Note on Algebraic Structure Count

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Three recursion relations for the algebraic structure count are deduced, which are closely analogous to the well-known recursion relation for the number of Kekulé structures. An efficient graphical method for the calculation of algebraic structure count is proposed.

It is a long known result [1] that the determinant of the adjacency matrix ($\mathbf{A}$) of a benzenoid graph is related to the number of the Kekulé structures (K) of the corresponding molecule as

$$\det \mathbf{A} = (-1)^{n/2} K^2 . \qquad (1)$$

For non-benzenoid (but alternant) systems, (1) is no more applicable and has to be replaced by

$$\det \mathbf{A} = (-1)^{n/2} L^2 \qquad (2)$$

with L being a certain integer [2].

In the above equations and later on, n denotes the number of vertices of the molecular graph. It may be assumed that n is even since otherwise $K = L = 0$.

The quantity L has been called [3, 4] the "algebraic structure count" (or "corrected structure count" [5, 6]). Its relation to the Kekulé structures has been extensively examined [6–8]. The algebraic structure count plays an important role in the topological theory of non-benzenoid conjugated molecules [6, 9–12].

Let e be an (arbitrary) edge of the molecular graph G. Then $G-e$ will denote the subgraph obtained by deleting this edge from G. In addition, $G-(e)$ will denote the subgraph obtained from G by deletion of the two vertices which are incident to G. Hence, if G has n vertices, then $G-e$ and $G-(e)$ have n and $n-2$ vertices, respectively.

The number of Kekulé structures of a molecular graph can be easily calculated by means of the recursion formula [6]

$$K(G) = K(G-e) + K(G-(e)) . \qquad (3)$$

On the other hand, no analogous regularity has been previously observed for the algebraic structure count. The aim of the present paper is to show that $L(G)$, $L(G-e)$ and $L(G-(e))$ conform to one of the following three relations:

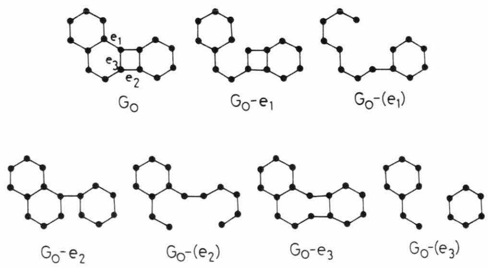
$$L(G) = L(G-e) + L(G-(e)) , \qquad (4)$$

$$L(G) = L(G-e) - L(G-(e)) , \qquad (5)$$

$$L(G) = L(G-(e)) - L(G-e) \qquad (6)$$

which, of course, closely resemble (3).

As a matter of fact, (4), (5) and (6) may apply in the case of alternant non-benzenoid systems. This is illustrated by the example of the molecular graph G_0, whose three edges are labelled by e_1, e_2 and e_3. The corresponding subgraphs $G_0 - e_i$ and $G_0 - (e_i)$, $i = 1, 2, 3$, are given as follows:



Direct calculation shows that $L(G_0) = 4$ (see later), whereas $L(G_0-e_1) = L(G_0-(e_1)) = L(G_0-(e_2)) = 2$, $L(G_0-e_2) = 6$, $L(G_0-e_3) = 0$ and $L(G_0-(e_3)) = 4$. Thus (4) holds in the case of the deletion of the edge e_1, (5) applies for the edge e_2, and (6) must be used if the edge e_3 is being deleted.

In order to deduce (4)–(6), recall that the characteristic polynomial $\Phi(G)$ of the graph G is defined via

$$\Phi(G) = \Phi(G, x) = \det(x\mathbf{I} - \mathbf{A}) , \qquad (7)$$

where $\mathbf{I}$ is the unit matrix of dimension n. Then, because of (2),

$$\Phi(G, 0) = (-1)^{n/2} L^2 . \qquad (8)$$

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The characteristic polynomial conforms to the relations [13]

$$\Phi(G) = \Phi(G-e) - \Phi(G-(e)) - 2\sum_Z \Phi(G-Z), \quad (9)$$

where the summation embraces all cycles Z which contain the edge e, and [14, 15]

$$\Phi(G-v_r)\,\Phi(G-v_s) - \Phi(G)\,\Phi(G-v_r-v_s) = \Big(\sum_W \Phi(G-W)\Big)^2, \quad (10)$$

where v_r and v_s are two vertices of G and the r.h.s. summation goes over all paths W which connect the vertices v_r and v_s. If v_r and v_s are adjacent vertices (joined by the edge e), then (10) can be rewritten in the form

$$\Phi(G-v_r)\,\Phi(G-v_s) - \Phi(G)\,\Phi(G-(e)) = \Big(\Phi(G-(e)) + \sum_Z \Phi(G-Z)\Big)^2. \quad (11)$$

Setting $x = 0$ into (9) and having (8) in mind, we get

$$L(G)^2 = L(G-e)^2 + L(G-(e))^2 + 2S, \quad (12)$$

where

$$S = \sum_Z (-1)^{(z/2)-1} L(G-Z)^2 \quad (13)$$

and z is the size of the cycles Z. (Note that if Z is of size $4m+2$, then $(-1)^{(z/2)-1} = +1$, and if Z is of size $4m$, then $(-1)^{(z/2)-1} = -1$. Cycles of odd size cannot occur in the molecular graphs of alternant systems.)

