Some Considerations About Bond Indices in Non-orthogonal Bases and the MO Calculation of Valence and Oxidation Number

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In order to guarantee the desired invariance properties of bond indices, we show the importance of expliciting the tensor character of the matrices concerned, so as to deal with a contraction in the tensor sense between a covariant index and a contravariant one. A straightforward definition of oxidation numbers is proposed. IEH calculations of valence and oxidation numbers for some appropriate examples are performed: they emphasize the role of "secondary" bonds in N and C-containing compounds; the hydrogen behaviour in half-bonds and strong H-bonds is satisfactorily accounted for; valence and oxidation number values are assigned to Fe, Co and Ni in a few complexes.

1. Introduction

The early π definition of Coulson bond order [1] was intended for the Hückel MO approximation. Under introduction of overlap, two generalizations were proposed by Chirgwin and Coulson [2] and by Löwdin [3]. The bond charge and overlap population concepts [4, 5] may be related to the X-ray evidence of an accumulation of charge along the bonds, even if there exists a recent warning in the sense that electron-rich atoms may exhibit a deficit in bond density [6].

When all valence electron methods were introduced, the non-orthogonal approximation (EH, IEH) with the three mentioned formulations, gave rise to different orbital-orbital bond order matrices. For CNDO and variations of it, the density matrix was the charge-bond order matrix. Neither of the methods met difficulties in the calculation of atomic charges, while difficulties did appear when some kind of measure of the bond between atoms A and B was attempted. The orbital-orbital matrix must be reduced to a smaller atom-atom matrix, and this is straightforward only for the Mulliken population analysis, which remains the most accepted alternative even in *ab initio* approaches.

As, however, the overlap population disappears for orthogonal bases, Wiberg indices have been introduced in this approximation [7]; they may in turn be generalized to non-orthogonal bases, as an option to the Mulliken population analysis [8].

We show here that the same ideas which lead to an MO definition of valence [9, 10, 11] may be easily adapted to calculate oxidation numbers. In order that each atomic orbital contributes with a certain weight factor in building the bond index [12], we impose certain requirements on this weight.

To discuss the tensor character of the matrices involved, we present a unified formulation of the above mentioned bond populations. Bond indices are usually required to fulfil certain invariance properties. For these to hold, the transformations should involve a contraction in the tensor sense, with subscripts and superscripts indicating unequivocally the correct variances. We show that the reduction of the orbital-orbital matrix to an atom-atom matrix, when using non-orthogonal bases, must be carried out according to the definition of tensor contraction.

Finally, we apply the valence and oxidation number definitions to some compounds in an IEH calculation. We choose as our examples molecules with "secondary" bonds, strong hydrogen bonding and a few transition metal complexes.

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2. Bond Index, Valency and Oxidation Number

Some years ago, an MO definition of valence V was proposed [9, 10], utilizing Wiberg's bond indices W_{AB} between atoms A and B [7], in CNDO calculations:

$$V_A = \sum_{B \neq A} W_{AB}. \tag{1}$$

This expression was introduced at the same time [13], in IEH calculations with Löwdin orthogonalization. It involves bond indices both between bonded atoms and not formally bonded ones. Recently, this approach to the valency concept has been reproposed [14, 15]. In these and other works [16], valency is extensively applied to molecules containing elements of the first and second rows of the periodic table.

Quantum mechanically, thus, valency ceases to appear as an integral number. With expression (1), it is possible to give a quantitative estimate of valency in cases where classically it would be difficult to do so, such as bridge-linked hydrogen or transition metal complexes.

References [9, 13, 14] deal with orthogonal (or orthogonalized) bases, for which Wiberg indices are intended. As Mulliken's overlap population reduces to zero in this approximation, we have shown [8] that, when using a non-orthogonal basis, the Wiberg indices must be compared with a suitable generalization, different from Mulliken's population analysis. A unified presentation of these populations is now required, to be able to compare the various indices.

As has been remarked [14], Wiberg makes use of the density matrix **P**. When the basis set is not an orthogonal set, it is known [17] that, if **S** is the overlap matrix, the first order density matrix is **PS**. For closed shell problems (i.e. for which the wavefunction is represented by a single Slater determinant) we find useful to define a matrix **Π** such that

$$\mathbf{PS} = 2\,\mathbf{\Pi}. \tag{2}$$

If a is an orbital centered on atom A, b one centered on atom B, and x_{ia} the coefficient of a in the i-th wavefunction of a doubly occupied level, we have

$$\Pi_{ab} = \sum_i x_{ia} y_{ib} = \sum_i \sum_c x_{ia} x_{ic} S_{cb}. \tag{3}$$

Let us underline that **Π** is not a symmetric matrix and $\mathbf{\Pi}^{\dagger}$ is an equally valid expression for the density matrix. Both are idempotent [18]:

$$\mathbf{\Pi}^2 = \mathbf{\Pi}; \quad (\mathbf{\Pi}^{\dagger})^2 = \mathbf{\Pi}^{\dagger} \tag{4}$$

and we shall see that this property is worth being exploited.

The orbital-orbital Mulliken matrix **M**

$$M_{ab} = 2P_{ab} S_{ab} \tag{5}$$

is not the density matrix for non-orthogonal bases, for it is not **PS**.

Chirgwin and Coulson define, for the bond order matrix, the symmetric part of **PS** [2]; in AVE calculations, *it does not lend itself to contraction.* We have proposed an alternate way to build an orbital-orbital symmetric matrix [8, 12]:

$$I_{ab} = 4\Pi_{ab}\Pi^{\dagger}_{ab} = 4\Pi_{ab}\Pi_{ba} \tag{6}$$

which, when contracted, is the appropriate generalization of the Wiberg bond index W_{AB}. **W** is the atom-atom matrix obtained contracting the density matrix as follows:

$$W_{AB} = \sum_{a \in A} \sum_{b \in B} P^2_{ab}. \tag{7}$$

The analogous atom-atom matrix obtained from **PS** is [8, 12]

$$I_{AB} = 4 \sum_{a \in A} \sum_{b \in B} \Pi_{ab}\Pi_{ba} \tag{8}$$

which has the desired properties. It has been shown that, for closed shell systems [19]

$$\sum_{b \neq a} P^2_{ab} = 2q_a - q^2_a, \tag{9}$$

$q_a = P_{aa}$ being the electronic charge in orbital a. This is easily generalized to non-orthogonal cases [11, 20]

$$4 \sum_{b \neq a} \Pi_{ab}\Pi_{ba} = 2q_a - q^2_a \tag{10}$$

where q_a is the Chirgwin-Coulson charge

$$q_a = 2 \sum_i x_{ia} y_{ia} \tag{11}$$

which for closed shells we have shown to be equal to that arising from **Π** [8]:

$$q_a = 2 \sum_c \Pi_{ac}\Pi_{ca}. \tag{12}$$

Expression (9) goes to zero if $q_a = 2$ or 0 (lone-pair or empty orbital) and is maximum for $q_a = 1$. It seems then an appropriate measure of the extent to which an atomic orbital shares its q_a electrons [7, 14]. Hence, so is (10).

