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On a SC Method for Determining Bond Orders in Alternant Hydrocarbons

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A method proposed by Hall allowing direct calculation of bond orders of even AH without computing first the MO's is extended a) so as to take into account some states which include singly occupied MO's and b) to odd AH.

An elegant method to compute bond orders $p_{\mu\nu}$ in even alternant hydrocarbons (AH) has been proposed by Hall [1]. He formulates equations which allow direct estimation of P without first calculating the molecular orbitals (MO's).

He applied this method to states in which the MO's are doubly occupied, such that each one has its associated MO (found by changing the signs of alternate atomic orbitals) unoccupied [1, 2]. They correspond to bond order matrices with non-zero determinant.

Hall's method is here extended a) so as to include certain states containing singly occupied MO's and b) to odd AH. It is also shown how to assign the solutions obtained to a corresponding system of occupation numbers.

The occupied MO's are expressed as linear combinations of N standard equivalent orbitals [1]

$$\Psi = \Phi_1 U + \Phi_2 V \tag{1}$$

Φ_1 and Φ_2 are the standard equivalent orbitals of starred and unstarred atoms. When N is even U and V are square matrices ($\frac{1}{2}N \times \frac{1}{2}N$). For N odd, U has $\frac{1}{2}(N+1)$ rows and $\frac{1}{2}(N-1)$ columns, V is a square matrix of dimension $\frac{1}{2}(N-1) \times \frac{1}{2}(N-1)$. The eigenvalue equation equation is:

$$BV = UE; \quad B'U = VE \tag{2}$$

where E is a diagonal matrix containing the eigenvalues corresponding to the occupied energy levels, and B is the part of the Hamiltonian connecting neighbouring atoms belonging to different sets (The prime denotes the transposed matrix).

If (U, V) correspond to E, $(U, -V)$ correspond to $-E$ and we shall denote by X^0 the eigenvector of the zero eigenvalue, which contains the standard equivalent orbitals belonging to odd atoms and satisfies

$$B'X^0 = 0\,. \tag{3}$$

One obtains the formulae corresponding to N even by putting X^0 identically zero.

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If $c_{i\mu}$ is the coefficient of the i-th eigenvector belonging to atom μ, we may write the orthonormalization as:

$$\sum_{\mu} c_{i\mu} c_{j\mu} = 2\delta_{ij} \tag{4}$$

which yield

$$\left.\begin{aligned} U'U + V'V &= 2I \\ U'U - V'V &= 0 \end{aligned}\right\} U'U = I = V'V, \qquad X^{0\prime}X^0 = 2 \quad U'X^0 = UX^{0\prime} = 0 \tag{5}$$

and

$$\sum_{i} c_{i\mu} c_{i\nu} = 2\delta_{\mu\nu} \tag{6}$$

from which

$$\begin{aligned} VV' &= I, \\ UU' + \tfrac{1}{2}X^0 X^{0\prime} &= I. \end{aligned} \tag{7}$$

We represent $\boldsymbol{P}$ by the $N \times N$ matrix

$$\boldsymbol{P} = \left(\begin{array}{c|c} U(n_l + n_h)U' + X^0 n_0 X^{0\prime} & U(n_l - n_h)V' \\ \hline V(n_l - n_h)U' & V(n_l + n_h)V' \end{array}\right) \tag{8}$$

n_l is a diagonal matrix with half the occupation numbers of the lowest energy levels and n_h a diagonal matrix with half the occupation numbers of the associated highest energy levels. n_0 is half the occupation number of the zero energy level. We shall consider states with $n_l + n_h = I$, $n_0 = \frac{1}{2}$, for which $\boldsymbol{P}$ reduces to:

$$\boldsymbol{P} = \begin{pmatrix} I & P \\ P' & I \end{pmatrix} \qquad n = n_l - n_h \tag{9}$$

where

$$P = UnV'. \tag{10}$$

For N even P is a square matrix $\frac{1}{2}N \times \frac{1}{2}N$. For N odd, it has $\frac{1}{2}(N+1)$ rows and $\frac{1}{2}(N-1)$ columns.

