Topological Properties of Bond Order

Ivan Gutman[1]

Institut für Quantenchemie, Berlin

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Integral topological formulas are obtained, relating the bond order with the characteristic polynomials of the molecular graph and its certain subgraphs. Several properties of the bond order are proved.

In the classical work of Coulson and Longuet-Higgins[2] the various π-electron characteristics of conjugated molecules were expressed as functions of the secular determinant and/or its minors. Those formulas of Coulson and Longuet-Higgins depending only on the secular determinant and/or its principal minors could be later simply reformulated in the language of graph spectral theory as formulas depending on the characteristic polynomials of the molecular graph and/or its subgraphs. This, on the other hand, enabled the application of the mathematical apparatus of graph theory in the study of total π-electron energy[3], charge distribution[4] and atom self-polarizability[5].

Bond orders are the most-important π-electron quantities which depend on the non-principal minors of the secular determinant and where, consequently, the application of graph-theoretical arguments is less straightforward. In the present paper we offer formulas which overcome this gap and from which a number of topological properties of bond orders can be deduced.

First we need the following graph-theoretical definitions[6]. A molecular graph G has N vertices. Let r and s be two vertices of G and e_{pq} the edge between the vertices p and q. Let further W and Z denote a path of the length w and a cycle of the size z, respectively. Then the subgraphs $G-e_{pq}$, $G-r,s$, $G-W$ and $G-Z$ are obtained from G by deletion of e_{pq}, r,s, W and Z, respectively. They have N, $N-2$, $N-w-1$ and $N-z$ vertices. Note that if p and q are not adjacent vertices, there is no edge e_{pq} in G and $G-e_{pq} \equiv G$.

For the purpose of the present consideration it is convenient to write the characteristic polynomial of a graph H in the form

$$P(H,x) = \sum_j (-1)^j \, b_{2j}(H) \, x^{N-2j} + \sum_j (-1)^j \, b_{2j+1}(H) \, x^{N-2j-1}$$

and to introduce the functions $A(H)$ and $B(H)$ as

$$P(H, i\,x) = i^N \left[A(H) - i\,B(H) \right]$$

where $i = \sqrt{-1}$. Hence,

$$A(H) = \sum_j b_{2j}(H) \, x^{N-2j}\,; \qquad B(H) = \sum_j b_{2j+1}(H) \, x^{N-2j-1}\,. \tag{1}$$

For brevity we shall write sometimes $b_j(G) = b_j$, $A(G) = A$ and $B(G) = B$. The fact that $b_N(G) = [\mathrm{ASC}(G)]^2$, with $\mathrm{ASC}(G)$ being the algebraic structure count[7] of the conjugated system G, will be important in the later discussion.

From Eq. (1) is seen that if N is even (odd), A is an even (odd) and B an odd (even) function of x. Moreover, for positive values of x, $A(G) > 0$ for all G because of $b_{2j} \geqq 0$.

Topological Formula for Bond Order

In order to find a relation between the bond order and the characteristic polynomials of the molecular graph and its subgraphs we use the equation[2]

$$\frac{\partial E}{\partial \beta_{rs}} = 2\,p_{rs} \tag{2 a}$$

where E is the total π-energy. In graph-theoretical notation, Eq. (2 a) reads

$$\left. \frac{\partial E_k}{\partial k} \right|_{k=k_0} = 2\,p_{rs} \tag{2 b}$$

where E_k is the total π-electron energy corresponding to the graph G_k, obtained from G by introducing an edge of weight k between the vertices r and s. If r and s are adjacent, then $k_0 = 1$. Otherwise, it is $k_0 = 0$.

Requests for reprints should be sent to Dr. I. G., Institut für Quantenchemie, Freie Universität Berlin, Holbeinstrasse 48, *D-1000 Berlin 45*, Germany.

Combining Eq. (2 b) with one of the available integral expressions for total π-energy[3], one gets the desired formula for p_{rs}. It is convenient to start from[3]

$$E_k - E = \left\langle \log \frac{P(G_k, i\,x)}{P(G, i\,x)} \right\rangle . \tag{3}$$

