On the density matrix definition of valency

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In a recent article Gopinathan and Jug have proposed a definition of atomic valency which had previously been given by Armstrong, Perkins and Stewart for closed shell molecules. The validity and interpretation of this definition for open shell systems is discussed. A new parameter for structural analysis, the free electron index, is presented.

Key words: Atomic valency — Valency, density matrix definition of ~ — Free electron index

Recently, Gopinathan and Jug [1] have proposed the following definition of atomic valency for closed and open shell systems

$$V_A^{GJ} = \sum_{a \in A} \sum_{B \neq A} \sum_{b \in B} P_{ab}^2 \tag{1}$$

where V_A^{GJ} is the valency of atom A and P_{ab} is the density matrix element for orbitals a and b associated to atoms A and B respectively. We want to point out that this expression had already been given a long time ago by Armstrong et al. [2] for the closed shell case. This fact was omitted by the aforementioned authors. Armstrong et al. proposed a general expression for atomic valency

$$V_A^{APS} = \sum_{a \in A} 2P_{aa} - \sum_{a \in A} \sum_{b \in A} P_{ab}^2 \tag{2}$$

which reduces to Eq. (1) for a closed shell molecule due to the duodempotency property of the density matrix obtained using the orthogonal molecular orbitals in NDO-type theories. The authors suggested that the difference between Eqs. (2) and (1) should be interpreted as a measure of reactivity or free valency [2]

$$F_A^{APS} = \sum_{a \in A} 2P_{aa} - \sum_{B} \sum_{a \in A} \sum_{b \in B} P_{ab}^2. \tag{3}$$

The main difference between both definitions in the open shell case is that Eq. (1) is a measure of the number of simple bonds which arrive at the considered atom, as it may be seen if Eq. (1) is rewritten in terms of Wiberg's bond index B_{AB} [3]

$$V_A^{GJ} = \sum_{B \neq A} B_{AB} \tag{4}$$

$$B_{AB} = \sum_{a \in A} \sum_{b \in B} P_{ab}^2. \tag{5}$$

On the other hand, Eq. (2) is a measure of the capacity of bonding due not only to the real bonds but to the nonbonded electrons as well. In a subsequent paper [4] Gopinathan and Jug have applied their definition to closed and open shell molecular systems and, in order to have a means of measuring chemical reactivity, they have defined a free valency index

$$F_A^{GJ} = V_A^r - V_A^{GJ} \tag{6}$$

where V_A^r is a reference valency which the authors define as "an integer value around which the computed valency of A is distributed in a large number of compounds" [4]. This definition implies that a molecule would react in such a way as to achieve the reference valency for each considered atom, irrespective of their different properties in different kinds of molecules. In Table 1 we show MNDO [5] calculations of methyl radical and nitric oxide. As may be seen, in the methyl radical example the value of V_A^{APS} represents the tetravalency of carbon, while the value of the corresponding V_A^{GJ} indicates that carbon is bonded by simple covalent bonds to three hydrogen atoms. The values of F_A^{APS} and F_A^{GJ} indicate the existence of an odd electron or subvalency. In the nitric oxide example V_A^{GJ} does not differentiate between both atoms since obviously they are linked by the same number of bonds, while V_A^{APS} indicates that the nitrogen atom has an increased bonding capacity as it is well known. Both F_A^{APS} and F_A^{GJ} show that the nitrogen atom is more reactive than the oxygen atom.

For a closed shell system, obviously, $F_A^{APS} = 0$ so that in the scheme of Armstrong et al. one must rely on the value of V_A^{APS} to measure chemical reactivity.

We want also to point out an incorrect partitioning of electron density in the article of Armstrong et al. [2]. They have started from the following relationship between B_{AB} and the total number of electrons N

$$\sum_B \sum_A B_{AB} = \sum_a \sum_b P_{ab}^2 = \text{Tr}\,(P^2) = \text{Tr}\,(2P) = 2N \tag{7}$$

Table 1. Valencies and free valencies from MNDO calculations for methyl radical and nitric oxide

Molecule	Atom	V_A^{APS}	V_A^{GJ}	F_A^{APS}	F_A^{GJ}
Methyl radical	C	3.900	2.997	0.903	1.003
Nitric oxide	N	2.787	2.141	0.646	0.859
	O	2.495	2.141	0.354	−0.141

For the definition of the quantities see text

and they have partitioned N in the following way

$$N = \sum_A \sum_{B<A} B_{AB} + \sum_A \frac{B_{AA}}{2} = \sum_A \sum_{B<A} N^b_{AB} + \sum_A N^a_A \tag{8}$$

where $N^a_A = B_{AA}/2$ is the number of electrons on atom A and $N^b_{AB} = B_{AB}$ is the number of electrons in bond $A - B$. We consider that this definition is not adequate because N^b_{AB} takes a value of 1 for a covalent two electron bond and not 2 as one would expect.

