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MOLECULAR INVARIANTS: ATOMIC GROUP VALENCE

by

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### Abstract

Molecular invariants may be deduced in a very compact way through Grassmann algebra. In this work, a generalized valence is defined for an atomic group; it reduces to the known expressions for the case of an atom in a molecule. It is the sum of the correlations between the fluctuations of the atomic charges  $q_C$  and  $q_D$  (C belongs to the group and D does not) around their average values. Numerical results agree with chemical expectation.

Key words : Molecular invariants - Atomic group valence - Grassmann algebra

## 1. Introduction

In MO calculations, molecular quantities of chemical significance are often associated with scalars (invariants in the tensor sense) [1]. Among them, we may recall:

- the Mulliken charge  $q_A$  of atom A in a molecule [2];
- the bond index  $I_{AB}$  between atoms A and B [1,3];
- the self-charge  $I_{AA}$  [1,3], which measures the softness  $s_A$  of atom A in the molecule [4];
- the valence  $V_A$  of atom A [5,6].

The valence of atomic groups is mentioned in chemistry, understood as an integer. However, to our knowledge, this quantity has not been explicitly defined. This is what we intend to do in this note, making use of the properties of a multilinear alternating space; the latter has proven very convenient in the treatment of fermionic systems. An alternative formulation of the wavefunction antisymmetry has been recently proposed [7], through an  $n$ -linear map in the Hilbert spaces  $\mathcal{X}$  defined by

$$\Lambda^n \mathcal{X} : \mathcal{X} \times \mathcal{X} \times \dots \times \mathcal{X} \longrightarrow \mathcal{Y} \quad (1)$$

where  $\mathcal{Y}$  is a multilinear alternating space.

We shall show that the definition of inner product in an  $n$ -linear alternating space may be used in order to define the concept of atomic group valence, or generalized valence  $V_G$ . We shall also see that the known Armstrong-Semenov [5,6] formula for  $V_A$  is a particular case of  $V_G$ . We report some examples in different kinds of compounds.

## 2. Inner product of $n$ -vectors in the Hilbert-Grassmann space

Let us generalize the inner product to  $n$ -vectors in a multilinear alternating space  $\mathcal{G}$ . In a vector  $n$ -dimensional space  $E$  the inner product is a symmetrical and positive bilinear form  $F$

$$F = (\xi_a \cdot \xi^b) = (\xi^b \cdot \xi_a) \quad (2)$$

where  $\xi_a$  are covariant and  $\xi^b$  contravariant vectors, i.e.  $\xi_a \in E$ ,  $\xi^b \in E^\dagger$  [8].

We may suppose  $E \approx \mathcal{K}$ . In (1), it is possible to define an inner product in each space [9]. Thus, being  $n$  an integer, let us consider the  $2n$  linear form  $\Gamma$  defined by

$$\Gamma (\xi_1, \dots, \xi_n; \xi^1, \dots, \xi^n) = \det(\xi_a \cdot \xi^b) \quad (3)$$

where  $(\xi_a \cdot \xi^b)$  is the inner product between the elements  $\xi_a \in \mathcal{X}$  and  $\xi^b \in \mathcal{X}^\dagger$ . There exists a linear transformation linking  $\mathcal{X}$  and  $\mathcal{X}^\dagger$ , through the metric tensor  $S$ , that is the overlap matrix of the problem [1].

If  $x_{ia}$  ( $x^{ia}$ ) are the covariant (contravariant) coefficients of spin-orbital  $a$  in the  $i$ -th MO, the first-order reduced density matrix is [1]

$$\Pi_a^b = \sum_i x_{ia} x^{ib} \quad (4)$$

where  $i$  runs over the occupied MO's. The form  $\Gamma$  may be written as

$$\Gamma = \det(\xi_a \cdot \xi^b) = \det(\Pi_a^b) \quad , \quad (5)$$

for the  $\xi_a$  ( $\xi^a$ ) mean

$$\xi_a = (x_{1a} \dots x_{ia} \dots x_{occ,a}) \quad ; \quad \xi^a = \begin{pmatrix} x_1^a \\ \vdots \\ x_i^a \\ \vdots \\ x_{occ}^a \end{pmatrix} \quad (6)$$

In (5),

$$(\xi_a \cdot \xi^b) = \Pi_a^b \quad (7)$$

is a bilinear alternating form both in the rows and in the columns of the matrix  $\Pi$ , hence  $\Gamma$  is alternating separately in the  $\xi_a$ 's and in the  $\xi^b$ 's.

Now, (3) (i.e. (5)) is the most general inner product between all the  $\xi$ 's. This is a very powerful tool. Here, in order to build the quantities with which we are concerned, we shall need only the simple, known inner products (7). The number  $n$ , the dimension of  $\Gamma$ , is given by the number of atomic orbitals used in (4).