The notation $\langle F \rangle$ is defined elsewhere[3,8]. The k-dependence of $P(G_k, x)$ is[9]

$$P(G_k, x) = P(G - e_{rs}, x) - k^2 P(G - r, s, x) - 2\,k \sum_Z P(G - Z, x) \tag{4}$$

where the summation goes over all cycles in G_k containing the edge e_{rs}. Substitution of Eq. (4) back into (3) and (2 b) gives straigthforwardly

$$p_{rs} = \frac{1}{2} \left\langle \frac{(A\,\alpha + B\,\beta)\,(A\,\alpha' + B\,\beta') + (A\,\beta - B\,\alpha)\,(A\,\beta' - B\,\alpha')}{(A\,\alpha + B\,\beta)^2 + (A\,\beta - B\,\alpha)^2} \right\rangle \Bigg|_{k = k_0} \tag{5}$$

where

$$\alpha = \alpha(k) = A(G - e_{rs}) + k^2 A(G - r, s) + 2\,k \sum_Z \omega_A(Z)\,,$$

$$\beta = \beta(k) = B(G - e_{rs}) + k^2 B(G - r, s) + 2\,k \sum_Z \omega_B(Z)\,,$$

and

$$\omega_A(Z) = \begin{cases} (-1)^{z/2-1} A(G - Z) & \text{for even } z\,, \\ (-1)^{(z-1)/2} B(G - Z) & \text{for odd } z\,, \end{cases}$$

$$\omega_B(Z) = \begin{cases} (-1)^{z/2-1} B(G - Z) & \text{for even } z\,, \\ (-1)^{(z+1)/2} A(G - Z) & \text{for odd } z\,. \end{cases}$$

Two cases are to be considered. Either r and s are adjacent or not. In the first case it is $k_0 = 1$ and Eq. (5) is further simplified due to the fact that[10] $\alpha(1) = A(G)$ and $\beta(1) = B(G)$. Therefore, for adjacent r and s

$$p_{rs} = \left\langle \frac{A(G - r, s)\,A + B(G - r, s)\,B}{A^2 + B^2} \right\rangle + \sum_Z \left\langle \frac{A\,\omega_A(Z) + B\,\omega_B(Z)}{A^2 + B^2} \right\rangle . \tag{6}$$

If r and s are not adjacent, we have to substitute $k_0 = 0$ in Eq. (5), which becomes

$$p_{rs} = \sum_Z \left\langle \frac{A\,\omega_A(Z) + B\,\omega_B(Z)}{A^2 + B^2} \right\rangle \tag{7}$$

due to the fact that for non-adjacent r and s it is $A(G - e_{rs}) \equiv A$ and $B(G - e_{rs}) \equiv B$.

The summation in (7) goes over all cycles in G_k containing the edge e_{rs}. But these cycles correspond exactly to paths between r and s in the graph G. Therefore Eq. (7) can be rewritten as

$$p_{rs} = \sum_W \left\langle \frac{A\,\omega_A(W) + B\,\omega_B(W)}{A^2 + B^2} \right\rangle . \tag{8}$$

In this case the summation is over all paths connecting r and s, and

$$\omega_A(W) = \begin{cases} (-1)^{w/2} B(G - W) & \text{for even } w\,, \\ (-1)^{(w-1)/2} A(G - W) & \text{for odd } w\,, \end{cases}$$

$$\omega_B(W) = \begin{cases} (-1)^{w/2+1} A(G - W) & \text{for even } w\,, \\ (-1)^{(w-1)/2} B(G - W) & \text{for odd } w\,. \end{cases}$$

Fortunately, formula (8) is valid also in the case of r and s being adjacent. Namely, if we take into account that e_{rs} is a path (of length one) between r and s, Eq. (6) is transformed into (8). Hence, Eq. (8) is the required topological formula valid for the bond order between arbitrary atoms in arbitrary conjugated systems.

Special Case: Alternant Molecules

In alternant molecules Eq. (8) is essentially simplified since it is $B(G) \equiv 0$ and $B(G - W) \equiv 0$ for all W.

$$p_{rs} = \sum_W^{\text{odd}} (-1)^{(w-1)/2} \left\langle \frac{A(G - W)}{A(G)} \right\rangle . \tag{9}$$

Because of the absence of odd-membered cycles, the paths between two vertices are either all even or all odd. Then from Eq. (9) follows that *if the distance between two sites in an alternant hydrocarbon is even,* $p_{rs} = 0$. But this is just another formulation of the well known property that the bond orders vanish between two stared (or two unstared) atoms.

In acyclic systems, the path connecting the vertices r and s is unique and Eq. (9) reduces to

$$p_{rs} = (-1)^{(d_{rs}-1)/2} \left\langle \frac{A(G - W)}{A(G)} \right\rangle \tag{10}$$

with d_{rs} being the distance between the vertices r and s. A result equivalent to Eqs. (9) and (10) was recently obtained by Hosoya and Hosoi[11] using another way of reasoning.