If N_A is the number of valence electrons which atom A furnishes to the molecule, and q_A the electronic charge in A:

$$q_A = \sum_{a \in A} q_a \tag{13}$$

then its charge Q_A will be

$$Q_A = N_A - q_A . \tag{14}$$

Equation (13) may also be written as

$$q_A = (1/2) \sum_{B} I_{AB} = (1/2)\, I_{AA} + (1/2) \sum_{B \neq A} I_{AB} \tag{15}$$

which emphasizes the separation of the total charge of an atom among its self-charge and its active charge [21] distributed along both the effective and the formal bonds which link it to the other atoms in the molecule. The extension of formula (1) to non-orthogonal bases leads to a valence [11]

$$V_A = \sum_{B \neq A} I_{AB} \tag{16}$$

which is twice the atom's active charge. If (10) is written in terms of active charge for an atom contributing only one orbital to the basis, we shall have

$$q_A - q_A^2/2 = (1/2) \sum_{B \neq A} I_{AB} . \tag{17}$$

That is, the active charge will be close to 0.5 for atoms like hydrogen which have $q_A \simeq 1$ [8, 22].

Due to the idempotency of the density matrix, it is easily seen that q_A in (13) and (15) *coincides with Mulliken's gross atomic population, with a quite different partition of self-charge and active charge.* As Mulliken's atomic population is the expectation value of the atomic charge operator for any LCAO-type wavefunction [11, 17], this important property is thus preserved. The present bond population gives results according to the classical expectations [8, 18]. For instance, CH_4 has an I_{CH} value of 0.999 in the IEH approximation, while the Mulliken overlap population is 0.794 [23].

It is tempting to relate the generalized bond indices I_{AD} to another classical concept, namely the oxidation number Ξ_A of atom A, which we define as

$$\Xi_A = (|Q_A|/Q_A) \sum_{D} I_{AD} , \tag{18}$$

where Q_A is the net charge in A and the sum is carried out over the atoms with polarity different from that of atom A. It is understood that if $Q_A = 0$, $\Xi_A = 0$.

This definition, appropriate for neutral species, ensures that oxidation numbers in a molecule add up to zero. We shall see (Sect. 4) that in usual cases the fractional values obtained are close or equal to the integrals predicted in classical approaches. Despite the difficulty which arises in the balance of oxidation-reduction equations, it permits to assign an oxidation number in cases *a priori* ambiguous. Expression (18) is more simple and straightforward than the appealing *ab initio* approach to oxidation numbers which has been recently published [24]. Contrary to that study, our expression (18) may lead to dramatic changes in oxidation numbers, as happens classically. Small variations of electronic densities may switch the polarities and yield very different oxidation numbers. We shall see in the discussion that in a few cases this happens for different calculations of the same molecule.

The introduction of a weight factor in our bond index I [12] (see Appendix), together with a suitable parameterization, may avoid negative bond and orbital populations.

Let us introduce a weight factor ω_{ab} in expression (8):

$$I_{AB} = 4 \sum_{a \in A} \sum_{b \in B} \Pi_{ab} \Pi_{ba} \omega_{ab} . \tag{19}$$

We define orbital and atomic charges

$$q_a = \sum_{c} \omega_{ac} \Pi_{ac} \Pi_{ca}; \quad q_A = \sum_{a \in A} q_a \tag{20}$$

which are no more equal to the Chirgwin-Coulson ones.

Let us write ω_{ab} in the form

$$\omega_{ab} = \Omega_a + \Omega_b . \tag{21}$$

In an N-electron system, we must have:

$$\sum_{a, A} q_a = N . \tag{22}$$

Hence, by (20)

$$\begin{aligned} \sum_{a,c} \omega_{ac} \Pi_{ac} \Pi_{ca} &= \sum_{a,c} (\Omega_a \Pi_{ac} \Pi_{ca} + \Omega_c \Pi_{ac} \Pi_{ca}) \\ &= 2 \sum_{a} \Omega_a \sum_{c} \Pi_{ac} \Pi_{ca} = N , \end{aligned} \tag{23}$$

and, as $\mathbf{\Pi}$ is idempotent:

$$2\sum_a \Omega_a(\Pi^2)_{aa} = 2\sum_a \Omega_a \Pi_{aa} = N. \tag{24}$$

So that, if we define the Ω's as proportional to the orbital electronegativity χ_a,

$$\Omega_a = \chi_a / K; \quad K = (2/N) \sum_{a,\,\mathrm{A}} \chi_a \Pi_{aa}. \tag{25}$$

If all electronegativities are equal, $\chi_a = \chi$; as the trace of the density matrix is $N/2$, and in this case $K = \chi$, K represents a sort of mean electronegativity of the orbitals included in the basis. The form given to ω in (21) ensures that an orbital with larger electronegativity will contribute more heavily to the bond index and the electronic charge.

3. Tensor Character of Bond Indices

Since the classical Chirgwin-Coulson study [2], little attention has been payed to the covariant or contravariant character of the indices appearing in the expressions involved. For example, in [25], the expectation value of any one-electron property in a basis $\{\varphi\}$ is written as

$$\langle \mathcal{O} \rangle = \sum_{ab} P_{ab}\, \mathcal{O}'_{ab} = \sum_{ab} \mathcal{O}_{ab}; \quad \mathcal{O}'_{ab} = \langle \varphi_b | \mathcal{O} | \varphi_a \rangle. \tag{26}$$

The summations over a and b are contracted as in (7) to obtain smaller sums over centres. Now, in order that expression (26) represents effectively a contraction in the tensor sense, the indices a and b should be written so as to manifest the invariance, i.e. they should display the proper variance: covariance (subscripts) or contravariance (superscripts). For the contraction must be carried out between a covariant index and a contravariant one, which have different transformation properties.

If any physical meaning is to be attached to a bond population, it must be invariant under a unitary transformation of the basis.

In the Wiberg index of (7),

$$P_{ab} = \sum_i c_{ia}\, c_{ib} \tag{27}$$

is an element of the density matrix in an orthonormal basis; the covariant components of the i-th wavefunction c_{ia} coincide with the contravariant c^{ia}, so that the distinction is immaterial here. Note that i is only a label for the wavefunction and has nothing to do with the variances of indices a and b. In (7), hence, P^2_{ab} ca be written as

$$P^2_{ab} = \sum_{ij} c_{ia}\, c_{ib}\, c^{ja}\, c^{jb} \tag{28}$$

and under contraction in a and b a scalar (invariant) is obtained.

For a non-orthogonal basis, the elements of the density matrix are given by

$$2\Pi^a_b = 2\sum_i x^{ia}\, y_{ib}, \tag{29}$$

where x^{ia} are the elements of a tensor which is contravariant of order one and y_{ib} is similarly covariant. Thus, the square of the mixed tensor Π^a_b, represented by an idempotent matrix, is itself a tensor and not a scalar.

