CHEMICAL GRAPH POLYNOMIALS. 1

THE POLYNOMIAL DESCRIPTION OF GENERALIZED CHEMICAL GRAPHS

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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 polynomials\(^1\) 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: \(v_1, v_2, \ldots, v_n\), \(m\) edges and \(r\) cycles: \(C_1, C_2, \ldots, C_r\). 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 \(v_i\).

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

$$
\mathrm{Ch}(G, x) = \det (xI - A) = \sum_{n=0}^{N} a_n x^{N-n} \quad (1)
$$

where $I$ is the unit matrix and $A$ is the adjacency matrix of the graph $G$.

The coefficients $a_n$ of the characteristic polynomial $\mathrm{Ch}(G, x)$ 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 Sachs 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 and to vertex- and edge-weighted graphs, that is to say to those graphs which may be used to represent heteroconjugated molecules.

Hosoya defined the acyclic (matching) polynomial as:

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

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 $\mathrm{Ch}(G, x)$ and $\mathrm{Ac}(G, x)$. This connection is done by the $\mu$-polynomial, $\mu(G, t, x)$, which continuously transforms $\mathrm{Ac}(G, x)$ into $\mathrm{Ch}(G, x)$ when the parameter $t$ changes from zero to unity. Gutman and Polansky defined the $\mu$-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) graph $G_x$ is a graph which has the loop $l_t$, located at the vertex $v_t$, weighted with the quantity $a_t$ 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

$$p(l_i) = a_i$$

(5)

that of an weighted edge is equal to

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

(6)

that of an weighted cycle is equal to

$$p(c_s) = \prod b_{ij}$$

(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:

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

(8)

Thus, the generalized $\mu$-polynomial is defined as

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

(9)

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

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

(10)

and the generalized acyclic polynomial has the following expression

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

(11)

4. RECURRENCE RELATIONS

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

**Proposition 1.**

$$\mu(G_s) = \mu(G) - a \mu(G - v_i) -$$

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

(12)
\[ \text{Ch}(G_g) = \text{Ch}(G) - \alpha \text{Ch}(G - v_i) - \] 
\[- \sum_{j=1}^{\sigma_i} (b_{ij}^2 - 1) \text{Ch}(G - v_i - v_j) - 2 \sum_{j=1}^{f} p(C_j) \left( \text{Ch}(G - C_j) - \alpha \text{Ch}(G - v_i - v_j) - \sum_{j=1}^{\sigma_i} (b_{ij}^2 - 1) \text{Ch}(G - v_i - v_j) \right) \] 
\[ \text{Ac}(G_g) = \text{Ac}(G) - \alpha \text{Ac}(G - v_i) - \sum_{j=1}^{\sigma_i} (b_{ij}^2 - 1) \text{Ac}(G - v_i - v_j) \] 
\[ (13) \]

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

From the previously known recurrence relations for \( \mu(G) \), \( \text{Ch}(G) \) and \( \text{Ac}(G) \) :

\[ \mu(G) = \mu(G - v_i) - \mu(G - v_i - v_j) - 2 \sum_{j=1}^{f} \mu(G - C_j) \] 
\[ \text{Ch}(G) = \text{Ch}(G - v_i) - \text{Ch}(G - v_i - v_j) - 2 \sum_{j=1}^{f} \text{Ch}(G - C_j) \] 
\[ \text{Ac}(G) = \text{Ac}(G - v_i) - \text{Ac}(G - v_i - v_j) \] 
\[ (14) \]

we obtain

\[ \mu(G_g) = \mu \left( G - \sum_{j=1}^{\sigma_i} e_{ij} \right) - \alpha \mu(G - v_i) - \] 
\[- \sum_{j=1}^{\sigma_i} b_{ij}^2 \mu(G - v_i - v_j) - 2 \sum_{j=1}^{f} p(C_j) t_{ij} \mu(G - C_j) \] 
\[ \text{Ch}(G_g) = \text{Ch} \left( G - \sum_{j=1}^{\sigma_i} e_{ij} \right) - \alpha \text{Ch}(G - v_i) - \] 
\[- \sum_{j=1}^{\sigma_i} b_{ij}^2 \text{Ch}(G - v_i - v_j) - 2 \sum_{j=1}^{f} p(C_j) \text{Ch}(G - C_j) \] 
\[ (15) \]