As any element of $n = n_l - n_h$ must be ± 1 or 0 when $n_l + n_h = I$ we have $n^3 = n$, therefore

$$PP'P = UnV'VnU'UnV' = Un^3V' = UnV' = P = PP'P. \tag{11}$$

For those cases with N even in which P has an inverse ($\det P \neq 0$) we deduce from (11)

$$PP' = I \tag{12}$$

which is the relation considered by Hall [1].

Instead of using (12), as Hall did, we shall use (11) which is more general and is valid also even though $\det P = 0$.

Multiplying the first of Eq. (2) from the right by nU', we get

$$BP' = UEnU'; \quad \text{i. e. } BP' = \text{symmetric} \tag{13}$$

and

$$Tr\,BP' = Tr\,UEnU' = Tr\,En \tag{14}$$

which is half the total π energy.

Eqs. (11) and (13) determine P and Eq. (14) is then used to assign P to the different possible states.

Introducing a suitable electron interaction one can follow Hall, replacing B by a Hamiltonian F [1]. For example, for butadiene and pentadienyl we have respectively

$$F = \begin{pmatrix} c+ap_{12} & dp_{14} \\ 1+bp_{23} & c+ap_{12} \end{pmatrix} F = \begin{pmatrix} c+ap_{12} & dp_{14} \\ 1+bp_{23} & 1+bp_{23} \\ dp_{14} & c+ap_{12} \end{pmatrix} \tag{15}$$

where

$$a = -(12|12)/2\beta_{23}; \quad b = -(23|23)/2\beta_{23}; \quad d = -(14|14)/2\beta_{23}; \quad c = \beta_{12}/\beta_{23}$$

and $(\mu\nu|\mu\nu)$ is the Coulomb integral between atomic orbitals on atoms μ and ν.

When making the above mentioned replacement ($B \rightarrow F$) the total π-energy (substracting the self-interaction) is calculated by means of [3]:

$$E_\pi = 2Tr(FP') - Tr((F-B)P') = Tr(FP') + Tr(BP') \tag{16}$$

Results and Discussions[1]

Tables 1 and 4 show the solutions corresponding to the Hamiltonian B for trans-butadiene and pentadienyl, together with the assignments by means of (14). The results are obviously the same as those obtained with Hückel's wave functions. Similarly, Tables 2 and 5 report the solutions and assignments for the Hamiltonian F for trans-butadiene and pentadienyl. The values of a, b, c, d for trans-butadiene are taken from Pariser and Parr [4]. With the geometrical configuration we have adopted for pentadienyl, it should not be too far from reality to suppose, as we have done, the same values for its parameters. It may be pointed out that the states $1^2 3^2$ and $1^1 2^2 4^1$ are inverted with respect to Hückel's approximation (Table 1). This is not surprising, since the introduced electron correlation may alter Hückel's ordering.

For pentadienyl, Hückel's approximation predict a constant $|p_{23}|$ value for nearly all states; this feature, as can be expected is removed in Table 5. In this molecule, the ordering is not altered with respect to Hückel's.

Table 3 reports Hall's values for trans-butadiene, which should be the same as the first part of our Table 2. This is essentially the case for states $1^2 2^2$ and $3^2 4^2$. But states $1^2 3^2$ and $2^2 4^2$ are strikingly different. Our solutions were not obtained by Hall, due to the fact that his representation for P, namely $p_{12} = p_{34} = \sin\varphi$, $p_{14} = -p_{23} = \cos\varphi$, is not the most general representation for a unitary matrix (it does not include inversion). The solutions we have found are of the form $p_{12} = p_{34} = 0$, $p_{23} = p_{14} = \pm 1$. This type of solutions are (for certain molecules) much more general than the present approach suggests. Instead, Hall writes two matrices which are not solutions of the problem.

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[1] The detailed calculation is available on request.