Equation (8) may be written in the form

$$I_{\mathrm{AB}} = 4 \sum_{a \in \mathrm{A}} \sum_{b \in \mathrm{B}} \Pi^a_b\, \Pi^b_a \tag{30}$$

which emphasizes that the contraction is carried out between covariant and contravariant indices, as it should. The introduction of a weight factor as in the previous section does not affect this discussion. In (25), the χ's are scalars, therefore the summation is actually a tensor contraction.

The Mulliken matrix $\mathbf{M}$ is similarly

$$M_{\mathrm{AB}} = 2 \sum_{a \in \mathrm{A}} \sum_{b \in \mathrm{B}} \varrho^{ab}\, S_{ab}, \tag{31}$$

where

$$\varrho^{ab} = \sum_i x^{ia}\, x^{ib}. \tag{32}$$

M_{AB} is also invariant, for the metric tensor S is a covariant tensor of order two.

In [14] the density matrix is most appropriately divided into atomic and interatomic blocks. Now, in the light of what precedes, matrices $\mathbf{M}$, $\mathbf{W}$, and $\mathbf{I}$, rather than $\mathbf{P}$, are suited to be divided into atomic blocks. For instance, $\mathbf{I}$ may be written as

$$\mathbf{I} = \begin{bmatrix} \mathbf{I}_{\mathrm{AA}} & \mathbf{I}_{\mathrm{AB}} \cdots \mathbf{I}_{\mathrm{AL}} \\ \mathbf{I}_{\mathrm{BA}} & \mathbf{I}_{\mathrm{BB}} \cdots \mathbf{I}_{\mathrm{BL}} \\ \vdots & \vdots \\ \mathbf{I}_{\mathrm{LA}} & \mathbf{I}_{\mathrm{LB}} \cdots \mathbf{I}_{\mathrm{LL}} \end{bmatrix} \tag{33}$$

with $\mathbf{I}_{\mathrm{AB}} = \mathbf{I}^{\dagger}_{\mathrm{BA}}$.

Let us underline that diagonal submatrices are square and symmetric, but the non-diagonal ones may happen to be rectangular and, even in the square case, they are usually not symmetric.

It has been remarked that Coulson bond orders do not lead to a useful definition of valence [16]. We are now in a position to understand why the Chirgwin-Coulson submatrices built from

$$C_{ab} = \sum_i \left(x^{ia}\, y_{ib} + x^{ib}\, y_{ia}\right) \tag{34}$$

lead to meaningless values if summed over a and b, for this sum is not a contraction in the tensorial sense. The same happens with **P**, so that for orthogonal bases an atom-atom bond index cannot be directly obtained from it and the sum of squares (i.e. a contraction) must be introduced. Only the traces of the diagonal submatrices *do* give rise to scalars in both cases.

Matrices of proper variance written in the form (33) may be contracted according to (26) within the blocks, giving scalar quantities which fulfil the desired requirements for bond indices. In a quite straightforward manner, the invariance properties of **W** [14] may be shown to hold for **I**.

4. Applications

As valence in the MO approach has been extensively discussed for compounds containing first and second-row elements [9, 10, 13, 15, 26], we shall rather focus our attention on a few systems to which it may be interesting to apply definitions (16) and (18).

Unless explicitly mentioned, all results are obtained through an IEH approach [27], molecular geometry is taken from [28], orbital exponents are Slater's and the ionization potentials, as well as the iteration parameters related to them, are derived from [29].

a) C and N-Containing Compounds: "Secondary" Bonds

Table 1 shows bond indices, net charge, valence and oxidation numbers for some carbon and nitrogen containing molecules, where significant contribution to valence comes from "secondary" bonds [10], that is pairs of "non-bonded atoms" with high I_{AB} values.

Halgren et al. [16] have studied localized molecular orbital structures for systems not well represented by single Lewis formulae, as occurs with those calculated here. They link MO formulations to valence bond (VB) ones, and analyze valence in connection with apparent violations of the octet rule.

For nitrous oxide N_2O, the bond indices obtained are more consistent with the well-behaved VB structures [16]:

$$:\mathrm{N}\equiv\overset{(+)}{\mathrm{N}}-\overset{(-)}{\ddot{\underset{\cdot\cdot}{\mathrm{O}}}}: \qquad :\overset{(-)}{\mathrm{N}}=\overset{(+)}{\mathrm{N}}=\ddot{\underset{\cdot\cdot}{\mathrm{O}}} \tag{35}$$

than with the controversial structure involving pentavalent nitrogen

$$:\mathrm{N}\equiv\mathrm{N}=\ddot{\underset{\cdot\cdot}{\mathrm{O}}} \tag{36}$$

which would violate the octet rule [16].

The left most nitrogen attains a valence $\simeq 3$ through a significant "long bond" [30] NO contribution, which is also responsible for the oxygen value. The central nitrogen has a higher value, but all three valences stand below the limits given by the parabolic curve of [9], which are respectively 3.75 for N and 3.0 for O. The central nitrogen has a polarity different from that of the other two atoms; thus its valency coincides with the oxidation number, while N_1 shows a negative value for Ξ.

The "increased valence" structures of dinitrogen tetroxide N_2O_4 have been studied from the VB

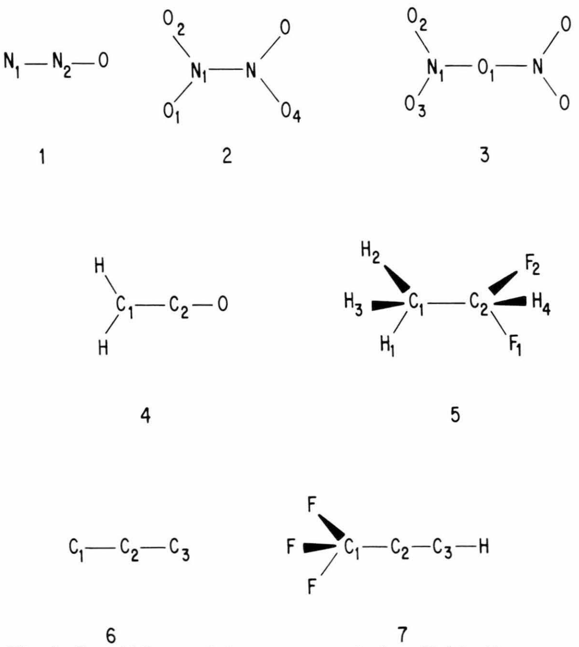

Fig. 1. C and N-containing compounds (see Table 1).

Table 1. N and C-containing systems.