Set now $x = 0$ into (11). Since n is even, the graphs $G-v_r$ and $G-v_s$ have an odd number of vertices and therefore $\Phi(G-v_r, 0) = \Phi(G-v_s, 0) = 0$. Consequently, we get from (11)

$$L(G)^2\,L(G-(e))^2 = [L(G-(e))^2 + S]^2. \quad (14)$$

Eliminating the auxiliary quantity S from (12) and (14), we arrive at an identity connecting $L(G)$, $L(G-e)$ and $L(G-(e))$:

$$4L(G)^2\,L(G-(e))^2 = [L(G)^2 + L(G-(e))^2 - L(G-e)^2]^2. \quad (15)$$

The above relation can be further transformed into

$$\begin{aligned}&[L(G) - L(G-(e)) - L(G-e)]\\ &\cdot[L(G) - L(G-(e)) + L(G-e)]\\ &\cdot[L(G) + L(G-(e)) - L(G-e)]\\ &\cdot[L(G) + L(G-(e)) + L(G-e)] = 0. \quad (16)\end{aligned}$$

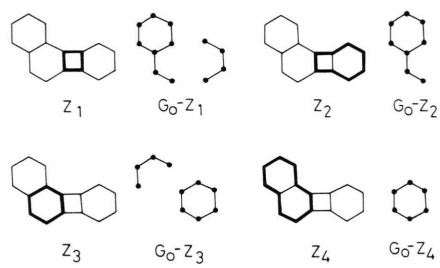
Since the last factor on the left-hand side of (16) is evidently non-zero, we conclude that the condition (15) implies the validity of either (4) or (5) or (6).

A detailed analysis of the relation (15) shows that formula (5) holds if the term $L(G-(e)) + S$ is negative (or zero). Formulas (4) and (6) hold when $L(G-(e)) + S$ is positive (or zero). Presently we are not able to determine the conditions which would make possible to predict whether (4) or (6) will apply for a given edge e of a given graph G.

In spite of their simple algebraic form, the recursion formulas (4)−(6) are of little value for the actual calculation of the algebraic structure count.

For practical purposes, (12) provides a much more efficient method of calculation of the algebraic structure count.

The use of (12) will be illustrated by the example of the graph G_0. The edge which will be deleted is e_3. There are four cycles in G_0 which contain e_3. They will be labelled by Z_1, Z_2, Z_3 and Z_4. The corresponding cycle-deleted subgraphs are given as follows:



We already know that $L(G_0-e_3) = 0$ and $L(G_0-(e_3)) = 4$. A simple calculation shows that in addition $L(G_0-Z_1) = L(G_0-Z_2) = L(G_0-Z_3) = L(G_0-Z_4) = 2$. Since $z_1 = 4$, $z_2 = 8$, $z_3 = 6$ and $z_4 = 10$, we have

$$L(G_0)^2 = 0^2 + 4^2 + 2(-2^2 - 2^2 + 2^2 + 2^2) = 16$$

and therefore $L(G_0) = 4$.

[1] M. J. S. Dewar and H. C. Longuet-Higgins, Proc. Roy. Soc. London **A 214,** 482 (1952).
[2] For the theory of the determinant of the adjacency matrix of a molecular graph see: A. Graovac and I. Gutman, Math. Chem. Mülheim **6,** 49 (1979).
[3] C. F. Wilcox, Tetrahedron Letters 795 (1968).
[4] C. F. Wilcox, J. Amer. Chem. Soc. **91,** 2732 (1969).
[5] W. C. Herndon, Tetrahedron **29,** 3 (1973).
[6] For review of Kekulé structures, algebraic structure count and related topics see: W. C. Herndon, J. Chem. Educ. **51,** 10 (1974).
[7] A. Graovac, I. Gutman, N. Trinajstić, and T. Živković, Theoret. Chim. Acta **26,** 67 (1972).
[8] D. Cvetković, I. Gutman, and N. Trinajstić, J. Chem. Phys. **61,** 2700 (1974).
[9] The topological theory of conjugated molecules is exposed in: A. Graovac, I. Gutman, and N. Trinajstić, Topological Approach to the Chemistry of Conjugated Molecules, Springer-Verlag, Berlin 1977.
[10] C. F. Wilcox, Croat. Chem. Acata **47,** 87 (1975).
[11] I. Gutman, N. Trinajstić, and C. F. Wilcox, Tetrahedron **31,** 143 (1975).
[12] C. F. Wilcox, I. Gutman, and N. Trinajstić, Tetrahedron **31,** 147 (1975).
[13] E. Heilbronner, Helv. Chim. Acta **36,** 170 (1953).
[14] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. London **A 192,** 16 (1947).
[15] For a recent application of Eq. (10) see: I. Gutman, Z. Naturforsch. **36 a,** 1112 (1981).