### 3. Valence of an atomic group

Let us define, for an atom A in a molecule, the invariants required for our purposes, in terms of the quantities introduced in the former section. As we shall restrict to closed-shell cases, we do not need a spin label.

$$I_{AA} = \sum_{\alpha, \alpha' \in A} (\xi_\alpha \cdot \xi^{\alpha'}) (\xi_{\alpha'} \cdot \xi^\alpha) \quad (8)$$

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$$I_{AB} = \sum_{\substack{a \in A \\ b \in B}} (\xi_a \cdot \xi^b) (\xi_b \cdot \xi^a) \quad ; \quad V_A = \sum_B I_{AB} \quad (9)$$

$$q_A = \frac{1}{2}(I_{AA} + V_A) \quad (10)$$

The quantity  $I_{AA}$  is related to  $s_A$ . We have introduced (10) the softness of an atomic group  $G$  by including the bond indices  $I_{AB}$ , linking atoms within the group, in its self-charge  $I_G$ . If  $G = \{ A_1 A_2 \dots A_L \}$ :

$$I_G = \sum_{A, B \in G} \sum_{\substack{a \in A \\ b \in B}} (\xi_a \cdot \xi^b) (\xi_b \cdot \xi^a) \quad (11)$$

$$V_G = \sum_{\substack{A \in G \\ B \in G}} \sum_{\substack{a \in A \\ b \in B}} (\xi_a \cdot \xi^b) (\xi_b \cdot \xi^a) \quad (12)$$

and hence

$$q_G = \frac{1}{2}(I_G + V_G) \quad (13)$$

From (9) and (12),

$$V_G = \sum_{\substack{A \in G \\ B \notin G}} I_{AB} \quad (14)$$

That is, the group valence is the sum of the bond indices between atoms inside and outside the group. In other words [4,11]  $V_G$  is given by the sum of the correlations between the fluctuations of the charges  $q_A$  (A belonging to G) and  $q_B$  (B not belonging to G) from their average values. If the group reduces to one atom, we meet again formula (9) for  $V_A$  which is, as we mentioned, the known expression introduced independently in Refs. [5] and [6]. Eq. (14) gives a quantitative meaning to the intuitive notion of group valence.

It is verified that

$$q_G = \sum_{i=1}^L q_{A_i} \quad (15)$$

Let us remark that, therefore, the atomic charges of the group are additive, while neither  $I_G$  nor  $V_G$  are obtained through the respective sums of  $I_{AA}$  or  $V_A$ .



#### 4. Results and discussion

The expressions above may be used both in semiempirical and in ab initio calculations. We have seen that, for other similar invariants [10], the results for different methods do not involve qualitative distinctions. We shall hence show results for  $V_G$  obtained with the CNDO/2 approach; let us recall that when employing an orthogonal basis the bond indices  $I_{AB}$  are the Wiberg indices [12]. There is no loss of generality in this choice, for the physical meaning of a quantity cannot depend of the basis being or not an orthogonal one [13].

We have reported in the Table the valence for a few atomic groups in different (mostly organic) compounds. Group valence is generally supposed to have a single integer value, unlike atomic valence which may classically have different possibilities. It is seen that the non-integer values obtained agree well with chemical expectation.  $V_G$  shows the peculiarity of each group within the molecule. In homologous series,  $V_G$  of a certain group seems to tend towards a constant value, after an initial greater variation when going from one to two carbons in the chain. This is found also for other atomic groups not shown here, as carboxyl in the acid series.

The methyl group has the highest  $V_G$  value in toluene, due probably to hyperconjugation. The lowest value of the Table is meth-

anol's, but in  $FCH_3$  it is even smaller ( 0.98 ). Valence for hydroxyl exhibits an appreciable range of variation ( 0.99 - 1.29 ).

For the amine group, formamide has its highest value, originated in the "secondary" bond between N and O [14]. "Secondary" bonds have been shown to explain that oxygen uses to have a valence greater than the classical value of two [1], hence it is not surprising that the carbonyl group is also more than divalent.  $V_{CO}$  is particularly high for thymine (not appearing in the Table), i.e. 2.49; we have instead  $V_{CH_3} = 1.13$  in this molecule, similar to other ones in the Table.

Another group not reported is the nitrosyl group. In  $N_2O$ ,  $N_2O_4$  and  $N_2O_5$  we have respectively  $V_{NO} = 2.89$ , 2.69 and 2.73. The first molecule has too a large "secondary" NO bond index.

From the Table, three values arise for the phenyl group valence ( in toluene, phenol and aniline ). For diphenyl, as expected, we obtain a high value of 1.19.

In short, the groups studied have varying non-integer valence values corresponding to the integers of the classical patterns.

Table 1. Valence  $V_G$  for some atomic groups

MOLECULE	$V_{CH_3}$	$V_{OH}$	$V_{NH_2}$	$V_{CO}$
$H_2O$		0.98		
$H_2O_2$		1.01		
$CH_3OH$	1.07	1.07		
$CH_3CH_2OH$	1.11	1.06		
$CH_3(CH_2)_2OH$	1.11	1.05		
$CH_3(CH_2)_3OH$	1.11	1.05		
$HCHO$				1.97
$CH_3CHO$	1.14			2.11
$CH_3CH_2CHO$	1.11			2.12
$CH_3(CH_2)_2CHO$	1.11			2.12
$CH_3COCH_3$	1.14			2.22
$HCOOH$		1.29		2.23
$CH_3COOH$	1.15	1.18		2.26
$CH_3CH_2COOH$	1.11	1.19		2.28
$CH_3(CH_2)_2COOH$	1.11	1.19		2.26
$C_6H_5CH_3$	1.18			
$C_6H_5OH$		1.13		
$C_6H_5NH_2$			1.28	
$NH_3$			0.99	
$N_2H_4$			1.06	
$NH_2OH$			1.04	
$CH_3NH_2$			1.03	
$NCONH_2$			1.29	2.24

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