\[ \text{Ac}(G_g) = \text{Ac} \left( G - \sum_{j=1}^{\sigma_i} e_{ij} \right) - \alpha \text{Ac}(G - v_i) - \sum_{j=1}^{\sigma_i} b_{ij}^2 \text{Ac}(G - v_i - v_j) \] 
\[ (16) \]

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

**Proposition 2.**

\[ \mu(G_g) = \mu \left( G - \sum_{j=1}^{\sigma_i} e_{ij} \right) - \alpha \mu(G - v_i) - \] 
\[- \sum_{j=1}^{\sigma_i} b_{ij}^2 \mu(G - v_i - v_j) - 2 \sum_{j=1}^{f} p(C_j) t_{ij} \mu(G - C_j) \] 
\[ \text{Ch}(G_g) = \text{Ch} \left( G - \sum_{j=1}^{\sigma_i} e_{ij} \right) - \alpha \text{Ch}(G - v_i) - \] 
\[- \sum_{j=1}^{\sigma_i} b_{ij}^2 \text{Ch}(G - v_i - v_j) - 2 \sum_{j=1}^{f} p(C_j) \text{Ch}(G - C_j) \] 
\[ (17) \]

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

**Proposition 3.**

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

\[ \mu(G_g) = \mu \left( G - \sum_{j=1}^{\sigma_i} e_{ij} \right) - \alpha \mu(G - v_i) - \sum_{j=1}^{\sigma_i} b_{ij}^2 \mu(G - v_i - v_j) \] 
\[ (21) \]

\[ \text{Ch}(G_g) = \text{Ch} \left( G - \sum_{j=1}^{\sigma_i} e_{ij} \right) - \alpha \text{Ch}(G - v_i) - \sum_{j=1}^{\sigma_i} b_{ij}^2 \text{Ch}(G - v_i - v_j) \] 
\[ (22) \]

\[ \text{Ac}(G_g) = \text{Ac} \left( G - \sum_{j=1}^{\sigma_i} e_{ij} \right) - \alpha \text{Ac}(G - v_i) - \sum_{j=1}^{\sigma_i} b_{ij}^2 \text{Ac}(G - v_i - v_j) \] 
\[ (23) \]
The expansion of the \( \mu \)-polynomial is given in (24) in terms of the \( \mu \)-polynomials of its subgraphs, corresponding to the decomposition of the graph \( G \) and its vertex \( v_i \):

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

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

**Proposition 4.**

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

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

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

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

In the following propositions, previously established equalities will be presented for the case of the generalized graph \( G_g \).

**Proposition 5.**

\[
\mu(G_g) = \text{Ac}(G_g) - 2 \sum p(C_i) t_i \text{Ac}(G_g - C_i) +
\]

\[
+ 4 \sum p(C_i) p(C_j) t_i t_j \text{Ac}(G_g - C_i - C_j) -
\]

\[
- 8 \sum p(C_i) p(C_j) p(C_k) t_i t_j t_k \text{Ac}(G_g - C_i - C_j - C_k) + \ldots \tag{28}
\]

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:

\[
(-1)^{s-2s} \sum \left( \prod_{1}^{s} p(C_j) \prod_{1}^{s} t_j \text{Ac}(G_g - C_1 - C_2 - \ldots - C_s) \right)
\]

