

CHEMICAL GRAPH POLYNOMIALS. 1

THE POLYNOMIAL DESCRIPTION OF GENERALIZED CHEMICAL GRAPHS

OVIDIU IVANCIUC *

Polytechnic Institute "Traian Vuia", Faculty of Chemical
Technology, Timișoara, România

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An alternative formulation of the Sachs formula which relates the structure of a generalized graph and its μ , and acyclic polynomials is given. Some recurrence relations for the generalized μ , characteristic and acyclic polynomials are presented.

1. INTRODUCTION

The graph theoretical polynomials¹ play a significant role in the area of topological chemistry, with applications to diverse areas such as the topological resonance theory (TRE)^{2,3} and the topological effect on molecular orbitals (TEMO).⁴ The most used graph theoretical polynomials are the characteristic, the acyclic (matching) and the μ -polynomial. We will present a slightly different formulation of the Sachs formula applied to generalized graphs. Some expressions for the generalized μ , characteristic and acyclic polynomials are obtained.

2. NOTATION AND TERMINOLOGY

We shall use the standard graph notation and terminology. G will denote a graph with n vertices: v_1, v_2, \dots, v_n , m edges and r cycles: C_1, C_2, \dots, C_r . We denote by t_i the weight associated to the cycle C_i . The edge connecting the vertices v_i and v_j is denoted by e_{ij} . The subgraph $G - v_i$ is obtained from the graph G by deletion of the vertex v_i . The subgraph $G - e_{ij}$ is obtained from the graph G by deletion of the edge e_{ij} . The subgraph $G - C_i$ is obtained from the graph G by deleting all the vertices of the cycle C_i . Two cycles, C_i and C_j , are disjoint if they have no vertex in common. We will denote by g_i the degree (the number of neighbours) of the vertex v_i .

* Correspondence address: strada N. Grigorescu, 18/2, 2750 Hunedoara, Romania

The characteristic polynomial of the graph G may be expressed as follows

$$\text{Ch}(G, x) = \det |x\mathbf{I} - \mathbf{A}| = \sum_{n=0}^N a_n x^{N-n} \quad (1)$$

where \mathbf{I} is the unit matrix and \mathbf{A} is the adjacency matrix of the graph G .⁵

The coefficients a_n of the characteristic polynomial $\text{Ch}(G, x)$ may be computed without using the unpractical procedure of the expansion of the determinant but from the topology of the molecular graph. Such a procedure was given by Sachs⁶ in the following expression:

$$a_n = \sum_{s \in S_n} (-1)^{c(s)} 2^{r(s)} \quad (2)$$

where s is a Sachs graph, S_n is the set of all Sachs graphs with n vertices, $c(s)$ is the total number of components in s , and $r(s)$ is the number of cycles in s . The components of a Sachs graph are combinations of isolated bonds (K_2) and cycles (C_m). Recently the Sachs formula was extended to vertex-weighted graphs^{7,8} and to vertex- and edge-weighted graphs^{9,10}, that is to say to those graphs which may be used to represent heteroconjugated molecules.

Hosoya defined¹¹ the acyclic (matching) polynomial as:

$$\text{Ac}(G, x) = \sum_{k=0}^N (-1)^k P(G, k) x^{N-2k} \quad (3)$$

where $P(G, k)$ is the number of ways of choosing k disjoint edges from G .

From the two definitions one could hardly anticipate any connection between $\text{Ch}(G, x)$ and $\text{Ac}(G, x)$. This connection is done by the μ -polynomial, $\mu(G, t, x)$, which continuously transforms $\text{Ac}(G, x)$ into $\text{Ch}(G, x)$ when the parameter t changes from zero to unity. Gutman and Polansky defined¹² the μ -polynomial as

$$\mu(G, t, x) = \sum_{n=0}^N \sum_{s \in S_n} (-1)^{c(s)} 2^{r(s)} x^{N-n} T(s) \quad (4)$$

where $T(s)$ is the product of the individual weights of the $r(s)$ cycles of the Sachs graphs s .

