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Short Communications

About Direct Obtainment of π SC Bond Orders

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A method for direct obtainment of SC bond orders is shown for π even systems with a twofold symmetry axis not crossing a π center. Two sets of equations are stated, one referring to symmetric and the other to antisymmetric basis functions. Pauli matrices are used for solving the 4-electron case.

Key words: Bond order – Excited states of hydrocarbons – Diazoethane

Direct calculation of SC bond orders without previous obtainment of MO's has been little explored. It has been developed for ground and excited states of hydrocarbons under certain conditions [1, 2]. SC π bond order equations and an oddity property [2] are formulated here for conjugated molecules possessing a twofold symmetry axis not passing through any of the N π-electron centers. The calculated bond orders can be assigned unequivocally to the corresponding electronic states. A Hamiltonian is proposed which involves a compromise between the fundamental and excited states.

For the 4-electron case, the question may be stated under a form seldom used in this kind of problem, employing Pauli matrices. These lead to a set of transcendental equations which are solved numerically. We are interested in applying formalisms which have proved to be useful in other fields. Elsewhere we will use the basic matrices of the SU_3 group.

The existence of a twofold symmetry axis leads to basis functions which are symmetric or antisymmetric with respect to the axis. This in turn allows the splitting of the secular equations in the two sets (with the notation of [2]):

$$JP^{+} = \text{symmetric}; \qquad KP^{-} = \text{symmetric} \tag{1}$$

where

$$J_{\mu\nu} = H_{\mu\nu} + H_{\mu,N+1-\nu}; \qquad K_{\mu\nu} = H_{\mu\nu} - H_{\mu,N+1-\nu}; \qquad P^{\pm}_{\mu\nu} = \sum_{i_\pm} n^{i_\pm} x^{i_\pm}_{\mu} x^{i_\pm}_{\nu} \tag{2}$$

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H is the effective Hamiltonian, x^i_μ the coefficient of atomic orbital μ in the ith MO whose occupation number is n^i, and the signs + or – label respectively the symmetric or antisymmetric levels.

As $n^i = 0, 1$ or 2,

$$(n^i)^3 - 3(n^i)^2 + 2(n^i) = 0 \tag{3}$$

The symmetry implies that the $P^\pm$ matrices repeat (in the case of P^- changing signs) their $N/2$ first columns. It is therefore enough to consider $P^\pm$ $N/2$-dimensional matrices, for we shall have for bond orders $P_{\mu\nu}$:

$$P_{\mu\nu} = P^+_{\mu\nu} + P^-_{\mu\nu}; \qquad P_{\mu,N+1-\nu} = P^+_{\mu\nu} - P^-_{\mu\nu} \qquad (\mu, \nu = 1 \ldots N/2) \tag{4}$$

If I is the unit matrix, it is easily seen that (3) leads to

$$(2P^\pm - I)^3 = 2P^\pm - I = Q^\pm \tag{5}$$

Our bond order equations are then

$$\begin{aligned} JQ^+ &= \text{sym.} \qquad & KQ^- &= \text{sym.} \\ (Q^+)^3 &= Q^+ \qquad & (Q^-)^3 &= Q^- \end{aligned} \tag{6}$$

These equations give the bond orders of all the states satisfying the conditions mentioned in [2].

By means of

$$\mathrm{Tr}(JP^+) = \tfrac{1}{2} \sum_{i_+} n^{i_+} E^{i_+}; \qquad \mathrm{Tr}(KP^-) = \tfrac{1}{2} \sum_{i_-} n^{i_-} E^{i_-} \tag{7}$$

the assignment of the corresponding state is made.

Note the auxiliary relations (with obvious meaning for $N^\pm$):

$$\mathrm{Tr}P^\pm = \tfrac{1}{2}N^\pm; \qquad \mathrm{Tr}Q^\pm = N^\pm - \tfrac{1}{2}N; \qquad \mathrm{Tr}(Q^+ + Q^-) = 0 \tag{8}$$

We introduce electron interaction through a Fock matrix of the PPP type [4], extensively used for electronically excited states of conjugated molecules [5].

$$H_{\mu\mu} = H^0_{\mu\mu} + \tfrac{1}{2}P_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\sigma\neq\mu} (P_{\sigma\sigma} - 1)(\mu\sigma|\mu\sigma): \qquad H_{\mu\nu} = H^0_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}(\mu\nu|\mu\nu) \tag{9}$$