The inversion of this identity yields

**Proposition 6.**

\[
\text{Ac}(G_g) = \mu(G_g) + 2 \sum p(C_i) t_i \mu(G_g - C_i) +
\]

\[
+ 4 \sum p(C_i) p(C_j) t_i t_j \mu(G_g - C_i - C_j) +
\]

\[
+ 8 \sum p(C_i) p(C_j) p(C_k) t_i t_j t_k \mu(G_g - C_i - C_j - C_k) + \ldots \tag{29}
\]
In (29) summation goes over all single, pairs, triplets, etc. of mutually disjoint cycles in \( G_\nu \). The term corresponding to the summation over \( s \) mutually disjoint cycles in \( G_\nu \) is:

\[
2^s \sum \left( \prod_{i} p(C_i) \prod_{j} t_j^{\mu(G_\nu - C_1 - C_2 - \ldots - C_\nu)} \right)
\]

We express the \( \mu \)-polynomial in terms of the characteristic polynomial, thus obtaining

**Proposition 7.**

\[
\mu(G_\nu) = \text{Ch}(G_\nu) + 2 \sum p(C_i)(1 - t_i) \text{Ch}(G_\nu - C_i) +
\]

\[
+ 4 \sum p(C_i)p(C_j)(1 - t_i)(1 - t_j) \text{Ch}(G_\nu - C_i - C_j) + \quad (30)
\]

\[
+ 8 \sum p(C_i)p(C_j)p(C_k)(1 - t_i)(1 - t_j)(1 - t_k) \text{Ch}(G_\nu - C_i - C_j - C_k) + \ldots
\]

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

\[
2^s \sum \left( \prod_{i} p(C_i) \prod_{j} (1 - t_j) \text{Ch}(G_\nu - C_1 - C_2 - \ldots - C_\nu) \right)
\]

The identity (30) can be inverted leading to

**Proposition 8.**

\[
\text{Ch}(G_\nu) = \mu(G_\nu) - 2 \sum p(C_i)(1 - t_i)\mu(G_\nu - C_i)
\]

\[
+ 4 \sum p(C_i)p(C_j)(1 - t_i)(1 - t_j)\mu(G_\nu - C_i - C_j) \quad (31)
\]

\[
- 8 \sum p(C_i)p(C_j)p(C_k)(1 - t_i)(1 - t_j)(1 - t_k)\mu(G_\nu - C_i - C_j - C_k) + \ldots
\]

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

\[
(-1)^s 2^s \sum \left( \prod_{i} p(C_i) \prod_{j} (1 - t_j)\mu(G_\nu - C_1 - C_2 - \ldots - C_\nu) \right)
\]

**Proposition 9.**

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

\[
\text{Ch}(G_\nu) = \Delta c(G_\nu) - 2 \sum p(C_i)\Delta c(G_\nu - C_i) +
\]

\[
+ 4 \sum p(C_i)p(C_j)\Delta c(G_\nu - C_i - C_j) - \quad (32)
\]

\[
- 8 \sum p(C_i)p(C_j)p(C_k)\Delta c(G_\nu - C_i - C_j - C_k) + \ldots
\]
The term corresponding to the summation over $s$ mutually disjoint cycles in $G_g$ is

$$(-1)^{2s} \sum \left( \prod_{j=1}^{s} p(C_j) \Delta c(G_g - C_1 - C_2 - \ldots - C_s) \right)$$

**Proposition 10.**

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

$$\Delta c(G_g) = \text{Ch}(G_g) + 2 \sum p(C_i) \text{Ch}(G_g - C_i) +$$

$$+ 4 \sum p(C_i)p(C_j) \text{Ch}(G_g - C_i - C_j) +$$

$$+ 8 \sum p(C_i)p(C_j)p(C_k) \text{Ch}(G_g - C_i - C_j - C_k) + \ldots$$

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

$$2^s \sum \left( \prod_{j=1}^{s} p(C_j) \text{Ch}(G_g - C_1 - C_2 - \ldots - C_s) \right)$$