3. THE GENERALIZED GRAPH AND POLYNOMIALS

The generalized (vertex- and edge-weighted)¹⁰ graph G_g is a graph which has the loop l_i , located at the vertex v_i , weighted with the quantity a_i and the edge e_{ij} weighted with the quantity b_{ij} . We define the generalized set of Sachs graphs as the set formed by loops L , isolated bonds

K_2 , and cycles C_m . The contribution of a loop is equal to

$$p(l_i) = a_i \tag{5}$$

that of an weighted edge is equal to

$$p(e_{ij}) = b_{ij}^2 \tag{6}$$

that of an weighted cycle is equal to

$$p(c_i) = \prod b_{ij} \tag{7}$$

where the multiplication goes over all edges in the cycle, and finally, the contribution of a Sachs graph, $p(s)$, is obtained by the multiplication of the contributions of the components of the Sachs graph:

$$p(s) = \prod_{i=1}^{c(s)} p_i \tag{8}$$

Thus, the generalized μ -polynomial is defined as

$$\mu(G_g(t, x)) = \sum_{n=0}^N \sum_{s \in S_n} (-1)^{c(s)} 2^{r(s)} p(s) T(s) \tag{9}$$

From the above formula it follows that the generalized characteristic polynomial is given by

$$\text{Ch}(G_g(x)) = \sum_{n=0}^N \sum_{s \in S_n} (-1)^{c(s)} 2^{r(s)} p(s) \tag{10}$$

and the generalized acyclic polynomial has the following expression

$$\text{Ac}(G_g(x)) = \sum_{n=0}^N \sum_{s \in S_n} (-1)^{c(s)} p(s) \tag{11}$$

4. RECURRENCE RELATIONS

If the generalized graph G_g is obtained from the graph G by setting the weight of the vertex v_i equal to a and the weight of the edge e_{ij} , $j = \overline{1, g_i}$ equal to b_{ij} , the following equalities take place:

Proposition 1.

$$\begin{aligned} \mu(G_g) &= \mu(G) - a\mu(G - v_i) - \\ &- \sum_{i=1}^{g_i} (b_{ij}^2 - 1)\mu(G - v_i - v_j) - 2 \sum_{j=1}^f (p(C_j) - 1)t_j \mu(G - C_j) \end{aligned} \tag{12}$$

$$\text{Ch}(G_g) = \text{Ch}(G) - a\text{Ch}(G - v_i) - \quad (13)$$

$$- \sum_{j=1}^{g_i} (b_{ij}^2 - 1) \text{Ch}(G - v_i - v_j) - 2 \sum_{j=1}^f (p(C_j) - 1) (\text{Ch}(G - C_j)$$

$$\text{Ac}(G_g) = \text{Ac}(G) - a\text{Ac}(G - v_i) - \sum_{j=1}^{g_i} (b_{ij}^2 - 1) \text{Ac}(G - v_i - v_j) \quad (14)$$

The second summation in (12) and (13) goes over all f cycles in G which contain vertex v_i .

From the previously known recurrence relations for $\mu(G)$,¹² $\text{Ch}(G)$ ¹³ and $\text{Ac}(G)$ ^{11,14}:

$$\mu(G) = \mu(G - e_{ij}) - \mu(G - v_i - v_j) - 2 \sum t_j \mu(G - C_j) \quad (15)$$

$$\text{Ch}(G) = \text{Ch}(G - e_{ij}) - \text{Ch}(G - v_i - v_j) - 2 \sum \text{Ch}(G - C_j) \quad (16)$$

$$\text{Ac}(G) = \text{Ac}(G - e_{ij}) - \text{Ac}(G - v_i - v_j) \quad (17)$$

we obtain

Proposition 2.