Molecule	Bond	Bond index	Atom	Net charge	Valence	Oxid. number
1) N_2O	N−N	2.095	N_1	− 0.081	2.96	− 2.09
Nitrous oxide	N_1-O	0.868	N_2	0.137	3.65	3.65
	N_2-O	1.557	O	− 0.056	2.42	− 1.56
2) N_2O_4	N−N	0.622	N	0.196	3.58	2.96
Dinitrogen tetroxide	N_1-O_1	1.381	O	− 0.098	2.13	− 1.48
	O_1-O_2	0.619				
3) N_2O_5	N_1-O_1	0.889	N	0.240	3.55	2.60
Dinitrogen pentoxide	N_1-O_2	1.296	O_1	0.052	2.34	0.56
	O_2-O_3	0.600	O_2	− 0.133	2.05	− 1.44
4) C_2H_2O	C−C	1.727	C_1	− 0.033	3.94	− 3.60
Keten	C_1-O	0.331	C_2	0.105	3.81	3.76
	C_2-O	2.030	O	− 0.174	2.43	− 2.10
	C−H	0.940	H	0.051	1.00	0.97
5) $C_2H_4F_2$	C−C	0.967	C_1	0.027	3.97	0.04
Difluorethane	C_2-F	0.897	C_2	0.293	3.74	1.79
	C_1-H_1	0.983	F	− 0.290	0.99	− 0.94
	C_1-H_2	0.995	H_1	0.055	1.00	0.01
	C_2-H_4	0.968	H_4	0.095	0.99	0.02
6) C_3	C_1-C_2	1.972	C_1	− 0.006	2.50	− 1.98
	C_1-C_3	0.520	C_2	0.012	3.95	3.96
7) C_3HF_3	C_1-C_2	0.945	C_1	0.534	3.73	2.77
Trifluormethylacetylene	C_1-F	0.921	C_2	0.070	3.93	0.09
	C_2-C_3	2.882	C_3	0.042	3.96	0.08
	C_3-H	0.984	F	− 0.238	1.03	− 0.98
			H	0.068	0.99	0.00

viewpoint [30]. Our low I_{NN} value, almost σ as expected, indicates a weak N−N bond and reflects the stability of the NO_2 molecule forming the dimer [31]. The observation of the torsional mode frequencies in the infrared spectrum of gaseous N_2O_4 led to an estimate of an internal rotation potential function. Comparing with that of N_2O_3, it was suggested that there should exist a weak σ bond between the *cis* oxygens O_1-O_4 to lock the system into the planar conformation [31]. Our small value $I(O_1-O_4) = 0.011$ (half σ, half π) gives an MO meaning to the statement, derived from VB calculations, that this bond is too weak as to hinder the rotation about the N−N bond [32]. Let us remark the high I values of O_1-O_2 in N_2O_4 and of O_2-O_3 in N_2O_5, corresponding to secondary bonds and contributing heavily to the oxygen valence. According to Trindle and Sinanoglu [33], we could say that O_2 has a localization defect of 38.6 in N_2O_4 and 36.3 in N_2O_5. Other systems, not reported here, such as O_3 and linear CO_2, show the same high I_{OO} values for secondary bonds. These cannot simply be ascribed to an interaction between lone pairs; otherwise, it would be expected to find equivalently high I_{FF} values in OF_2, BF_3 and other systems: they are instead practically negligible, as I_{HH} in CH_2, OH_2, etc. Thus, the bonding characteristics of fluorine resemble those of hydrogen more than it could be expected from its electronic structure. It was recently pointed out that there is a close parallel between many properties of alkaline-earth metal hydrides and fluorides [34], suggesting that in such compounds fluorine behaves in a manner similar to hydrogen.

Let us present rapidly a related peculiar case. In [24], the oxidation number is associated with the *ab initio* spherically averaged electron density around the atoms in two series of chlorine and sulphur-containing compounds. In the case of S_2F_2, there exists some perplexity as to which of the three possibilities shown in Fig. 2 should be considered preferable. The authors give arguments supporting formula II, although they also say that chemical intuition could favour I or III. In our IEH calculations we have choosen to introduce d orbitals only in the transition metals of Table 4, so that we have run a CNDO calculation of this molecule. Again, I_{FF} is negligible. Table 2 shows the other results. It is

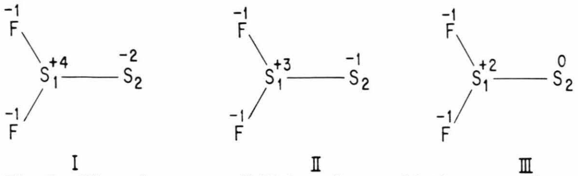

Fig. 2. The three possibilities for oxidation numbers mentioned in [24].

Table 2. CNDO results for S_2F_2 (see Figure 2).

Bond	Bond index	Atom	Net charge	Valence	Oxid. number
S−S	2.259	S_1	0.374	4.88	2.35
S−F	1.176	S_2	0.040	2.64	0.11
		F	− 0.207	1.25	− 1.23

seen that they are decidedly close to formula III, due to the equal polarity of the sulphur atoms.

The C-containing compounds show no unexpected valence values. We find the classical values 2 and 4 in CH_2 and CH_4 respectively. As, from (15) and (16), valence was shown to be twice the active charge, it follows from the total charge value (~ 4) that very nearly three electrons in methylene and two in methane belong to the carbon's self-charge. In between, we found a few instances of $V_C = 2.5-2.75$ but the majority of the results lies in the range 3.4−3.85.

The oxidation numbers are less clear *a priori* in these compounds. In keten, the high oxidation numbers of C_1 and C_2 are due to their different polarity, together with the I_{CC} value. If the polarity were the same, their oxidation numbers would be respectively around −2 and 2. In $C_2F_2H_4$, C_2 is linked at atoms of three different electronegativity sets. As C_1 has the same polarity as the methyl hydrogens and as C_2, its oxidation number is practically zero, with the very small contribution from I_{AD} values corresponding to non-bonded atoms. In C_3HF_3, the influence of the fluorine atoms bonded to C_1 is extended to the three carbon atoms, affecting their oxidation numbers. Now, if a CNDO calculation is performed for the latter system, C_1 reverts its polarity: $Q(C_1) = -0.08$; $Q(C_2) = 0.42$; $\Xi(C_1) = -3.97$; $\Xi(C_2) = 2.85$.

The short life species C_3 shows a strong secondary interaction between the extreme carbons which give rise to a higher valence than the classical one. The hybridizations are respectively $sp^{1.66}(C_1)$ and $sp^{2.5}(C_2)$, which would correspond to differences in electronegativity in agreement with the polarity obtained, which in turn explains the Ξ values. In this case too CNDO reverts the polarity, for it gives $Q(C_1) = 0.080$ and $Q(C_2) = -0.159$. The hybridizations would be respectively $sp^{1.4}$ and $sp^{3.0}$, predicting electronegativities in disagreement with the charges.

These are two of the very few examples where IEH and CNDO results diverge. When such uncertainties arise, certainly the question should be settled through more rigorous calculations. However, IEH polarity deserves perhaps more confidence than the CNDO one, since it arises from self-consistency in electronic charges instead of self-consistency in the total energy. *Ab initio* predictions are not more reliable by themselves, for they may be strongly basis dependent [11, 26]; the STO-3G calculations which we performed in the Gauss 70 approximation do not resolve the present ambiguities.

It is seen that small variations in the charges (whether due to the method applied or whether to parameterization) may alter polarity and thus yield very different oxidation numbers; we are hence faced with the kind of dramatic changes predicted classically, as we mentioned in Section 2.

The introduction of a weight factor for this group of compounds does not alter the trends described. As expected, it tends to polarize the charge distribution and to decrease bond indices values.

