Note an Bond Orders

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Both the Coulson bond order and the contribution of an electron to bond order are decomposed into through-path interactions. These through-path interactions are strictly additive functions of the molecular topology.

The concept of mobile bond order was introduced to the molecular orbital theory of conjugated systems many years ago [1] and its basic properties were established in the classical paper [2]. Recently [3], using graph-theoretical methods, some additional topological properties of the bond order have been deduced. In particular, it has been shown that the bond order between two atoms is an additive function of the contributions coming from the interactions of these two atoms through all possible paths in the molecular network. In the present paper we report some further investigations along these lines. However, whereas the considerations in [3] were restricted to non-charged \( \pi \)-electron systems whose all bonding MO’s are doubly occupied and all antibonding MO’s are empty, the results of the present paper hold for \( \pi \)-electron systems with arbitrary number of \( \pi \)-electrons and with arbitrarily occupied MO’s.

Let the molecular graph of the conjugated system considered be denoted by \( G \) and its vertices by \( v_r \), \( r = 1, 2, \ldots, n \). The subgraph obtained by deletion of the vertex \( v_r \) from \( G \) will be denoted by \( G - v_r \). A path in the graph \( G \) is a sequence of mutually distinct vertices \( v_{q_0}, v_{q_1}, \ldots, v_{q_k} \) of the graph \( G \), such that \( v_{q_{i-1}} \) is adjacent to \( v_{q_i}, i = 1, \ldots, k \). This path is said to be of length \( k \) and to connect the vertices \( v_{q_0} \) and \( v_{q_k} \). If \( W \) is a path in \( G \), then \( G - W \) is the subgraph obtained by deletion of the vertices of \( W \) from \( G \).

For example, the vertices \( v_1 \) and \( v_6 \) in the naphthalene graph are connected by four paths: \( W_1, W_2, W_3 \) and \( W_4 \):

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be imposed on the value of the occupation numbers $Q_j$.

In [2] the following three relations (among many other) have been deduced:

$$\frac{\partial X_j}{\partial A_{rs}} = 2 C_{jr} \cdot C_{js} \quad (r \neq s) ; \quad (2)$$

$$\frac{\partial X_j}{\partial A_{rr}} = (C_{jr})^2 ; \quad (3)$$

$$\frac{\partial X_j}{\partial A_{rs}} = \Phi (G - v_r, x_j)/\Phi^{(1)} (G, x_j) , \quad (4)$$

where the partial derivative on the left-hand side of (2) is taken under the constraint $A_{rr} = A_{rs}$. In (4), $\Phi^{(1)} (G, x)$ denotes the first derivative of $\Phi (G, x)$ with respect to $x$. The above three formulas hold if $x_j$ is a non-degenerate eigenvalue of the molecular graph.

If $x_j$ is degenerate, then (2) – (4) are to be modified as follows. Let the eigenvectors $C_{j1}, C_{j2}, \ldots, C_{jd}$ be degenerate, i.e. let the eigenvalues $x_{j1}, x_{j2}, \ldots, x_{jd}$ be all mutually equal. Assuming that $d \geq 2$ we have

$$\sum_{i=1}^{d} \frac{\partial X_j}{\partial A_{rs}} = 2 \sum_{i=1}^{d} C_{jir} \cdot C_{jis} \quad (r \neq s) \quad (5)$$

$$\sum_{i=1}^{d} \frac{\partial X_j}{\partial A_{rr}} = \sum_{i=1}^{d} (C_{jir})^2 \quad (6)$$

$$\frac{\partial X_j}{\partial A_{rs}} = \Phi^{(d-1)} (G - v_r, x_j)/\Phi^{(d)} (G, x_j)$$

$$\frac{\partial X_j}{\partial A_{rr}} = 0 \quad \text{for} \quad i = 2, \ldots, d . \quad (7)$$

Here and later $\Phi^{(m)} (G, x)$ denotes the $m$-th derivative of the polynomial $\Phi (G, x)$.

Combining (2), (3) and (4) we arrive at

$$\left( \frac{\partial X_j}{\partial A_{rs}} \right)^2 = 4 \frac{\partial X_j}{\partial A_{rr}} \cdot \frac{\partial X_j}{\partial A_{ss}}$$

and

$$C_{jr} \cdot C_{js} = [\Phi (G - v_r, x_j) \cdot \Phi (G - v_s, x_j)]^{1/2} / \Phi^{(1)} (G, x_j) . \quad (8)$$

The relations (8) and (9) seem not have been noticed in the chemical literature.

We shall use now the graph-theoretical identity [2, 5]

$$\Phi (G - v_r, x) \cdot \Phi (G - v_s, x) - \Phi (G, x) \quad (10)$$

$$\cdot \Phi (G - v_r - v_s, x) = \left[ \sum_{W} \Phi (G - W, x) \right]^2$$

in which the right-hand side summation goes over all paths in $G$, connecting the vertices $v_r$ and $v_s$. Since $\Phi (G, x_j)$, for $x = x_j$ (10) reduces to

$$\Phi (G - v_r, x_j) \cdot \Phi (G - v_s, x_j) = \left[ \sum_{W} \Phi (G - W, x_j) \right]^2 , \quad (11)$$

which substituted back into (9) yields

$$C_{jr} \cdot C_{js} = \sum_{W} t_{rs} (j, W) \quad (12)$$

with

$$t_{rs} (j, W) = \Phi (G - W, x_j)/\Phi^{(1)} (G, x_j) . \quad (13)$$

Note that (11) has another solution leading to $t_{rs} (j, W) = - \Phi (G - W, x_j)/\Phi^{(1)} (G, x_j)$. It can be shown [6] that the solution given by (13) is the correct one.