$$\mu(G_g) = \mu \left(G - \sum_{j=1}^{g_i} e_{ij} \right) - a\mu(G - v_i) - \quad (18)$$

$$- \sum_{j=1}^{g_i} b_{ij}^2 \mu(G - v_i - v_j) - 2 \sum_{j=1}^f p(C_j) t_j \mu(G - C_j)$$

$$\text{Ch}(G_g) = \text{Ch} \left(G - \sum_{j=1}^{g_i} e_{ij} \right) - a \text{Ch}(G - v_i) - \quad (19)$$

$$- \sum_{j=1}^{g_i} b_{ij}^2 \text{Ch}(G - v_i - v_j) - 2 \sum_{j=1}^f p(C_j) \text{Ch}(G - C_j)$$

$$\text{Ac}(G_g) = \text{Ac} \left(G - \sum_{j=1}^{g_i} e_{ij} \right) - a \text{Ac}(G - v_i) - \sum_{j=1}^{g_i} b_{ij}^2 \text{Ac}(G - v_i - v_j) \quad (20)$$

The second summation in (18) and (19) goes over all f cycles in G which contain vertex v_i .

Proposition 3.

If every edge e_{ij} , $j = \overline{1, g_i}$, is a bridge then :

$$\mu(G_g) = \mu \left(G - \sum_{j=1}^{g_i} e_{ij} \right) - a\mu(G - v_i) - \sum_{j=1}^{g_i} b_{ij}^2 \mu(G - v_i - v_j) \quad (21)$$

$$\text{Ch}(G_g) = \text{Ch} \left(G - \sum_{j=1}^{g_i} e_{ij} \right) - a \text{Ch}(G - v_i) - \sum_{j=1}^{g_i} b_{ij}^2 \text{Ch}(G - v_i - v_j) \quad (22)$$

$$\text{Ac}(G_g) = \text{Ac} \left(G - \sum_{j=1}^{g_i} e_{ij} \right) - a \text{Ac}(G - v_i) - \sum_{j=1}^{g_i} b_{ij}^2 \text{Ac}(G - v_i - v_j) \quad (23)$$

The expansion of the μ -polynomial is given in (24) in terms of the μ -polynomials of its subgraphs, corresponding to the decomposition of the graph G and its vertex v_i ¹⁵

$$\mu(G) = x\mu(G - v_i) - \sum_{j=1}^{g_i} \mu(G - v_i - v_j) - 2 \sum_{j=1}^f t_j \mu(G - C_j) \quad (24)$$

where the second summation goes over all f cycles which contain vertex v_i . For the generalized graph G_g we obtain

Proposition 4.

$$\mu(G_g) = (x - a)\mu(G - v_i) - \sum_{j=1}^{g_i} b_{ij}^2 \mu(G - v_i - v_j) - 2 \sum_{j=1}^f p(C_j) t_j \mu(G - C_j) \quad (25)$$

$$\text{Ch}(G_g) = (x - a) \text{Ch}(G - v_i) - \sum_{j=1}^{g_i} b_{ij}^2 \text{Ch}(G - v_i - v_j) - 2 \sum_{j=1}^f p(C_j) \text{Ch}(G - C_j) \quad (26)$$

$$\text{Ac}(G_g) = (x - a) \text{Ac}(G - v_i) - \sum_{j=1}^{g_i} b_{ij}^2 \text{Ac}(G - v_i - v_j) \quad (27)$$

where the second summation in (25) and (26) goes over all f cycles which contain vertex v_i .

In the following propositions, previously established¹² equalities will be presented for the case of the generalized graph G_g .

Proposition 5.

$$\begin{aligned} \mu(G_g) = & \text{Ac}(G_g) - 2 \sum p(C_i) t_i \text{Ac}(G_g - C_i) + \\ & + 4 \sum p(C_i) p(C_j) t_i t_j \text{Ac}(G_g - C_i - C_j) - \\ & - 8 \sum p(C_i) p(C_j) p(C_k) t_i t_j t_k \text{Ac}(G_g - C_i - C_j - C_k) + \dots \end{aligned} \quad (28)$$

In (28) summation goes over all single, pairs, triplets, etc. of mutually disjoint cycles in G_g . The term corresponding to the summation over s mutually disjoint cycles in G_g is:

$$(-1)^{s2^s} \sum \left(\prod_1^s p(C_j) \prod_1^s t_j \text{Ac}(G_g - C_1 - C_2 - \dots - C_s) \right)$$

The inversion of this identity yields

Proposition 6.

