ISSN 0029-3865

CBPF-NF-010/86

DIRECT CONSEQUENCES OF THE BOND INDEX STATISTICAL INTERPRETATION

by

Paulo Pitanga[1], Mario Giambiagi and
Myriam S. de Giambiagi

Centro Brasileiro de Pesquisas Físicas - CBPF/CNPq
Rua Dr. Xavier Sigaud, 150
22290 - Rio de Janeiro, RJ - Brasil

[1]Instituto de Física
Universidade Federal do Rio de Janeiro
Cidade Universitária, Ilha do Fundão
21910 - Rio de Janeiro, Brasil

ABSTRACT

The statistical interpretation of bond index, valence and charge fluctuation is connected with the hardness-softness concept developed by Pearson, Parr and co-workers. It is shown that the MO self-charge of an atom is its softness in the molecule. For all pairs (A,B) of atoms in a molecule, a reciprocal relation is obtained for the rate of change of the electronic charge in A with respect to the chemical potential of B.

Key-words: Bond index; Charge fluctuation; Valence; Hardness-softness.

In non-orthogonal bases, the first-order reduced density matrix is a mixed second order tensor [1]

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

where $x^{\underline{i}\underline{a}}$ are the contravariant coefficients and $x_{\underline{i}\underline{a}}$ the co-variant ones of orbital $\underline{a}$ in the $\underline{i}$-th molecular orbital of a doubly occupied level (restricting to the closed-shell case).

The atomic charge q_A of atom A in an N-electron system ($\sum_A q_A = N$) is

$$q_A = (1/2)\ I_{AA} + (1/2) \sum_{B\neq A} I_{AB} \quad (I_{AB} = 4 \sum_{\substack{\underline{a}\varepsilon A \\ \underline{b}\varepsilon B}} \Pi_{\underline{a}}^{\underline{b}}\ \Pi_{\underline{b}}^{\underline{a}}) \qquad (2)$$

where the first term is the self-charge and the second one the active charge [1,2]. This is the Mulliken atomic population, with a quite different partition among self and active charges; q_A is the invariant associated with the first-order density matrix [3].

Eq.(2) may be also stated as

$$q_A = \langle\hat{q}_A\rangle = (1/2)(I_{AA} + V_A) \qquad (3)$$

where $\hat{q}$ is the electronic density operator and V_A, the valence of atom A, is [3]

$$V_A = \sum_{B\neq A} I_{AB} \qquad (4)$$

We have shown that the bond index I_{AB} between atoms A and B is the scalar associated with the spinless second-order density matrix d [4]:

$$I_{AB} = q_A\, q_B - \sum_{\substack{\underset{\sim}{a}\varepsilon A \\ \underset{\sim}{b}\varepsilon B}} d^{\underset{\sim}{a}\underset{\sim}{b}}_{\underset{\sim}{b}\underset{\sim}{a}} = <\hat{q}_A>\, <\hat{q}_B> - <\hat{q}_A \hat{q}_B> \qquad (5)$$

which may be written as [4]

$$- I_{AB} = <(\hat{q}_A - <\hat{q}_A>)(\hat{q}_B - <\hat{q}_B>)> \qquad (6)$$

Therefore, V_A is the sum of the correlations between the fluctuation in A and those of all the other atoms.

If in (6) A is made equal to B, we have [4]

$$<\hat{q}_A^2> - <\hat{q}_A>^2 = - I_{AA} \qquad (7)$$

The kind of fluctuations we have described have different sense from those which have been obtained in a work partitioning the Mulliken electronic density in orbital regions [5]. In this one, chemical bonds correspond to weak relative charge fluctuations. Instead, we infer a bond when, in addition to a large fluctuation, we have a large correlation between the charge fluctuations in a pair of atoms; our bond indices belong to the atomic population through its active charge.

We shall now relate the above mentioned concepts to what is tempting to call a thermodynamical formalism. The grand partition function Γ for quantum statistics is, in our notation,

$$\Gamma = \mathrm{Tr}\,\exp\,[-\beta(F - \sum_L \mu_L \hat{q}_L)]\,;\quad G = -(1/\beta)\,\ln\,\Gamma \qquad (8)$$

where G is the Gibbs function, F the Helmholtz free energy, $\beta = 1/kT$ and μ_L the chemical potential of atom L. It is then straightforward to show that

$$<\hat{q}_A> = -\,\partial G/\partial \mu_A \qquad (9)$$

and that [6]

$$-\partial^2 G/\partial\mu_A^2 = \beta(\langle\hat{q}_A^2\rangle - \langle\hat{q}_A\rangle^2) \tag{10}$$

Similarly, we can easily show that

$$-\partial^2 G/\partial\mu_A\partial\mu_B = \beta(\langle\hat{q}_A\hat{q}_B\rangle - \langle\hat{q}_A\rangle\langle\hat{q}_B\rangle) \tag{11}$$

or, by (5)

$$\partial^2 G/\partial\mu_A\partial\mu_B = \beta I_{AB} \tag{12}$$

and also

$$V_A = (1/\beta) \sum_{B\neq A} \partial^2 G/\partial\mu_A\partial\mu_B \tag{13}$$

As I_{AB} and V_A are numbers, the derivatives in eqs.(12) and (13) must be the values of the corresponding functions at a certain point; this is most naturally defined as the equilibrium point where all atomic chemical potentials (electronegativities) are equal, for they must be so in the molecule [7]: $\mu_A = \mu_B = \mu$. Expression (13) opens a new thermodynamical outlook for the valence concept.

