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 π-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 π-electron systems with arbitrary number of π-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:

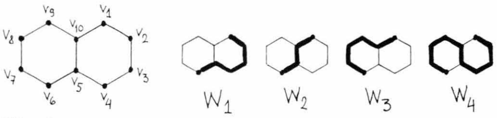

Fig. 1.

Let $\boldsymbol{A} = \| A_{rs} \|$ be the adjacency matrix of G and let x_j and $\boldsymbol{C}_j$, $j = 1, 2, \ldots, n$ be its eigenvalues and eigenvectors [4]. Then, $\boldsymbol{A}\, \boldsymbol{C}_j = x_j\, \boldsymbol{C}_j$. Throughout the present paper we shall assume that all the eigenvectors of $\boldsymbol{A}$ are real. The components of the vector $\boldsymbol{C}_j$ are denoted by $C_{j1}, C_{j2}, \ldots, C_{jn}$.

The characteristic polynomial [4] of $\boldsymbol{A}$ is denoted by $\Phi\,(G, x)$. Of course, $\Phi\,(G, x_j) = 0$.

The eigenvectors and eigenvalues of $\boldsymbol{A}$ are closely related to the Hückel molecular orbitals and energy levels [4]. According to [1], the bond order P_{rs} between two conjugated atoms r and s is given by

$$P_{rs} = \sum_{j=1}^{n} g_j\, C_{jr} \cdot C_{js}\,, \tag{1}$$

where g_j is the occupation number of the j-th MO. The quantity $C_{jr} \cdot C_{js}$ is interpreted as the contribution of one π-electron in the j-th MO to the order of the bond between atoms r and s. This contribution may be either positive or negative or zero.

One should note that if the j-th MO is degenerate, then $C_{jr} \cdot C_{js}$ does not have a unique numerical value. The sum of the terms $C_{jr} \cdot C_{js}$ over all degenerate MO's is, on the other hand, unique. As a consequence, the bond order (as defined via (1)) is physically meaningful only if all degenerate molecular orbitals are occupied with equal number of electrons.

Therefore in the following we shall require that if $x_i = x_j$, then also $g_i = g_j$. No other restriction will

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be imposed on the value of the occupation numbers g_j.

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

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

$$\frac{\partial x_j}{\partial A_{rr}} = (C_{jr})^2\,; \tag{3}$$

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

where the partial derivative on the left-hand side of (2) is taken under the constraint $A_{rs} = A_{sr}$. 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 $\boldsymbol{C}_{j_1}, \boldsymbol{C}_{j_2}, \ldots, \boldsymbol{C}_{j_d}$ be degenerate, i.e. let the eigenvalues $x_{j_1}, x_{j_2}, \ldots, x_{j_d}$ be all mutually equal. Assuming that $d \geqq 2$ we have

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

$$\sum_{i=1}^{d} \frac{\partial x_{j_i}}{\partial A_{rr}} = \sum_{i=1}^{d} (C_{j_i r})^2 \tag{6}$$

$$\frac{\partial x_{j_1}}{\partial A_{rr}} = \Phi^{(d-1)}\,(G - v_r, x_{j_1})/\Phi^{(d)}\,(G, x_{j_1})$$

$$\frac{\partial x_{j_i}}{\partial A_{rr}} = 0 \quad \text{for } i = 2, \ldots, d\,. \tag{7}$$

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

$$\left(\frac{\partial x_j}{\partial A_{rs}}\right)^2 = 4 \frac{\partial x_j}{\partial A_{rr}} \cdot \frac{\partial x_j}{\partial A_{ss}} \tag{8}$$

and

$$C_{jr} \cdot C_{js} = [\Phi\,(G - v_r, x_j) \cdot \Phi\,(G - v_s, x_j)]^{1/2}/\Phi^{(1)}\,(G, x_j)\,. \tag{9}$$

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

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

$$\Phi\,(G - v_r, x) \cdot \Phi\,(G - v_s, x) - \Phi\,(G, x) \cdot \Phi\,(G - v_r - v_s, x) = \left[\sum_W \Phi\,(G - W, x)\right]^2 \tag{10}$$

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

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

which substituted back into (9) yields

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

with

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

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

$$\frac{1}{d} \sum_{i=1}^{d} C_{j_i r}\, C_{j_i s} = \sum_W t_{rs}\,(j_i, W) \tag{14}$$

with

$$t_{rs}\,(j_i, W) = \Phi^{(d-1)}\,(G - W, x_{j_i})/\Phi^{(d)}\,(G, x_{j_i}) \tag{15}$$

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

The total bond order can be thus written in the form

$$P_{rs} = \sum_W T_{rs}\,(W)\,, \tag{16}$$

where

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

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 π-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 $j \leqq n/2$ 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 and W_7, connecting the vertices v_1 and v_2 of the naphthalene graph.

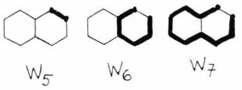

Fig. 2.

For the calculation of $t_{rs}(j, W)$ 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:

$$\begin{array}{ll} x_1 = 2.3028\,, & x_{10} = -x_1\,, \\ x_2 = 1.6180\,, & x_9 = -x_2\,, \\ x_3 = 1.3028\,, & x_8 = -x_3\,, \\ x_4 = 1.0000\,, & x_7 = -x_4\,, \\ x_5 = 0.6180\,, & x_6 = -x_5\,, \end{array}$$

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

$$\Phi(G - W_5, x) = x^8 - 8x^6 + 19x^4 - 16x^2 + 4$$

$$\Phi(G - W_6, x) = x^4 - 3x^2 + 1$$

$$\Phi(G - W_7, x) = 1\,.$$

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

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

The $T_{12}(W_i)$-values were obtained using formula (17) and assuming $g_j = 2$ for $j \leqq 5$ 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 π-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 $t_{rs}(j, W)$ and $T_{rs}(W)$ (some of them have been briefly mentioned in the preceeding text). A detailed graph-theoretical analysis of the dependence of the quantities t_{rs} and T_{rs} on molecular topology is in preparation.

[1] C. A. Coulson, Proc. Roy. Soc. London **A169,** 413 (1939).
[2] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. London **A191,** 39 (1947).
[3] I. Gutman, Z. Naturforsch. **32a,** 765 (1977).
[4] A. Graovac, I. Gutman, and N. Trinajstić, Topological Approach to the Chemistry of Conjugated Molecules, Springer-Verlag, Berlin 1977.
[5] For a detailed discussion of (10) and its origin see: I. Gutman, Z. Naturforsch. **36a,** 1112 (1981).
[6] C. D. Godsil, to be published.