TWO SIMPLE SYMMETRY-DEPENDENT RULES IN CONJUGATED SYSTEMS

Myriam Segre de Giambiagi and Mario Giambiagi
Centro Brasileiro de Pesquisas Físicas
Av. Wenceslau Braz, 71
22290 Rio de Janeiro, RJ, BRASIL

It has recently been remarked [1] the increasing difficulty in obtaining new simple but generally valid rules for conjugated systems. We have established some symmetry-related theorems and corollaries about π bond orders of such systems [2,3,4]. In ref. (2) we generalized to non-or -thogonal basis and non alternant molecules the complementarity condition introduced in orthogonal basis for alternant hydrocarbons [5]. We later found particular solutions for the bond order matrix, independently from the approximations used [3], and properties of the molecular orbitals' (MO) contributions [4] under certain symmetry conditions. We now present two simple bond order properties in systems with a twofold symmetry axis which (I) crosses two π centers; (II) does not cross any π center. From these relations simple structural "a priori" properties follow.

The mobile LCAO bond order is defined as [6]

$$P_{\mu\nu} = \frac{1}{2} \sum_i n_i (x_{i\mu} y_{i\nu} + x_{i\nu} y_{i\mu}); \quad y_{i\nu} = \sum_\rho S_{\nu\rho} x_{i\rho} \qquad (1)$$

where $x_{i\mu}$ is the coefficient of atom μ in the i-th MO; n_i is the i-th occupation number and $S_{\nu\rho}$ is the overlap between the atomic orbitals ν and ρ.

I) When a molecule has a twofold symmetry axis not passing through any of its N π-electron centers, there exist "a priori" known solutions for the P matrix of certain excited states[3]. We shall now show that these "a priori" solutions exist also, under different form, if the twofold symmetry axis crosses two π-electron centers. The labelling is such that the symmetry establishes an equivalence between the μ and the $N+2-\mu$ atomic orbitals. As μ goes from 1 upto N, we must add the convention that N+1 is equivalent to 1 (cyclic numeration), in order to ensure that the first and the (N/2+1)-th atomic orbitals are equivalent to themselves.

We have

$$Tr\ P = N \tag{2}$$

and, defining a matrix Q by

$$Q = P - I \tag{3}$$

I being the unit matrix. It is easily seen[3] that Q must satisfy

$$Q^3 = Q \tag{4}$$

and, being H the Hamiltonian matrix,

$$HQ = symmetric \tag{5}$$

As

$$H_{\mu,N+2-\nu} = H_{\nu,N+2-\mu} \tag{6}$$

bearing in mind the cyclic convention, two non-trivial (i.e.

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besides $Q = 0$) solutions for Q are

$$Q_{\mu\nu} = \pm\delta_{\mu,N+2-\nu}$$ (7)

if we suppose $\delta_{1,N+1} = 1$ by definition.
We have then

$$P^{\pm}_{\mu\nu} = \delta_{\mu\nu} \pm \delta_{\mu,N+2-\nu}$$ (8)

with $P^+P^- = 0$ and $P^+ + P^- = 2I$.

These particular solutions do not imply unitary charges[3]. Let us write

$$P^{\pm} = \begin{pmatrix} A^{\pm} & B^{\pm} \\ B^{\pm} & A^{\pm} \end{pmatrix}$$ (9)

where A and B are submatrices of the form

$$A^+ = \begin{pmatrix} 2 & & \\ & 1 & \\ & & \ddots \\ & & & 1 \end{pmatrix}; A^- = \begin{pmatrix} 0 & & \\ & 1 & \\ & & \ddots \\ & & & 1 \end{pmatrix}; B^{\pm} = \begin{pmatrix} & & & 0 \\ & & \pm 1 & \\ & \ddots & & \\ 0 & \pm 1 & & \end{pmatrix}$$ (10)

It is a straighforward matter to show that P^+ correspond to having all symmetric functions doubly occupied, where

$$x^+_{j\mu} = x^+_{j,N+2-\mu}$$ (11)

the coefficients of the atoms on the axis being simply equal

to themselves. And $\underset{\sim}{P^-}$ to the antisymmetric ones

$$x^-_{j\mu} = - x^-_{j,N+2-\mu} \tag{12}$$

so that the atoms on the axis must have zero coefficients.

These solutions do not lead us to states of the neutral molecule M, but of the corresponding double ions: $\underset{\sim}{P^+}$ of M^{2-} and $\underset{\sim}{P^-}$ of M^{2+}. They have electronic π charges of 2 (0) for the atoms on the axis, and unitary π charges for the other atoms. The mobile bond orders are + 1 (- 1) if they relate symmetrically equivalent centers, and zero otherwise.

The particular solutions are independent of the nature of the atoms building the system, i.e. it happens as if in these states electronegativity does not matter. Now, a molecule such as pyridine (Fig. 1a) has still a very nearly zero[3] π dipole moment μ (not exactly zero due to the difference in the interatomic distances); but a molecule such as azulene (Fig. 1b) has μ quite different from zero. It is always $\mu^+ + \mu^- = 0$, of course, as the states corresponding to the particular solutions are complementary[2]. II) If the twofold symmetry axis does not pass through any of the N π-electron centers, there are N/2 symmetric and N/2 antisymmetric MO's. Labelling is now such that the symmetry establishes an equivalence between the μ and the $N+1-\mu$ atomic orbitals[3].