By (9) and (10) we have that

$$\partial\langle\hat{q}_A\rangle/\partial\mu_A\big|_{\mu_A=\mu} = \beta(\langle\hat{q}_A^2\rangle - \langle\hat{q}_A\rangle^2) \tag{14}$$

that is, by (7)

$$\partial\langle\hat{q}_A\rangle/\partial\mu_A\big|_{\mu_A=\mu} = -\beta I_{AA} \tag{15}$$

In turn, this is related to hardness η or softness $\underline{s}$, such as defined by Parr et al. in the density functional formulation[8,9].

$$\underline{s}_A = 1/\eta_A = \partial\langle\hat{q}_A\rangle/\partial\mu_A\big|_{\mu_A=\mu} \tag{16}$$

Eq. (16) may then give a quantitative meaning to the statement that "each atom has its own effective hardness in a molecule (whereas electronegativities of all atoms are the same)" [9]. Let us underline that even hydrogen, from this point of view, exhibits variating hardnesses; its self-charge covers a surprisingly large range in compounds such as hydrocarbons, azines and borazarobenzenes [2]. We conclude that, as regards the reactivity aspect of hardness [9], the significant quantity is the self-charge rather than the total charge.

In actual calculations, we must remember to get rid of isolated pairs and core electrons in order to estimate hardness through I_{AA}, for they contribute in an additive constant to q_A and are hence independent of μ_A. For doubtful cases, they are easily identified by calculating the $2\Pi^{a'}_{\underline{a}}$ eigenvalues.

The ensemble molecular formulation may be found in Ref. [10]. However, the "thermodynamical" treatment must be dealt with some caution, keeping aware of the recent developments in local thermodynamics [9,11]. Our formulation seems to involve an intermediate level, neither local (functions of the space coordinates) nor global (numbers referred to the molecule as a whole) in the sense used in density functional theory [9]. Quantities such as q_A and I_{AB} are associated with zones within a molecule, so that they could be better named zonal quantities.

As a corollary, either of eq.(9) or of eq.(12), we arrive at the inciting equilibrium condiiton

$$\partial\langle\hat{q}_A\rangle/\partial\mu_B|_{\mu_A=\mu_B=\mu} = \partial\langle\hat{q}_B\rangle/\partial\mu_A|_{\mu_A=\mu_B=\mu} \qquad (17)$$

Thus, for <u>all pairs</u> (A,B) of atoms in a molecule, we have a reciprocal relation for the rate of change of the electronic charge in A with respect to the chemical potential of B.

Acknowledgement

We are deeply indebted to Dr. Robert G. Parr for having called our attention on the relation with softness. We also acknowledge the generous discussions carried out with Drs. André Julg and Pierre Claverie.

References

[1] M.S. de Giambiagi, M. Giambiagi and F.E. Jorge, Z. Naturforsch. 39a(1984)1259.

[2] M. Giambiagi, M.S. de Giambiagi, D.R. Grempel and C.D. Heymann, J. Chim. Phys. 72(1975)15.

[3] I. Mayer, Chem. Phys. Lett. 97(1983)270.

[4] M.S. de Giambiagi, M. Giambiagi and F.E. Jorge, Theoret. Chim. Acta 68(1985)337.

[5] A. Julg and P. Julg, Intern. J. Quantum Chem. 13(1978)483; see also P. Claverie and S. Diner in: Localalization and delocalization in quantum chemistry, Vol.2, eds. O. Chalvet et al. (D. Reidel, Dordrecht, 1976), p. 395.

[6] K. Huang, Statistical mechanics (Wiley, N.York,1963),p.179.

[7] P. Politzer and H. Weinstein, J. Chem. Phys. 71(1979)4218 and Refs. therein.

[8] R.G. Parr and R.G. Pearson, J. Am. Chem. Soc. 105(1983)7512.

[9] M. Berkowitz, S.K. Ghosh and R.G. Parr, J. Am. Chem. Soc. 107(1985)6811; W. Yang and R.G. Parr, Proc. Natl. Acad. Sci. USA 82(1985)6723.

[10] R. McWeeny, Rev. Mod. Phys. 32(1960)335.

[11] S.K. Ghosh, M. Berkowitz and R.G. Parr, Proc. Natl. Acad. Sci. USA 81(1984)8028.