A zero oxidation number is usually ascribed to ozone [35]. We have obtained $\Xi = 2.55$ for the central atom ($Q = 0.112$, $V = 2.55$) and $\Xi = -1.28$ for the two non-bonded oxygens ($Q = -0.06$, $V = 1.96$). The dipole moment obtained is 0.85 D, of which 0.49 D arise from the hybridization moment. From Stark and Stark-Zeeman J rotational transitions, a dipole moment of 0.53 D is obtained [36]. Even if the hybridization moment could perhaps account for this value, let us note that CNDO charges [15] are more polarized than ours and valences farther apart. As neither charges nor valences [15, 16] predict any equivalence for the three oxygen atoms, we think that oxidation numbers should also be non-equivalent. Several systems of Table 1, as well as S_2F_2 and O_3, conflict thus with the axiom [35]: "If there is no serious reason to do otherwise, identical oxidation numbers are ascribed to atoms of the same element in a given compound." It seems that the axiom holds for atoms of the same element which are equivalent under symmetry operations.

b) Symmetrical Hydrogen Bridging

Many years have elapsed since Pauling's suggestion [37] that symmetrical bridging hydrogen bonds may be considered half-bonds for compounds such as $(HF_2)^-$ and boranes. Plenty of theoretical and experimental work has been devoted in more recent time to other compounds with similar structure [38, 39]. Experimental evidence of a single very high-field hydrogen in the ^1H NMR has been given, for example, for μ-hydrido bridging in cycloalkyl cations [40]. We shall limit our discussion to a few relevant systems.

The values of diborane agree with previous results for bond indices and valence [13, 15, 37]. Our estimation of I in the HB system is 0.998, somewhat higher than the diborane four equivalent I_{BH} values, and dividing itself exactly in halves across the bridge, where H holds its valence value one. The difficulty in defining formal oxidation numbers for this molecule has been explicitly recognized by Jørgensen [35], who states that it is "not easy to handle in any satisfactory manner". Formula (18) may thus contribute to elucidate this problem. We see that oxidation numbers in Table 3 are quite different from valences and classically not predictable, as the H and B electronegativities are very close to each other.

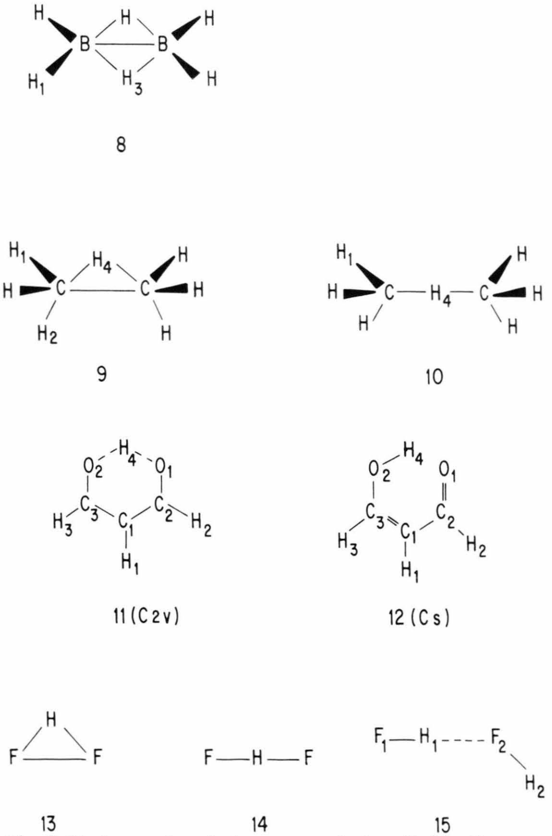

Fig. 3. Hydrogen bonded compounds (see Table 3).

The C_2H_7 anion and cation [41] are other examples of these half-bonds. This cation, used as a model for more complex systems such as the dimethylcyclodecyl cation [40], has been described as having a C−C bond [42] which, according to the I_{CC} values, would be rather weak (so would be for the anion). On occupying the a_{1u} MO when going from cation to anion, the magnitudes related to carbon suffer variations larger than those related to hydrogen; this MO has mostly carbon contribution. For the same process, an *ab initio* calculation predicts shortening of the CH terminal bonds. Although we are not relating here I to the interatomic distance, it is seen that ΔI_{CH} (cation → anion) points in the same direction; the opposite is obtained with the MINDO/3 method [41], perhaps because MINDO/3 is not suitable for calculating hydrogen bonded systems [43].

Malonaldehyde is one of the more usual molecules calculated in order to analyze intramolecular hydrogen bonding, considering the symmetric situation as the limiting case [38]. The C_s and C_{2v} structures are those of Fig. 3 and geometry is taken from [44]. Both structures show close parallelism in their valences and oxidation numbers, which would have been difficult to predict classically. In a couple of compounds related to the present ones it is suggested that, when symmetry constraints are left aside, the C_{2v} structure relaxes into the C_s one [41]. The delocalization pictured by the I values of C_1-C_2 and O_1-C_2 corresponding to Fig. 3-11 is indeed quite uniform. Passing from C_{2v} to C_s, this uniformity is replaced by a certain alternance in the bond indices and the O_2-H_4 index increases at the expense of the O_1-H_4 one. However, rather than a disappearance of the O_1-H_4 bond, it looks as if this symmetric bridge turns into a usual hydrogen bond. The potential barrier between the two possible C_s conformers, with the C_{2v} one as transition state, is

Table 3. Hydrogen bonded systems.

Molecule	Bond	Bond index	Atom	Net charge	Valence	Oxid. number
8) B_2H_6	B−B	0.542	B	0.073	3.53	1.98
Diborane	$B-H_1$	0.984	H_1	−0.048	1.00	−0.99
	$B-H_3$	0.499	H_3	0.023	1.00	0.00
9) $(C_2H_7)^+$	C−C	0.364	C	0.152	3.82	
	$C-H_1$	0.982	H_1	0.088	0.99	
	$C-H_2$	0.962	H_2	0.092	0.99	
	$C-H_4$	0.485	H_4	0.152	0.98	
10) $(C_2H_7)^-$	C−C	0.255	C	−0.331	3.74	
	$C-H_1$	0.990	H_1	−0.053	1.00	
	$C-H_4$	0.501	H_4	−0.020	1.00	
11) $C_3O_2H_4$	C_1-C_2	1.385	C_1	0.024	3.97	0.20
Malonaldehyde (C_{2v})	C_1-H_1	0.987	C_2	0.087	3.85	1.50
	C_2-O_1	1.387	O_1	−0.238	2.46	−2.10
	C_2-H_2	0.972	H_1	0.039	1.00	0.00
	O_1-O_2	0.352	H_2	0.047	1.00	0.01
	O_1-H_4	0.488	H_4	0.145	0.98	0.98
12) $C_3O_2H_4$	C_1-C_2	1.295	C_1	0.025	3.97	0.21
Malonaldehyde (C_s)	C_1-C_3	1.481	C_2	0.083	3.84	1.58
	C_1-H_1	0.987	C_3	0.087	3.85	1.40
	C_2-O_1	1.514	O_1	−0.241	2.37	−2.05
	C_2-H_2	0.970	O_2	−0.230	2.47	−2.15
	C_3-O_2	1.275	H_1	0.041	1.00	0.00
	C_3-H_3	0.975	H_2	0.047	1.00	0.02
	O_1-O_2	0.321	H_3	0.048	1.00	0.01
	O_1-H_4	0.321	H_4	0.140	0.98	0.98
	O_2-H_4	0.656				
13) $(FHF)^+$	F−F	1.006	F	0.285	1.41	
	F−H	0.408	H	0.430	0.82	
14) $(FHF)^-$	F−F	0.201	F	−0.552	0.80	
	F−H	0.495	H	0.104	0.99	
15) $(HF)_2$	F_1-H_1	0.827	F_1	−0.309	0.90	−0.83
	F_1-F_2	0.078	F_2	−0.128	1.16	−1.07
	F_2-H_1	0.132	H_1	0.194	0.96	0.96
	F_2-H_2	0.939	H_2	0.243	0.94	0.94