$(\mu\nu|\mu\nu)$ being the Coulomb integrals between atomic orbitals on atoms μ and ν. We look for a Hamiltonian which is necessarily a compromise one, that is a compromise between ground state and all the excited states considered, on the same footing [3]. Certain excited states have unit charges independent of the nature of the atoms forming the conjugated frame, and obeying only the symmetry conditions imposed here [2b]. Two of these are the states with all symmetric (antisymmetric) levels doubly occupied. The third particular solution, corresponding also to unit charges, is the standard excited state [6], with one electron per level. If an explicit solution of Eqs. (6) is carried out

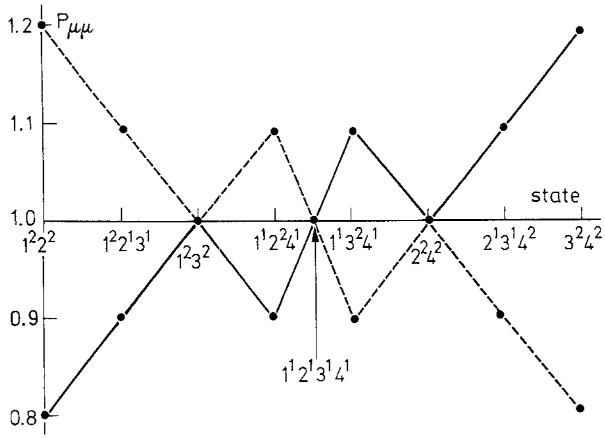

Fig. 1. Electronic densities for different states of diazoethane, Hückel approximation (——— P_{11}; - - - P_{22})

for the diazoethane molecule ($H_2C{=}N{-}N{=}CH_2$), the electronic charges of C and N follow the pattern of Fig. 1, in agreement with the complementarity relations [7]. Therefore, it does not seem unreasonable to assume - fully aware of the limitation implied by not considering configuration interaction - a compromise Hamiltonian with unit charges, which is strictly correct for the three intermediate states mentioned

$$H_{\mu\nu} = H^0_{\mu\nu} + P_{\mu\nu} C_{\mu\nu} \tag{10}$$

If J and K are given by (2), with H^0 instead of H, and $C^{\pm}_{\mu\nu} = C_{\mu\nu} \pm C_{\mu,N+1-\mu}$, the equivalent Eqs. (5) will be

$$[J + (C^+P^+) + (C^-P^-)]\,P^+ = \text{sym.}; \qquad [K + (C^-P^+) + (C^+P^-)]\,P^- = \text{sym.} \tag{11}$$

where (CP) are not products of C and P, but must be understood as $(CP)_{\mu\nu} = C_{\mu\nu}P_{\mu\nu}$. The equations for Q are then:

$$[J' + (C^+Q^+) + (C^-Q^-)]\,Q^+ = \text{sym.}; \qquad [K' + (C^-Q^+) + (C^+Q^-)]\,Q^- = \text{sym.} \tag{12}$$

where

$$J' = 2J + (C^+I) + (C^-I); \qquad K' = 2K + (C^-I) + (C^+I) \tag{13}$$

as J and K are symmetric, it is seen at once that particular solutions of (12) are

$$Q^{\pm} = \pm I; \qquad Q^{\pm} = 0 \tag{14}$$

The left-hand sides of Eqs. (7) become [8]

$$\begin{aligned} &\mathrm{Tr}\{[J + (C^+P^+) + (C^-P^-)]P^+\} + \mathrm{Tr}(JP^+) \\ &\mathrm{Tr}\{[K + (C^-P^+) + (C^+P^-)]P^-\} + \mathrm{Tr}(KP^-) \end{aligned} \tag{15}$$

Let us show that the solutions for diazoethane (the 4-electron case), writing the Q's in the form $q_0 + \mathbf{q} \cdot \sigma$. σ stands for the Pauli matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{16}$$

From $Q^3 = Q$:

$$q_0 = q_0^3 + 3q_0 \cdot \mathbf{q}^2; \qquad \mathbf{q} = (3q_0^2 + \mathbf{q}^2)\mathbf{q} \tag{17}$$

Three cases are immediately recognized

$$\begin{aligned} &1) \quad \mathbf{q} = 0;\ q_0 = q_0^3 \quad \Rightarrow q_0 = +I, -I, 0 \\ &2) \quad \mathbf{q} \neq 0; q_0 = 0 \quad \Rightarrow \mathbf{q}^2 = I \\ &3) \quad \mathbf{q} \neq 0; q_0 \neq 0 \quad \Rightarrow \mathbf{q}^2 = q_0^2 = I/4 \end{aligned} \tag{18}$$

Case 1) corresponds to the three particular solutions. Case 2) gives the states for which $\det P \neq 0$, and 3) those for which $\det P = 0$ [2a].