Therefore, we suggest the following definition

$$N^b_{AB} = 2B_{AB} \tag{9}$$

and rewriting Eq. (8)

$$N = \sum_A \sum_{B<A} 2B_{AB} + \sum_A \left(\frac{B_{AA}}{2} - \sum_{B<A} B_{AB} \right) \tag{10}$$

we find a new expression for the number of electrons in atom A

$$N^a_A = \frac{B_{AA}}{2} - \sum_{B \neq A} \frac{B_{AB}}{2} = \frac{B_{AA} - V^{APS}_A}{2} \tag{11}$$

where use has been made of Eq. (2) for a closed shell molecule. This quantity is a measure of the number of electrons on atom A which do not participate in bonds (i.e. lone pairs, unpaired electrons, etc.). We consider that this parameter, which we shall call free electron index, together with bond index and valency is indispensable for a correct description of molecular systems in terms of Lewis structural scheme.

For an open shell molecule, Eq. (7) is not valid since use has been made of the duodempotency of P, which does not hold for open shell systems. The correct expression for both closed and open shell molecules is

$$2N = \text{Tr}\,(2P) = \sum_a 2P_{aa} = \sum_A (V^{APS}_A + B_{AA}). \tag{12}$$

If we use the same definition for N^b_{AB} as above (Eq. (9)) we find

$$N = \sum_A \sum_{B<A} 2B_{AB} + \sum_A \left(\frac{V^{APS}_A + B_{AA}}{2} - \sum_{B \neq A} B_{AB} \right) \tag{13}$$

so that the new definition for the free electron index is

$$N^a_A = \frac{V^{APS}_A + B_{AA}}{2} - \sum_{B \neq A} B_{AB}. \tag{14}$$

It may be easily seen that Eq. (14) reduces to Eq. (11) for a closed shell molecule. In the Gopinathan-Jug scheme this last quantity may be calculated as $N^a_A = \delta_A - V^{GJ}_A$, with $\delta_A = \sum_{a \in A} P_{aa}$ the electronic density on atom A.

In Table 2, we show the N^a_A values obtained from MNDO calculations of several closed and open shell molecules. We also report the corresponding anisotropy

Table 2. Free electron indices (N_A^a) and anisotropies (L_A) from MNDO calculations

Molecule	Atom	N_A^a	L_A	Molecule	Atom	N_A^a	L_A
N_2	N	2.00	0.28	BH_3	B	−0.04	0.38
O_2 (triplet)	O	4.50	0.27	NO_2	N	1.52	0.19
O_2 (singlet)	O	4.00	0.77		O	4.29	0.39
CO	C	1.33	0.54	H_3O^+	O	3.44	0.36
	O	3.76	0.19	NH_3	N	2.26	0.51
NO (doublet)	N	2.83	0.44	CH_3NH_2	N	2.32	0.49
	O	3.88	0.29	$(CH_3)_2NH$	N	2.38	0.46
H_2O	O	4.39	0.64	$(CH_3)_3N$	N	2.50	0.46
SO_2	S	2.09	0.22	$C_6H_5NH_2$	N	2.19	0.47
	O	4.56	0.44	CH_3OH	O	4.33	0.57
HCN	C	0.20	0.01	CH_3CH_2OH	O	4.32	0.57
	N	2.11	0.31	C_6H_5OH	O	4.13	0.54
HNC	C	1.24	0.50	$CH_3OH^{\cdot-}$	O	4.68	0.46
	N	2.07	0.09		C	0.13	0.03
$CH_3^{\cdot}$	C	1.20	0.01				

[2] values (L_A) which measure the non-sphericity of electron density around an atom. It may be seen that the N_A^a values are close to the number of electrons in lone pairs or radicals which one could derive from Lewis formulae. For the amine series the free electron index increases in the order: aniline < ammonia < methylamine < dimethylamine < trimethylamine, corresponding to a decrease of electron density on the nitrogen atom in aniline compared with ammonia and a progressive increase of this quantity with the replacement of hydrogen atoms by methyl groups. We see that anisotropy does not mimic this tendency very well. The N_A^a value for methyl radical indicates clearly the existence of an unpaired electron, while anisotropy is almost null. The only atom in the table with a negative value of N_A^a is the boron atom in borane, in accordance with its known electronic deficiency. Finally we see that in phenol the oxygen atom has a lower value of N_A^a compared with the aliphatic alcohols, attributable to the delocalization of the lone pairs on the aromatic ring.

As Gopinathan and Jug [1] also reported an expression for the valency of an atomic orbital in a molecule from which they derived the atomic valency formula (1), we want to define the corresponding quantity in the formalism of Armstrong et al.

$$V_a^{APS} = 2P_{aa} - \sum_{b \in A} P_{ab}^2 \tag{15}$$

where V_a^{APS} is the valency of the atomic orbital a centred on atom A. Finally, we want to quote an extension of Armstrong et al. formulae to *ab initio* SCF-LCAO-MO calculations by Mayer [6] and an extension of the work of Gopinathan and Jug on the CI level [7].

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