very low [44]. This lowering compared with the usual chemical reactions may be related to the gradual transformation which we are inclined to favour.

Let us consider the well-known H-bond in FH... F. Cation and anion have different geometries; the FF distance is respectively 1.55 Å and 2.23 Å [41]. Nevertheless, the very different I_{FF} values cannot be ascribed to geometry, for if the anion is calculated with the cation's geometry, I_{FF} remains low (0.216). Nether can they be attributed to the mere occupation of the cation's HOMO, for all MO's in the anion change appreciably [45]. In FH, $I = 0.950$. Again, it parcels out quite nearly into halves both in the symmetric anion and cation. The enthalpy of formation calculated for the very strong hydrogen bond of $(FHF)^-$ (g) is about eight times as great as that of the usual hydrogen bonds [37]; our I values for these (0.05−0.08) [46, 47] are in good agreement with the above estimate. In the dimer, $I(F_2-H_1)$ indicates a hydrogen bond stronger than the usual ones. Under dimerization, the charge lost by the FH bond goes practically to the bridge. We have discussed the electronic distribution along a XH... Y bond when dealing with nucleic acids; we found there that, when the base pair is formed, the NH group of the separate bases weakens its bond, transfering a fraction of an electron to H ... Y [22].

When passing from cations to the corresponding anions, not only for the kind of systems studied in this section, the discussion usually proceeds in the framework of frozen MO's. In this scheme, the role of HOMO and LEMO receives the utmost attention. If MO's are allowed to "thaw", it turns out that alterations in each energy level must be assigned to the variation in the occupation number of the *other* levels [45]. Thus, the building of the anion by populating the cation's LEMO may affect all the occupied levels. The MO modification is less pronounced but cannot be disregarded.

c) Transition Metal Complexes

Carbonyl complexes are attractive cases for applying the definitions of valence and oxidation number to transition metals; we choose here $Fe(CO)_5$, $HCo(CO)_4$ and $Ni(CO)_4$. In the case of iron we compare with results obtained for ferrocene. The geometry for this molecule, as in [12], is supposed to be an eclipsed D_{5h}; the staggered D_{5d} is not consistent with experimental data, a quite low barrier being opposed to internal rotation [48]. We have chosen for $Fe(CO)_5$ the trigonal bipyramidal structure, on the grounds given in [49]. For $HCo(CO)_4$ we adopted the configuration of Figure 4 [37]. For ferrocene, the calculation is carried out with a weight factor for the reasons explained in [12]. For the other complexes, a weight factor is not required; for all of them, the ionization potentials with the related iteration parameters are derived from [50].

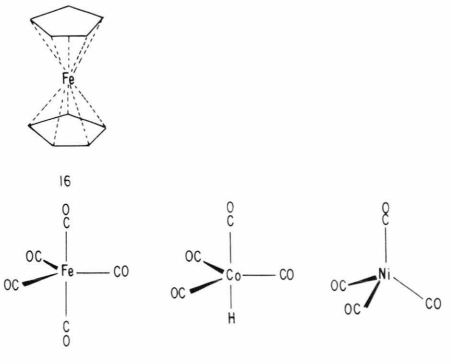

Fig. 4. Ferrocene, $Fe(CO)_5$, $HCo(CO)_4$, and $Ni(CO)_4$ (see Table 4).

We see that iron has quite different valence depending on whether the ligand is C_5H_5 or CO. In the first case a classical one is predicted, while in the second the valence is nearly twice, close to the 5.78 value originally assigned to iron by Pauling [51]. The Fe−C distance in ferrocene is 2.05 Å; in $Fe(CO)_5$ it is 1.84 Å. Although the dependence of I on distance is by no means straightforward, it could affect greatly the values of I(Fe−C). This is not the case, however. If ferrocene is calculated with a Fe−C distance of 1.84 Å, I(Fe−C) goes to 0.335 and V_{Fe} to 3.90, still far from that appearing in $Fe(CO)_5$; I_{CC} is not modified much (1.215), that is the cyclopentadienyl structure is not affected by drawing it near the iron atom. Both for cobalt and nickel we obtain valence values close to 8.

The multiple bonding of the iron-group transition metals has been exhaustively analyzed by Pauling a

Table 4. Transition metal complexes (the subscript a stands for axial and e for equatorial).

Molecule	Bond	Bond index	Atom	Net charge	Valence	Oxid. number
16) $Fe(C_5H_5)_2$	Fe−C	0.272	Fe	1.153	3.20	2.72
Ferrocene	Fe−H	0.048	C	− 0.132	4.00	− 1.22
	C−C	1.264	H	0.017	1.05	0.95
	C−H	0.947				
17) $Fe(CO)_5$	Fe−C_e	0.963	Fe	0.281	5.84	1.12
Iron pentacarbonyl	Fe−C_a	0.916	C_e	0.072	3.48	2.31
	Fe−O_e	0.227	C_a	0.087	3.51	2.32
	Fe−O_a	0.220	O_e	− 0.137	2.58	− 2.53
	C_e−O_e	2.229	O_a	− 0.130	2.58	− 2.55
	C_a−O_a	2.234				
18) $HCo(CO)_4$	Co−C_e	1.775	Co	0.765	8.18	1.29
Cobalt tetracarbonyl	Co−C_a	1.562	C_e	0.055	3.78	1.92
hydride	Co−H	0.860	C_a	0.100	3.77	2.10
	C_e−O_e	1.653	O_e	− 0.253	2.42	− 2.04
	C_a−O_a	1.750	O_a	− 0.225	2.45	− 2.10
			H	− 0.046	1.00	− 0.93
19) $Ni(CO)_4$	Ni−C	1.660	Ni	0.704	7.94	1.29
Nickel tetracarbonyl	Ni−O	0.325	C	0.045	3.75	1.96
	C−O	1.842	O	− 0.221	2.53	− 2.28

long time ago from the VB viewpoint [37]. In $Fe(CO)_5$, 80% of double character has been assigned to the Fe−C bonds, deriving from one single and four double bonds [49, 52]. In disagreement with these previous estimations, our $I(\mathrm{Fe-C})$ suggests a single bond.