Table 1. *Bond orders and π total energy for different states of butadiene (Hückel approximation)*

State	p_{12}	p_{23}	p_{14}	E_π (β units)	Order
$1^2 2^2$	0.8944	0.4473	-0.4473	4.472	1
$1^2 3^2$	0	1	1	2	4
$2^2 4^2$	0	-1	-1	-2	5
$3^2 4^2$	-0.8944	-0.4473	0.4473	-4.472	8
$1^2 2^1 3^1$	0.4472	0.7236	0.2764	3.236	2
$1^1 2^2 4^1$	0.4472	-0.2764	-0.7236	1.236	3
$1^1 3^2 4^1$	-0.4472	0.2764	0.7236	-1.236	6
$2^1 3^1 4^2$	-0.4472	-0.7236	-0.2764	-3.236	7

Table 2. *Bond orders and π total energy for different states of trans-butadiene with Hamiltonian F*

State	p_{12}	p_{23}	p_{14}	E_π (β_{23} units)	Order
$1^2 2^2$	0.9771	0.2127	-0.2127	11.558	1
$1^2 3^2$	0	1	1	5.247	3
$2^2 4^2$	0	-1	-1	1.247	5
$3^2 4^2$	-0.9239	-0.3826	0.3826	-2.964	8
$1^2 2^1 3^1$	0.4680	0.6758	0.3241	6.658	2
$1^1 2^2 4^1$	0.4963	-0.4396	-0.5604	4.416	4
$1^1 3^2 4^1$	-0.4457	0.2734	0.7266	-0.931	6
$2^1 3^1 4^2$	-0.4930	-0.5834	-0.4166	-2.608	7

Table 3. *Hall's bond orders for trans-butadiene*

State	p_{12}	p_{23}	p_{14}
$1^2 2^2$	0.9771	0.2127	-0.2127
$1^2 3^2$	0.9771	-0.2127	0.2127
$2^2 4^2$	-0.9239	0.3811	-0.3811
$3^2 4^2$	-0.9239	-0.3811	0.3811

We remark that in Tables 2 and 5 two "complementary states" [5] (I and II) do not in general obey the equation $P_I + P_{II} = 2I$, which is not unexpected as this is only valid when two complementary states are calculated with the same Hamiltonian. Hall's electronic correlation implies a different Hamiltonian for each state. In this sense the lack of complementarity may give a qualitative idea of the modification introduced by using for each state a Hamiltonian with appropriate electronic correlation.

One could wonder about which are the wave function coefficients (i. e. U and V) reproducing these bond orders. This is by no means a simple question and we shall not face it here. Some problems connected with it have been analyzed, among others, by Hall himself [2], Parr and Mulliken [6] and recently Messmer [7].

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Table 4. *Bond orders and π total energy for different states of pentadienyl (Hückel approximation)*

State	p_{12}	p_{23}	p_{14}	E_π (β units)	Order
$1^2 2^2 3^1$	0.7887	0.5773	−0.2113	5.464	1
$1^2 3^1 4^2$	−0.2113	0.5773	0.7887	1.464	4
$2^2 3^1 5^2$	0.2113	−0.5773	−0.7887	−1.464	5
$3^1 4^2 5^2$	−0.7887	−0.5773	0.2113	−5.464	8
$1^2 2^1 3^1 4^1$	0.2886	0.5773	0.2886	3.4636	2
$1^1 2^2 3^1 5^1$	0.5	0	−0.5	2	3
$1^1 3^1 4^2 5^1$	−0.5	0	0.5	−2	6
$2^1 3^1 4^1 5^2$	−0.2886	−0.5773	−0.2886	−3.4636	7

Table 5. *Bond orders and π total energy for different states of pentadienyl with Hamiltonian F*

State	p_{12}	p_{23}	p_{14}	E_π (β_{23} units)	Order
$1^2 2^2 3^1$	0.9009	0.4226	−0.0991	12.301	1
$1^2 3^1 4^2$	−0.2241	0.5897	0.7759	3.847	4
$2^2 3^1 5^2$	0.0571	−0.3282	−0.9429	1.542	5
$3^1 4^2 5^2$	−0.8692	−0.4768	0.1308	− 3.625	8
$1^2 2^1 3^1 4^1$	0.3522	0.5019	0.3522	6.351	2
$1^1 2^2 3^1 5^1$	0.5	0	−0.5	5.132	3
$1^1 3^1 4^2 5^1$	−0.5	0	0.5	− 1.820	6
$2^1 3^1 4^1 5^2$	−0.4168	−0.3906	−0.4168	− 2.659	7

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