Equation (9) can be viewed as a decomposition of the bond order into several contributions, each arising from a particular path. Their signs are simply $(-1)^{(w-1)/2}$ because all integrals on the right side of (9) are positive. Therefrom we have an interesting analogy to the Hückel $4m+2$ rule, namely that *all cycles of the size $4m+2$ containing the edge e_{rs} have an increasing, and all cycles of the size $4m$ containing e_{rs} a decreasing contribution to p_{rs}*.

Approximate Formula for the Components of Bond Order

It is seen from Eqs. (8) and (9) that the bond orders depend on a large number of topological parameters. In order to get a qualitative insight into this dependence and to estimate the order of magnitude of the various effects contributing to p_{rs}, the integrals $\langle A(G-W)/A(G)\rangle$ can be approximated using the method of Reference [3].

Knowing that $A(G-W)/A(G)$ is a bell-shaped function with the properties

$$A(G-W)/A(G) \to x^{-w-1} \quad \text{for} \quad x \to \infty$$

and

$$\begin{aligned} A(G-W)/A(G) &= b_{N-w-1}(G-W)/b_N(G) \\ &= [\mathrm{ASC}(G-W)/\mathrm{ASC}(G)]^2 \quad \text{for} \quad x=0 \end{aligned}$$

we have

$$\begin{aligned} \left\langle \frac{A(G-W)}{A(G)} \right\rangle &\doteq \left\langle \frac{b_{N-w-1}(G-W)}{b_N(G) + b_{N-w-1}(G-W)\, x^{w+1}} \right\rangle \\ &= \frac{2}{(w+1)\sin\dfrac{\pi}{w+1}} \left[\frac{\mathrm{ASC}(G-W)}{\mathrm{ASC}(G)}\right]^{2w/(w+1)}. \end{aligned} \tag{11}$$

For $w=1$, Eq. (11) becomes

$$\left\langle \frac{A(G-W)}{A(G)} \right\rangle \doteq p_{rs} \text{ (Pauling)} \tag{12}$$

because $\mathrm{ASC}(G-r,s)/\mathrm{ASC}(G)$ is just equal to the Pauling bond order [11, 12]. Hence, *the contribution of the path of length one to the (molecular orbital) bond order between two adjacent sites is approximately equal to the (resonance-theoretical) Pauling bond order.*

For larger paths formula (11) can be further approximated as

$$\left\langle \frac{A(G-W)}{A(G)} \right\rangle \doteq \frac{2}{\pi} \left[\frac{\mathrm{ASC}(G-W)}{\mathrm{ASC}(G)}\right]^2. \tag{13}$$

Two important consequences follow from the relations (11) – (13). Firstly, *the main topological factor determining the value of p_{rs} is the algebraic structure count* of the conjugated system and its certain fragments. Secondly, the contributions to p_{rs} coming from longer paths are not negligible and their magnitude is not a strictly decreasing function of the path length.

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[1] Permanent address: Department of Chemistry, Faculty of Sciences, University of Kragujevac, *J-34000 Kragujevac*, Yugoslavia.

[2] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. London A **191,** 39 [1947].

[3] I. Gutman, J. Chem. Phys. **66,** 1652 [1977] and references therein.

[4] I. Gutman and N. Trinajstić, Croat. Chim. Acta **48,** 19 [1976].

[5] I. Gutman and N. Trinajstić, J. Chem. Phys. **65,** 3796 [1976].

[6] For further details see the review: I. Gutman and N. Trinajstić, Topics Curr. Chem. **42,** 49 [1973].

[7] C. F. Wilcox, Tetrahedron Lett. 795 [1968]; J. Amer. Chem. Soc. **91,** 2732 [1969].

[8] S. Bosanac and I. Gutman, Z. Naturforsch. **32 a,** 10 [1977].

[9] A. Graovac, O. E. Polansky, N. Trinajstić, and N. Tyutyulkov, Z. Naturforsch. **30 a,** 1696 [1975]; J. Aihara, J. Amer. Chem. Soc. **98,** 6840 [1976].

[10] H. Hosoya, Theor. Chim. Acta **25,** 215 [1972].

[11] H. Hosoya and K. Hosoi, J. Chem. Phys. **64,** 1065 [1976].

[12] W. C. Herndon, J. Amer. Chem. Soc. **96,** 7605 [1974].