Formula (13) applies in the case of non-degenerate eigenvalues. If, however, $x_j$ is a $d$-times degenerate eigenvalue, then instead of (12) and (13) we have

$$\frac{1}{d} \sum_{i=1}^{d} C_{jir} \cdot C_{jis} = \sum_{W} t_{rs} (j, W) \quad (14)$$

with

$$t_{rs} (j, W) = \Phi^{(d-1)} (G - W, x_j)/\Phi^{(d)} (G, x_j) \quad (15)$$

for $i = 1, 2, \ldots, d$.

The total bond order can be thus written in the form

$$P_{rs} = \sum_{W} T_{rs} (W) , \quad (16)$$

where

$$T_{rs} (W) = \sum_{j=1}^{n} g_j t_{rs} (j, W) . \quad (17)$$

Hence both the bond order and the contribution of a single electron to the bond order are decomposed into interactions over particular paths of the molecular graph. The term $t_{rs} (j, W)$ represents the fraction of the effect of an electron (in the $j$-th MO) on the bonding between the atoms $r$ and $s$, which has been transmitted through the path $W$. Similarly, $T_{rs} (W)$ represents the collective effect of all electrons of the molecule considered on the $\pi$-bond between the atoms $r$ and $s$, transmitted through the path $W$. The total bond order is a simple additive function of these path-effects.
Formula (16) is a generalization of a previous result [3]. It can be shown, namely, that (16) reduces to (8) of [3] in the special case when \( g_j = 2 \) for \( j \leq n/2 \) and \( g_j = 0 \) for \( j > n/2 \).

In order to illustrate the results obtained in the present paper, we shall work out the details of the path-decomposition of the bond order \( P_{12} \) of naphthalene.

There are three paths \( W_5, W_6, W_7 \), connecting the vertices \( r_1 \) and \( r_2 \) of the naphthalene graph.

![Fig. 2.](image)

For the calculation of \( t_{ij} (j, W) \) we need the characteristic polynomial of the naphthalene graph:

\[
\Phi (G, x) = x^{10} - 11 x^8 + 41 x^6 - 65 x^4 + 43 x^2 - 9
\]

its zeros:

\[
\begin{align*}
x_1 & = 2.3028, & x_{10} & = -x_1, \\
x_2 & = 1.6180, & x_9 & = -x_2, \\
x_3 & = 1.3028, & x_8 & = -x_3, \\
x_4 & = 1.0000, & x_7 & = -x_4, \\
x_5 & = 0.6180, & x_6 & = -x_5,
\end{align*}
\]

and the characteristic polynomials of the subgraphs \( G - W_i, i = 5, 6, 7: \)

\[
\begin{align*}
\Phi (G - W_5, x) & = x^8 - 8 x^6 + 19 x^4 - 16 x^2 + 4 \\
\Phi (G - W_6, x) & = x^4 - 3 x^2 + 1 \\
\Phi (G - W_7, x) & = 1.
\end{align*}
\]

Since none of the eigenvalues of the naphthalene graph is degenerate, we can apply (13). Direct calculation gives then the following results:

\[
\begin{align*}
t_{12} (1, W_5) & = 0.05428, & t_{12} (1, W_6) & = 0.01400, \\
t_{12} (2, W_5) & = 0.14635, & t_{12} (2, W_6) & = 0.00000, \\
t_{12} (3, W_5) & = 0.09595, & t_{12} (3, W_6) & = -0.15267, \\
t_{12} (4, W_5) & = 0.00000, & t_{12} (4, W_6) & = 0.16667, \\
t_{12} (5, W_5) & = 0.02135, & t_{12} (5, W_6) & = 0.00000, \\
T_{12} (W_5) & = 0.63587; & T_{12} (W_6) & = 0.05598; \\
t_{12} (1, W_7) & = 0.00106, & t_{12} (1, W_8) & = 0.03271, \\
t_{12} (2, W_7) & = -0.03455, & t_{12} (2, W_8) & = -0.16667, \\
t_{12} (3, W_7) & = -0.12606, & t_{12} (4, W_8) & = 0.09045, \\
t_{12} (5, W_7) & = -0.16667, & T_{12} (W_8) & = 0.03271.
\end{align*}
\]

The \( T_{12} (W_i) \)-values were obtained using formula (17) and assuming \( g_j = 2 \) for \( j \leq 5 \) and \( g_j = 0 \) for \( j > 5 \). It is easy to see that for \( i = 5, 6, 7 \) and \( j = 1, 2, 3, 4, 5 \):

\[
t_{12} (j, W_i) = -t_{12} (11 - j, W_i).
\]

The sum \( T_{12} (W_5) + T_{12} (W_6) + T_{12} (W_7) = 0.72456 \) coincides with the bond order \( P_{12} \) calculated by standard methods.

In the present communication we have provided a complete set of formulas necessary for the decomposition of bond orders into contributions coming from various trough-path electron interactions. Although the essential results along these lines are (implicitly) contained already in the early work of Coulson and Longuet-Higgins [2], formulas necessary for practical calculation are, however, given here for the first time. We have exposed our approach using the language of graph theory and applying the Hückel molecular orbital model. Neither of both were necessary. All the statements given in the present work can be easily reformulated for the eigenvalues/eigenvectors of arbitrary Hermitean matrices. As a consequence the path-decomposition of bond orders can be reformulated within the framework of any molecular orbital approximation and is also not limited to \( \pi \)-electrons. The authors hope to be able to work on such a project in the forseen future.

The results of the present note need elaboration also in another direction. Many general regularities could be observed for the numbers \( t_{ij} (j, W) \) and \( T_{ij} (W) \) (some of them have been briefly mentioned in the preceeding text). A detailed graph-theoretical analysis of the dependence of the quantities \( t_{ij} \) and \( T_{ij} \) on molecular topology is in preparation.