$$\begin{aligned} \text{Ac}(G_g) = & \mu(G_g) + 2 \sum p(C_i) t_i \mu(G_g - C_i) + \\ & + 4 \sum p(C_i) p(C_j) t_i t_j \mu(G_g - C_i - C_j) + \\ & + 8 \sum p(C_i) p(C_j) p(C_k) t_i t_j t_k \mu(G_g - C_i - C_j - C_k) + \dots \end{aligned} \quad (29)$$

In (29) summation goes over all single, pairs, triplets, etc. of mutually disjoint cycles in G_g . The term corresponding to the summation over s mutually disjoint cycles in G_g is :

$$2^s \sum \left(\prod_1^s p(C_j) \prod_1^s t_j \mu(G_g - C_1 - C_2 - \dots - C_s) \right)$$

We express the μ -polynomial in terms of the characteristic polynomial, thus obtaining

Proposition 7.

$$\begin{aligned} \mu(G_g) &= \text{Ch}(G_g) + 2 \sum p(C_i)(1 - t_i) \text{Ch}(G_g - C_i) + \\ &+ 4 \sum p(C_i)p(C_j)(1 - t_i)(1 - t_j) \text{Ch}(G_g - C_i - C_j) + \quad (30) \\ &+ 8 \sum p(C_i)p(C_j)p(C_k)(1 - t_i)(1 - t_j)(1 - t_k) \text{Ch}(G_g - C_i - C_j - C_k) + \dots \end{aligned}$$

In (30) summation goes over all single, pairs, triplets, etc. of mutually disjoint cycles in G_g . The term corresponding to the summation over s mutually disjoint cycles in G_g is :

$$2^s \sum \left(\prod_1^s p(C_j) \prod_1^s (1 - t_j) \text{Ch}(G_g - C_1 - C_2 - \dots - C_s) \right)$$

The identity (30) can be inverted leading to
Proposition 8.

$$\begin{aligned} \text{Ch}(G_g) &= \mu(G_g) - 2 \sum p(C_i)(1 - t_i) \mu(G_g - C_i) \\ &+ 4 \sum p(C_i)p(C_j)(1 - t_i)(1 - t_j) \mu(G_g - C_i - C_j) \quad (31) \\ &- 8 \sum p(C_i)p(C_j)p(C_k)(1 - t_i)(1 - t_j)(1 - t_k) \mu(G_g - C_i - C_j - C_k) + \dots \end{aligned}$$

In (31) summation goes over all single, pairs, triplets, etc. of mutually disjoint cycles in G_g . The term corresponding to the summation over s mutually disjoint cycles in G_g is :

$$(-1)^s 2^s \sum \left(\prod_1^s p(C_j) \prod_1^s (1 - t_j) \mu(G_g - C_1 - C_2 - \dots - C_s) \right)$$

Proposition 9.

For $T = 1$ we obtain from (28)

$$\begin{aligned} \text{Ch}(G_g) &= \text{Ac}(G_g) - 2 \sum p(C_i) \text{Ac}(G_g - C_i) + \\ &+ 4 \sum p(C_i)p(C_j) \text{Ac}(G_g - C_i - C_j) - \quad (32) \\ &- 8 \sum p(C_i)p(C_j)p(C_k) \text{Ac}(G_g - C_i - C_j - C_k) + \dots \end{aligned}$$

The term corresponding to the summation over s mutually disjoint cycles in G_g is

$$(-1)^s 2^s \sum \left(\prod_1^s p(C_j) \text{Ac}(G_g - C_1 - C_2 - \dots - C_s) \right)$$

Proposition 10.

For $T = 0$ we obtain from (29)

$$\begin{aligned} \text{Ac}(G_g) &= \text{Ch}(G_g) + 2 \sum p(C_i) \text{Ch}(G_g - C_i) + \\ &+ 4 \sum p(C_i) p(C_j) \text{Ch}(G_g - C_i - C_j) + \\ &+ 8 \sum p(C_i) p(C_j) p(C_k) \text{Ch}(G_g - C_i - C_j - C_k) + \dots \end{aligned} \tag{33}$$

The term corresponding to the summation over s mutually disjoint cycles in G_g is

$$2^s \sum \left(\prod_1^s p(C_j) \text{Ch}(G_g - C_1 - C_2 - \dots - C_s) \right)$$

Proposition 11.

