.258	-0.0819	-0.1395	-0.0935	0.0829	0.0786	0.0807
	0.861	0.812	0.954						
fluoro-benzene	1.262	1.358	1.220	-0.0874	-0.1446	-0.0768	0.0840	0.0798	0.0841
	0.745	0.663	0.893						

Table 12. Six-center ring index for typical systems

System	I(ring)		
	CNDO	IEH	MOPAC
benzene	0.0888	0.0894	0.0883
pyridine	0.0880	0.0879	0.0875
borazine	0.0384	0.0547	–
$(S_3N_3)^-$	0.0054	0.0017	0.0078

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