Looking at the $I(\mathrm{Co-C})$ values, we could say that in this molecule the Co−C bonds have an average of 72% double character; double Co−C bonds have been predicted for $Co_2(CO)_8$ [52]. In an *ab initio* SCF-LCAO-MO calculation of this known catalyst, a negative $\mathrm{Co-C_e}$ overlap population (− 0.02) was obtained [53].

The double bond structure for $Ni(CO)_4$ was proposed first by Langmuir [54]. An experimental electron diffraction determination came to its support, yielding a result of 1.82 Å for the Ni−C distance, smaller than that advanced for models with a single Ni−C bond. Studying the hybrid orbitals for $Ni(CO)_4$ [55], the Ni−C bond was described as having 75% double character, in agreement with our $I(\mathrm{Ni-C})$ of 1.66. The metal-ligand back bonding, with feedback of the carbonyl $2\pi^*$ orbitals, is considered an important factor related to the mentioned structure [56, 57, 58]. Actually, the bonding mechanism between Ni and CO should be synergic [56], being preceeded by an electronic donation into the nickel 4s and 4p orbitals.

In carbon monoxide I_{CO} is 2.61 (close to the best *ab initio* value of 2.52 [11]), which can be discriminated thus:

$$I(\sigma):\ 0.894,\quad I(\pi):\ 0.858,\quad I(\pi'):\ 0.858. \tag{37}$$

These values suggest a sort of triple bonding in CO [16], while the I_{CO} values of Table 4 indicate that the CO bond resembles more a double one. This trend is not monotonous in relation to atomic number. Back donation should yield a decrease of the CO bond order, paralleling the bond strength [59]; we see that, in fact, the same holds for bond indices.

Let us examine the orbital charge distribution in order to have an insight into back bonding and other related problems. In Table 5 we show the metal's orbital charge distribution in the complexes considered here. As expected, the 3d population is always the highest, although those of the 4s and 4p orbitals are not negligible as often happens (particularly for 4s orbitals) in more sophisticated calculations [60, 61, 62]. The partition of the orbital charge into self and active charge is much more illustrative of these orbitals' performance. Even if the 3d charges are similar in the four compounds, their active charges (and the corresponding percentage of the orbital charge) are decidedly larger in the carbonyl complexes, concurring thus heavily to their high valences. On the other hand, the percentage of the orbital charge becoming active is strikingly high for 4s and 4p orbitals (perhaps because they are more diffuse), contributing "exhaustively" to

Table 5. Distribution of the metal orbital charge between self-charge and active charge for the complexes of Table 4. * Percentage of the orbital charge which goes into active charge. ** Percentage of valence for each atomic orbital.

Molecule		Metal orbital charge	Self-charge	Active charge	Percentage*	Percentage**
$Fe(C_5H_5)_2$	s	0.491	0.085	0.406	83	25
	p	0.788	0.073	0.715	91	45
	d	5.568	5.083	0.485	9	30
	total	6.847	5.241	1.606	23	100
$Fe(CO)_5$	s	0.227	0.026	0.221	97	7
	p	0.774	0.141	0.633	82	22
	d	6.718	4.629	2.089	31	71
	total	7.719	4.796	2.943	38	100
$HCo(CO)_4$	s	0.583	0.172	0.411	70	10
	p	1.969	0.683	1.286	65	31
	d	5.683	3.292	2.391	42	59
	total	8.235	4.147	4.088	50	100
$Ni(CO)_4$	s	0.556	0.155	0.401	72	10
	p	2.490	1.133	1.357	54	34
	d	6.249	4.034	2.215	35	56
	total	9.296	5.322	3.973	42	100

Table 6. Orbital contributions to charge from carbon and oxygen in metal carbonyls, compared with free CO. In the Fe and CO complexes, data are from axial C and O (on z axis), in CO, the σ component is on x axis.

Charge	$Fe(CO)_5$		$HCo(CO)_4$		$Ni(CO)_4$		CO	
	q_C	q_O	q_C	q_O	q_C	q_O	q_C	q_O
s	1.388	1.638	1.238	1.584	1.254	1.601	1.484	1.622
p_x	0.852	1.423	0.897	1.506	0.937	1.502	1.190	1.704
p_y	0.842	1.423	0.897	1.506	0.937	1.502	0.623	1.376
p_z	0.841	1.645	0.868	1.631	0.826	1.617	0.623	1.376
q_{tot}	3.913	6.129	3.900	6.227	3.954	6.222	3.921	6.079
Q	0.087	− 0.129	0.100	− 0.227	0.046	− 0.222	0.079	− 0.079

valence. The last column in the Table illustrates the weight of each orbital in the metal's valence: the 3d orbital is predominant in carbonyls and the 4p influence increases with atomic number. In ferrocene, the most important contribution to valence comes from the 4p orbitals, but their weight is comparable to that of 4s and 3d orbitals.

Table 6, together with Table 5, helps us to picture back bonding. From the distribution of the orbital charge in the metal, the following transitions from the reference state can be written for the metal carbonyls:

$$\begin{aligned} &\text{Fe:}\quad 3d^6\,4s^2 \quad 3d^{6.72}\,4s^{0.23}\,4p^{0.77} \\ &\text{Co:}\quad 3d^7\,4s^2 \quad 3d^{5.68}\,4s^{0.58}\,4p^{1.97} \\ &\text{Ni:}\quad 3d^8\,4s^2 \quad 3d^{6.25}\,4s^{0.56}\,4p^{2.49}. \end{aligned} \tag{38}$$

Table 6 compares the orbital charges of C and O in these compounds with the ones appearing in free CO. An enhancement in the π population and a decrease in σ population appear in the three complexes. However, (38) shows that the Ni and Co complexes reduce the 3d occupancy and enlarge the (s + p) one, while this does not happen in the iron complexes. The results indicate thus more back bonding in $Ni(CO)_4$ than in $HCo(CO)_4$ and no back bonding in $Fe(CO)_5$.

Let us note that in a direct variational method calculation of $Fe(CO)_5$ and its photochemical fragments, it has been hinted that the back bonding would not have the major role in bonding mechanism, contrary to expectation in other similar complexes [63]. We concur in finding that all MO's are almost entirely localized on the ligands, except for the highest ones; this does not happen for our Co and Ni complexes.

Let us remark that metals' negative orbital populations in sandwich compounds such as ferrocene have been ascribed to counterintuitive orbital mixing (COM) [64], i.e. inversion in the expected symmetry of the lowest energy levels. We have seen [12] that this does not explain by itself the appearance of negative orbital and bond populations, which may be overcome otherwise by the introduction of a weight factor in the bond index, combined with a suitable parameterization. The results obtained here lead us to infer that the weight factor may be considered a part of the parameterization. Actually, negative populations in atomic orbitals of metallic complexes may appear without COM [65]. Hence, even if in the present calculation for ferrocene we do not obtain either COM or negative populations (the charge in the $4p_z$ orbital of iron, which is frequently negative and is not shown explicitly in the Table, is 0.142), both facts are not necessarily related.