If the graph G_g possesses a single cycle C , then

$$\begin{aligned} \mu(G_g) &= \text{Ac}(G_g) - 2p(C)t \text{Ac}(G_g - C) \\ \mu(G_g) &= \text{Ch}(G_g) - 2p(C)(1-t) \text{Ch}(G_g - C) \\ \mu(G_g) &= (1-t) \text{Ac}(G_g) + t \text{Ch}(G_g) \end{aligned} \tag{34}$$

$$\begin{aligned} \text{Ch}(G_g) &= \mu(G_g) - 2p(C)(1-t) \mu(G_g - C) \\ \text{Ch}(G_g) &= \text{Ac}(G_g) - 2p(C) \text{Ac}(G_g - C) \\ \text{Ch}(G_g) &= \text{Ac}(G_g)(t-1)/t + \mu(G_g)/t \end{aligned} \tag{35}$$

$$\begin{aligned} \text{Ac}(G_g) &= \mu(G_g) + 2p(C)t \mu(G_g - C) \\ \text{Ac}(G_g) &= \text{Ch}(G_g) + 2p(C) \text{Ch}(G_g - C) \\ \text{Ac}(G_g) &= \text{Ch}(G_g)t/(t-1) + \mu(G_g)/(1-t) \end{aligned} \tag{36}$$

If the graph G_g possesses s undisjoint cycles,

$$\mu(G_g) = \text{Ac}(G_g) - 2 \sum_1^s p(C_i) t_i \text{Ac}(G_g - C_i) \tag{37}$$

$$\mu(G_g) = \text{Ch}(G_g) + 2 \sum_1^s p(C_i)(1-t_i) \text{Ch}(G_g - C_i)$$

$$\text{Ac}(G_g) = \mu(G_g) + 2 \sum_1^s p(C_i) t_i \mu(G_g - C_i) \quad (38)$$

$$\text{Ac}(G_g) = \text{Ch}(G_g) + 2 \sum_1^s p(C_i) \text{Ch}(G_g - C_i)$$

$$\text{Ch}(G_g) = \mu\gamma(G_g) - 2 \sum_1^s p(C_i)(1 - t_i)\mu(G_g - C_i) \quad (39)$$

$$\text{Ch}(G_g) = \text{Ac}(G_g) - 2 \sum_1^s p(C_i) \text{Ac}(G_g - C_i)$$

The following recurrence relation for the μ -polynomial was given in ¹²:

$$\mu(G \cdot H) = \mu(G)\mu(H - v_2) + \mu(G - v_1)\mu(H) - x\mu(G - v_1)\mu(H - v_2) \quad (40)$$

where v_1 and v_2 are vertices of the graphs G and H , respectively, and $G \cdot H$ represents the graph obtained by identifying v_1 with v_2 .

Let the weight of the vertex v_i obtained by identifying v_1 with v_2 be a and the weight of the incident edges $e_{ij}, j = \overline{1, g_i}$ be b_{ij} . We obtain the following

Proposition 12.

$$\begin{aligned} \mu(G_g \cdot H_g) &= \mu(G_g)\mu(H_g - v_2) + \\ &+ \mu(G_g - v_1)\mu(H_g) - (x + a)\mu(G_g - v_1)\mu(H_g - v_2) - \\ &- \sum_1^{g_1} (b_{1j}^2 - 1)\mu(G_g - v_1 - v_j)\mu(H_g - v_2) - \\ &- \sum_1^{g_2} (b_{2j}^2 - 1)\mu(G_g - v_1)\mu(H_g - v_2 - v_j) - \\ &- \sum (p(C_j) - 1)t_j\mu(G_g - C_j)\mu(H_g) - \sum (p(C_j) - 1)t_j\mu(G_g)\mu(H_g - C_j) \end{aligned} \quad (41)$$