The trace equations (8) limit the coupling of Q^+ and Q^- to those within the same case.

Writing all relevant matrices in terms of Pauli σ-matrices, as by relations (12) $Q^{\pm}$ commutes with the expressions between square brackets, the vectorial parts must verify

$$\begin{aligned} \lambda \mathbf{q}^+ &= \mathbf{j}' + (c^+\mathbf{q}^+) + (c^-\mathbf{q}^-) \\ \mu \mathbf{q}^- &= \mathbf{k}' + (c^-\mathbf{q}^+) + (c^+\mathbf{q}^-) \end{aligned} \tag{19}$$

All second components of symmetrical matrices must be set equal to zero; Eqs. (19) are equivalent to the following set of equations

$$\begin{cases} \lambda \sin\varphi_1 = A_1 + a_1 \sin\varphi_1 + a_2 \sin\varphi_2 \\ \lambda \cos\varphi_1 = A_3 + b_1 \cos\varphi_1 + b_2 \cos\varphi_2 \\ \mu \sin\varphi_2 = B_1 + a_2 \sin\varphi_1 + a_1 \sin\varphi_2 \\ \mu \cos\varphi_2 = B_3 + b_2 \cos\varphi_1 + b_1 \cos\varphi_2 \end{cases} \tag{20}$$

For case 2) $A_1 = j'_1; A_3 = j'_3; B_1 = k'_1; B_3 = k'_3$. For case 3) $A_1 = 2j'_1; B_1 = 2k'_1$ and A_3, B_3 are slightly different, involving q_0. These systems of transcendental equations are easily solved by a generalization of the *regula falsi* [9]. Eliminating λ and μ, Eqs. (20) may be reduced to a system of two transcendential equations, analogous to those of Ref. [2a], being equal to them when $\lambda = \mu$.

Table 1 gives $P_{\mu\nu}$ and the energy for different states of diazoethane, employing Pariser-Parr integrals for the calculation and $\beta_{CN} = 1.10, \beta_{NN} = 0.7, \alpha_N - \alpha_C = 1.2$, all in β_{CC} units. The energies follow the same sequence as those of butadiene [2a] and show also the same inversion, with respect to the Hückel calculation, in the $2^2 4^2$ and $1^1 3^2 4^1$ states. The $P_{\mu\nu}$ values for the states $1^2 3^2$ and $2^2 4^2$ are independent of the molecule and of the approximation [2b]. Electronic interaction amounts to more even charges than those of Fig. 1, except for the $1^1 3^2 4^1$ state, and obviously there is no reason for complementarity to hold [7].

Table 1. $P_{\mu\nu}$ and π total for different states of diazoethane with compromise Hamiltonian

State	P_{11}	P_{22}	P_{14}	P_{12}	P_{13}	P_{23}	E (in β_{CC} units)	Order
$1^2 2^2$	0.9203	1.0797	−0.2294	0.9699	−0.0189	0.2294	5.535	1
$1^2 3^2$	1	1	1	0	0	1	1.543	3
$2^2 4^2$	1	1	−1	0	0	−1	−1.257	5
$3^2 4^2$	1.1489	0.8511	0.2240	−0.9625	0.0347	−0.2240	−4.111	8
$1^2 2^1 3^1$	0.9370	1.0630	0.1941	0.4123	−0.0247	0.7039	1.679	2
$1^1 2^2 4^1$	0.9196	1.0804	−0.5804	0.4867	−0.0133	−0.4296	0.636	4
$1^1 3^2 4^1$	1.1492	0.8508	0.5731	−0.4710	0.0231	0.4269	−2.896	6
$2^1 3^1 4^2$	1.1201	0.8799	−0.2224	−0.3888	0.0657	−0.7776	−3.866	7

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