Symmetric and antisymmetric functions are separately normalized to 1/2, i.e.

$$\sum_{\mu=1}^{N/2} x_{i\mu}^{\pm} y_{j\mu}^{\pm} = \delta_{ij} \tag{13}$$

By (1) we have

$$P_{\mu,N+1-\nu} = \frac{1}{2} \sum_i n_i (x_{i\mu} y_{i,N+1-\mu} + x_{i,N+1-\mu} y_{i\mu}) \tag{14}$$

As $x_{i\mu}^{\pm} = \pm x_{i,N+1-\mu}^{\pm}$ and this is valid also for y,

$$\sigma = \sum_{\mu=1}^{N/2} P_{\mu,N+1-\mu} = \sum_{i\mu} n_i^+ x_{i\mu}^+ y_{i\mu}^+ - \sum_{i\mu} n_i^- x_{i\mu}^- y_{i\mu}^- \tag{15}$$

Therefore

$$\sigma = (N^+ - N^-)/2 \tag{16}$$

That is, in systems possessing a twofold symmetry axis not passing through any π center, the summation of the bond orders crossing the symmetry axis is equal to half the difference between the number of electrons occupying symmetric and antisymmetric levels. This holds not only for the ground state, but for excited states too.

From (16) it follows that for the ground state σ is equal to 0 or 1 if $N/2$ is respectively even or odd; if there exists a twofold symmetry axis not crossing any π center, and a second one which crosses two π centers, this one does not interfere and σ is still 0 or 1. This applies for example:

a - To linear polyenes. In the limiting case of butadiene

$(CH_2 = CH - CH = CH_2)$, $P_{14} + P_{23} = 0$, $\therefore P_{14} = - P_{23}$, a known property which, as others[4], is seen to hold for any mole_cule of the same symmetry.

b - To naphthalene, anthracene and in general linear poly-benzenic condensed hydrocarbons. For naphthalene (Fig.1c) $2P_{1,10} + 2P_{29} + P_{38} = 1$ and, as $P_{1,10}$ cannot be too diffe-rent from P_{38} we may write $3 P_{1,10} + 2 P_{29} \simeq 1$. The Dewar-type formal bond orders, which are not necessarily negati-ve for excited states, must be so in the ground state. Again, this trend is found in heteromolecules of the same symmetry.

c - To monocyclic azines of the due symmetry. That is, in pyridazine (Fig. 1d), pyrazine (Fig. 1e), s-tetrazine (Fig. 1f) and v-tetrazine (Fig. 1g), σ is 1. In benzene (Fig. 1h) $P_{16} + P_{25} + P_{34} = 1$; since $P_{34} = P_{12}$ and $P_{25} = P_{14}$, this involves that the summation of the bond orders around any one atom is 1, a classical property which holds also for the mesomeric method[7]. Similarly, for a planar cyclooc-tatetraene ring (Fig. 1i), this summation would be zero.

When there exist two non-equivalent twofold symme_try axes not crossing π centers, Eq. (16) is valid for each one of them. The wave-functions are either symmetric regar_ding one axis and antisymmetric with respect to the other one, or symmetric (antisymmetric) regarding both. We no longer know "a priori" if σ is 0 or 1 for the ground state.

BIBLIOGRAPHY

(1) I. Gutman: Chem. Phys. Lett., 58, 137 (1978).

(2) M.S. de Giambiagi and M. Giambiagi: Chem. Phys. Lett.,
    1, 563 (1968);
    R. Carbó, M.S. de Giambiagi and M. Giambiagi: Nuovo Ci-
    mento, 59B, 204 (1969).

(3) C.G. Bollini, J.J. Giambiagi, M. Giambiagi and M.S. de
    Giambiagi: Theoret. Chim. Acta, 22, 234 (1971).

(4) M. Giambiagi and M.S. de Giambiagi: Lett. Nuovo Cimen-
    to, 4, 845 (1972).

(5) A.D. MacLachlan: Mol. Phys., 2, 271 (1959).

(6) B.H. Chirgwin and C.A. Coulson: Proc. Roy. Soc., A201,
    196 (1950).

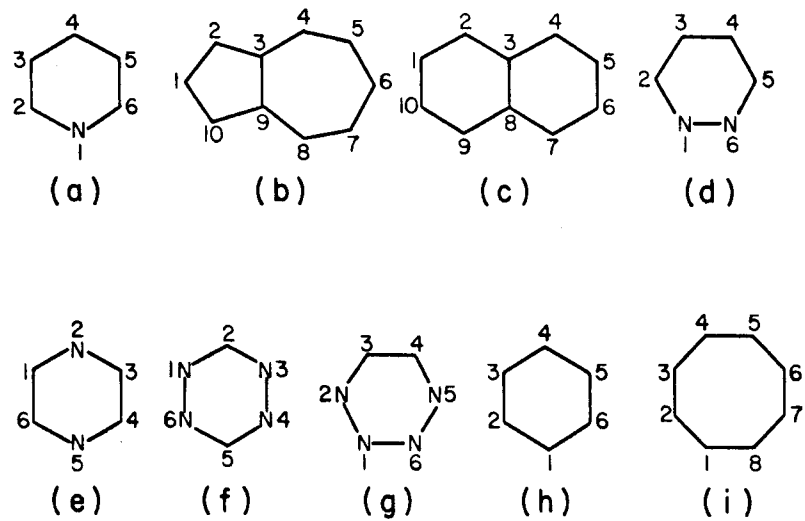(7) C.A. Coulson, P. & R. Daudel: La R. Sci. 85, 29 (1947).

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