$$\begin{aligned} \text{Ch}(G_g \cdot H_g) &= \text{Ch}(G_g) \text{Ch}(H_g - v_2) + \\ &+ \text{Ch}(G_g - v_1) \text{Ch}(H_g) - (x + a) \text{Ch}(G_g - v_1) \text{Ch}(H_g - v_2) - \\ &- \sum_1^{g_1} (b_{1j}^2 - 1) \text{Ch}(G_g - v_1 - v_j) \text{Ch}(H_g - v_2) - \\ &- \sum_1^{g_2} (b_{2j}^2 - 1) \text{Ch}(G_g - v_1) \text{Ch}(H_g - v_2 - v_j) - \\ &- \sum (p(C_j) - 1) \text{Ch}(G_g - C_j) \text{Ch}(H_g) - \sum (p(C_j) - 1) \text{Ch}(G_g) \text{Ch}(H_g - C_j) \end{aligned} \quad (42)$$

$$\begin{aligned}
\text{Ac}(G_g \cdot H_g) &= \text{Ac}(G_g) \text{Ac}(H_g - v_2) + \\
&+ \text{Ac}(G_g - v_1) \text{Ac}(H_g) - (x + a) \text{Ac}(G_g - v_1) \text{Ac}(H_g - v_2) - \\
&- \sum_1^{g_1} (b_{1j}^2 - 1) \text{Ac}(G_g - v_1 - v_j) \text{Ac}(H_g - v_2) - \\
&- \sum_1^{g_2} (b_{2j}^2 - 1) \text{Ac}(G_g - v_1) \text{Ac}(H_g - v_2 - v_j)
\end{aligned}$$

The third and fourth summation in (41) and (42) goes over all cycles in G_g which contain vertex v_1 , and over all cycles in H_g which contain vertex v_2 , respectively.

5. CONCLUSIONS

Several combinatorial relations between μ , characteristic and acyclic polynomials were extended to generalized graphs. The method exposed is in principle applicable to the description of heteroconjugated molecules in the framework of the HMO theory.

REFERENCES

- ¹ J. V. Knop and N. Trinajstić, *Int. J. Quantum Chem. : Quantum Chem. Symp.*, **14**, 503 (1980).
- ² I. Gutman, M. Milun and N. Trinajstić, *J. Amer. Chem. Soc.*, **99**, 1692 (1977).
- ³ J. Aihara, *J. Amer. Chem. Soc.*, **98**, 275 (1976).
- ⁴ O. E. Polansky and M. Zander, *J. Mol. Struct.*, **84**, 361 (1982).
- ⁵ D. H. Rouvray, in "Chemical Application of Graph Theory", A. T. Balaban, Ed. Academic, London, 1976, p. 175.
- ⁶ H. Sachs, *Publ. Math. Debrecen*, **1**, 119 (1963).
- ⁷ R. B. Mallion, N. Trinajstić and A. J. Schwenk, *Z. Naturforsch.*, **29a**, 1481 (1974).
- ⁸ R. B. Mallion, A. J. Schwenk and N. Trinajstić, *Croat. Chem. Acta*, **46**, 171 (1974).
- ⁹ A. Graovac, O. E. Polansky, N. Trinajstić and N. Tyutyulkov, *Z. Naturforsch.*, **30a**, 1696 (1975).
- ¹⁰ N. Trinajstić, "Chemical Graph Theory", vol. I, CRC Press, Boca Raton, 1983, p. 56.
- ¹¹ H. Hosoya, *Bull. Chem. Soc. Japan*, **44**, 2332 (1971).
- ¹² I. Gutman and O. E. Polansky, *Theoret. Chim. Acta (Berl.)*, **60**, 203 (1981).
- ¹³ D. Cvetcović, M. Doob and H. Hachs, "Spectra of Graphs — Theory and Application", Academic Press, New York, 1980.
- ¹⁴ I. Gutman and H. Hosoya, *Theoret. Chim. Acta (Berl.)*, **48**, 279 (1978).
- ¹⁵ O. E. Polansky, *Match*, **18**, 71 (1985).