The oxidation number value obtained for iron in ferrocene, through definition (18), is nearly 3; the oxidation state ascribed to the metal in this compound is two or three [35]. Taking into account that the weight factor emphasizes the polarization of the charge distribution, the iron charge may be considered in reasonable agreement with an experimental estimate of 0.73 [66].

As to the metals in the carbonyl complexes, the results for Ξ indicate a narrow range 1.1 − 1.3. An oxidation number equal to 1 is assigned to cobalt in this compound [35]. By measuring binding energies through X-ray photoelectron spectroscopy and applying the potential model, it is infered that hydrogen in $HCo(CO)_4$ is negatively charged [67], in agreement with our results. A value zero for the metals' oxidation number is sometimes alluded to in

$Fe(CO)_5$ and $Ni(CO)_4$ [68]; this would imply a zero net charge. But the metal charges in carbonyl complexes are *not* zero, even if they keep reasonably within the limits of the electroneutrality principle [37, 49], and the same happens in the abundant results quoted from the literature. For example, a direct variational method [63] gives ~ 0.5 for iron in $Fe(CO)_5$; nickel in $Ni(CO)_4$ appears with $Q = 0.24$ in an *ab initio* calculation [60] and 0.37 in an INDO one [61].

Some care must be taken in using the terms oxidation number and oxidation state. Cases exist where a clear-cut definition cannot be given for both concepts. Even when this is possible, they do not necessarily coincide [35]. There is also some confusion around the words valence and covalence [16]. It looks as if different (although similar) names were used in connection to similar (but not equal) underlying ideas. We find hence worthwhile to work with unambiguous concepts, and formulae (16) and (18) (as Armstrong's and related ones) serve this purpose well. In relation to this, the need of unifying the notion of binding has been recently underlined [69], without ignoring the difficulties encountered to incorporate quantum mechanics into a description of single and double bonds [70].

5. Conclusions

1) In non-orthogonal bases, the density matrix is a mixed second order tensor. An orbital-orbital matrix is built from it; in order that this matrix may contract to an atom-atom bond index matrix, the subscripts and superscripts should have their variance clearly defined.

2) Bond indices permit a straightforward definition for the oxidation number of an atom in neutral systems, which is useful in elucidating ambiguous cases.

3) For the C and N-containing compounds which we calculated, the contribution of "secondary" bonds to valence cannot be disregarded; it may amount to 1/3 of the total valence.

4) The MO valence definition explains satisfactorily the hydrogen behaviour in systems with half-bonds and strong H-bonds.

5) For iron in ferrocene, valence is 3.20 and oxidation number is 2.72. In metal carbonyl complexes, iron, cobalt and nickel have valences of 5.84, 8.18 and 7.94 respectively. The metal oxidation numbers are predicted to differ from zero being close to one.

Appendix

In [12] a weight factor was introduced in a different way. I_{AB} was defined as

$$I_{AB} = \sum_{a \in A} \sum_{b \in B} I'_{ab} I'_{ba} \tag{A.1}$$

where

$$I'_{ab} = 4 \sum_i \sum_c x_{ia} x_{ic} S_{cb} \omega_{cb} \tag{A.2}$$

and

$$\omega_{cb} = \chi_c / (\chi_c + \chi_b), \tag{A.3}$$

obeying

$$\omega_{cb} + \omega_{bc} = 1. \tag{A.4}$$

Condition (A.4) is customarily imposed on weighted linear populations [65, 71]. However, we shall show that in the present case this procedure is not satisfactory.

We have

$$q_A = (1/2) \sum_B I_{AB}. \tag{A.5}$$

It is useful to write

$$\begin{aligned} \omega_{cb} &= (1/2)(1 + \omega_{cb} - \omega_{bc}) \\ &= (1/2)(1 + \Delta_{cb}). \end{aligned} \tag{A.6}$$

Then

$$I_{AB} = 16 \sum_{a \in A} \sum_{b \in B} \sum_{ij} \sum_{cd} x_{ia} x_{ic} S_{cb} \omega_{cb} x_{jb} x_{jd} S_{da} \omega_{da}, \tag{A.7}$$

$$I_{AB} = 4 \sum_{a \in A} \sum_{b \in B} \sum_{ij} \sum_{cd} x_{ia} x_{ic} x_{jb} x_{jd} \cdot S_{cb} S_{da} (1 + \Delta_{cb})(1 + \Delta_{da}), \tag{A.8}$$

where *c*, *d* run over all orbitals of all atoms. From (A.5):

$$q_A = 2 \sum_{a \in A} \sum_{ij} \sum_{bcd} x_{ia} x_{ic} x_{jb} x_{jd} \cdot S_{cb} S_{da} (1 + \Delta_{cb})(1 + \Delta_{da}), \tag{A.9}$$

which, upon summing over A gives

$$\sum_{\mathrm{A}} q_{\mathrm{A}} = 2\sum_{ij}\sum_{abcd} x_{ia}\,x_{ic}\,x_{jb}\,x_{jd} \cdot S_{cb}\,S_{da}(1+\Delta_{cb}+\Delta_{da}+\Delta_{cb}\,\Delta_{da}). \qquad \text{(A.10)}$$

We shall now separate the four terms in (A.10). Taking into account (11), the first one is:

$$\begin{aligned} 2\sum_{ij}\sum_{ab} x_{ia}\,y_{ib}\,x_{jb}\,y_{ja} &= 2\sum_{i}\Big(\sum_{a} x_{ia}\,y_{ja}\Big)\sum_{j}\sum_{b} x_{jb}\,y_{ib} && \text{(A.11)} \\ &= 2\sum_{i}\delta_{ij}\sum_{j}\sum_{b} x_{jb}\,y_{ib} \\ &= \sum_{b}\Big(2\sum_{i} x_{ib}\,y_{ib}\Big) = N. && \text{(A.12)} \end{aligned}$$

So that

$$\sum_{\mathrm{A}} q_{\mathrm{A}} = N + 2\sum_{ij}\sum_{abcd} x_{ia}\,x_{ic}\,x_{jb}\,x_{jd} \cdot S_{cb}\,S_{da}(\Delta_{cb}+\Delta_{da}+\Delta_{cb}\,\Delta_{da}). \qquad \text{(A.13)}$$

The term linear in Δ_{cb} is odd in relation to an exchange in the indices b and c; therefore, it cancels when summing over all indices. The same applies to the term linear in Δ_{da}.

The last term does not disappear. For $i \neq j$, when b is exchanged with c, a must be also exchanged with d. We are thus left with an even function. The sum $\sum_{\mathrm{A}} q_{\mathrm{A}}$ differs from N in second order in S and in the Δ's which are in turn proportional to the electronegativity differences

$$\Delta_{cb} = (\chi_c - \chi_b)/(\chi_c + \chi_b). \qquad \text{(A.14)}$$

let us remark that for large molecules the error is of the same order of magnitude as the usual precision of IEH calculations.

Acknowledgement

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