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ABOUT THE CORRELATION BETWEEN ATOMIC CHARGE FLUCTUATIONS IN A MOLECULE*

by

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*Dedicated to Dr. Ricardo Ferreira

ABSTRACT

In this note, the features of the correlation between the
electronic charge fluctuations of a pair of atoms within a
molecule are analized. Through Schwarz's inequality for ran-
dom operators in the Hilbert space, the softness of an atom
in a molecule is related to its valence and to the softness
of the other atoms. It is concluded that in the general case
this correlation (from which in turn stems the chemical bond)
in non-linear.

Key words: Correlation between the electronic charge fluctua-
tions - Schwarz's inequality - Softness of an atom in a molecule.

In former works[1,2] we have shown that the index I_{AB}, which reflects suitably certain properties of the chemical bond between atoms A and B, is associated with the second-order reduced density matrix and correlates the electronic charge fluctuations of A and B:

$$-I_{AB} = <(\hat{q}_A - <\hat{q}_A>)(\hat{q}_B - <\hat{q}_B>)> \qquad (1)$$

where $\hat{q}_A$ is the electronic density operator and its mean value

$$<\hat{q}_A> = q_A \qquad (2)$$

is the Mulliken charge.

The valence of A is[3]

$$V_A = \sum_{B \neq A} I_{AB} \qquad (3)$$

If in eq. (1) we allow A to be equal to B,

$$-I_{AA} = <\hat{q}_A^2> - <\hat{q}_A>^2 \qquad (4)$$

verifying[4]

$$q_A = 1/2 (I_{AA} + \sum_{B \neq A} I_{AB}) = 1/2 (I_{AA} + V_A) \qquad (5)$$

On the other hand, I_{AA} leads to the softness s_A or the hardness η_A of A in a molecule[2]

$$s_A = 1/\eta_A = -\beta I_{AA} \qquad (6)$$

The usual approach for the softness-hardness concepts[5-7] is based upon valence state ionization potentials and electron affinities, and have recourse to the finite difference approximation, yielding thus a semiempirical scale. Our non-empirical

scale[2] permits the definition of functional group softness.
Both scales are not comparable[8].

Schwarz's inequality, as has been recently demonstrated,
is valid also for random operators in the Hilbert space[9];
for the mean values of two operators f and g:

$$<fg>^2 \leq <f^2><g^2> \tag{7}$$

where the equality holds if and only if f and g are propor-
tional. Let us apply the inequality to:

$$f = \hat{q}_A - <\hat{q}_A> \quad ; \quad g = \hat{q}_B - <\hat{q}_B> \tag{8}$$

By (1) and (4)

$$I_{AB}^2 \leq I_{AA}I_{BB} \quad \therefore \quad I_{AB} \leq (I_{AA}I_{BB})^{1/2} \tag{9}$$

i.e.

$$I_{AB}^2 \leq s_A s_B / \beta^2 \tag{10}$$

Adding all the inequalities (9) we have

$$\sum_{B \neq A}' I_{AB} \leq \sum_{B \neq A}' (I_{AA}I_{BB})^{1/2} \tag{11}$$

$$\sum_{B \neq A}' I_{AB} \leq I_{AA}^{1/2} \sum_{B \neq A}' I_{BB}^{1/2} \tag{12}$$

Therefore

$$I_{AA} \geq (\sum_{B \neq A}' I_{AB} / \sum_{B \neq A}' I_{BB}^{1/2})^2 \tag{14}$$

or also

$$s_A \geq (V_A / \sum_{B \neq A}' s_B^{1/2})^2 \tag{15}$$

which is an appealing relation between an atom's softness,

its valence and the softness of the other atoms in the molecule.

In the case of the equality in (7), we would have a linear correlation

$$\hat{q}_A - \langle\hat{q}_A\rangle = \alpha(\hat{q}_B - \langle\hat{q}_B\rangle) \tag{15}$$

Squaring and averaging, by (4),

$$I_{AA} = \alpha^2 I_{BB} \tag{16}$$

Expanding

$$\langle\hat{q}_A^2\rangle - \langle\hat{q}_A\rangle^2 = \alpha^2(\langle\hat{q}_B^2\rangle - \langle\hat{q}_B\rangle^2) = \langle(\alpha\hat{q}_B)^2\rangle - \langle\alpha\hat{q}_B\rangle^2 \tag{17}$$

$$\therefore \quad \hat{q}_A = \alpha\hat{q}_B \quad ; \quad q_A = \alpha q_B \tag{18}$$

And in that case it would be

$$(q_A/q_B)^2 = I_{AA}/I_{BB} = s_A/s_B \tag{19}$$

which we verified that is obeyed only by diatomic molecules either a) homonuclear or b) heteronuclear of the XH type. Hence in the general case the electronic charges and softnesses of the atoms in a molecule do not obey a simple relation such as eq. (19) would predict.

As, by eq. (19), s_A and s_B are equal only in the homonuclear case, the corollary according which the equalization of the electronegativities of the atoms in a molecule amounts necessarily to the equalization of their hardnesses[7], relies on too limiting hypotheses[6].

Let us remark that, mathematically, the sign of α in (15)

could both be positive and negative. However, by (18), as q_A and q_B have the same sign, α is always positive; as a consequence, the charge fluctuations have the same direction if their correlation is linear.

Thus, eq. (7) is generally an inequality. Hence, we shall have that generally the correlation between the charge fluctuations of atoms A and B in a bond AB is non-linear.

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