**Proposition 11.**

If the graph $G_g$ possesses a single cycle $C$, then

$$\mu(G_g) = \Delta c(G_g) - 2p(C) t \Delta c(G_g - C)$$

$$\mu(G_g) = \text{Ch}(G_g) - 2p(C) (1 - t) \text{Ch}(G_g - C)$$

$$\mu(G_g) = (1 - t) \Delta c(G_g) + t \text{Ch}(G_g)$$

$$\text{Ch}(G_g) = \mu(G_g) - 2p(C)(1 - t) \mu(G_g - C)$$

$$\text{Ch}(G_g) = \Delta c(G_g) - 2p(C) \Delta c(G_g - C)$$

$$\text{Ch}(G_g) = \Delta c(G_g)(t - 1)/t + \mu(G_g)/t$$

$$\Delta c(G_g) = \mu(G_g) + 2p(C) t \mu(G_g - C)$$

$$\Delta c(G_g) = \text{Ch}(G_g) + 2p(C) \text{Ch}(G_g - C)$$

$$\Delta c(G_g) = \text{Ch}(G_g)t/(t - 1) + \mu(G_g)/(1-t)$$

If the graph $G_g$ possesses $s$ undisjoint cycles,

$$\mu(G_g) = \Delta c(G_g) - 2 \sum_{j=1}^{s} p(C_i) t_i \Delta c(G_g - C_i)$$

$$\mu(G_g) = \text{Ch}(G_g) + 2 \sum_{j=1}^{s} p(C_i)(1 - t_i) \text{Ch}(G_g - C_i)$$
\[ \Delta c(G_g) = \mu(G_g) + 2 \sum_1^s \ p(C_i) t_i \mu(G_g - C_i) \]  

(38)

\[ \Delta c(G_g) = \text{Ch}(G_g) + 2 \sum_1^s \ p(C_i) \text{Ch}(G_g - C_i) \]  

(39)

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

The following recurrence relation for the \( \mu \)-polynomial was given in \(^{12}\):

\[ \mu(G \cdot H) = \mu(G) \mu(H - v_2) + \mu(G - v_1) \mu(H) - \mu(G - v_1) \mu(H - v_2) \]  

(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 \( e_{ij}, j = 1, g_i \) be \( b_{ij} \). We obtain the following

**Proposition 12.**

\[ \mu(G_g \cdot H_g) = \mu(G_g) \mu(H_g - v_2) + \]

\[ + \mu(G_g - v_1) \mu(H_g) - (x + a) \mu(G_g - v_1) \mu(H_g - v_2) - \]

\[ - \sum_1^{s_1} (b_{1j}^2 - 1) \mu(G_g - v_1 - v_j) \mu(H_g - v_2) - \]

\[ - \sum_1^{s_2} (b_{2j}^2 - 1) \mu(G_g - v_1) \mu(H_g - v_2 - v_j) - \]

\[ - \sum(p(C_i) - 1) t_i \mu(G_g - C_i) \mu(H_g) - \sum(p(C_i) - 1) t_i \mu(G_g) \mu(H_g - C_i) \]

\[ \text{Ch}(G_g \cdot H_g) = \text{Ch}(G_g) \text{Ch}(H_g - v_2) + \]

\[ + \text{Ch}(G_g - v_1) \text{Ch}(H_g) - (x + a) \text{Ch}(G_g - v_1) \text{Ch}(H_g - v_2) - \]

\[ - \sum_1^{s_1} (b_{1j}^2 - 1) \text{Ch}(G_g - v_1 - v_j) \text{Ch}(H_g - v_2) - \]

\[ - \sum_1^{s_2} (b_{2j}^2 - 1) \text{Ch}(G_g - v_1) \text{Ch}(H_g - v_2 - v_j) - \]

\[ - \sum(p(C_i) - 1) \text{Ch}(G_g - C_i) \text{Ch}(H_g) - \sum(p(C_i) - 1) \text{Ch}(G_g) \text{Ch}(H_g - C_i) \]
\[
\Delta c(G, H) = \Delta c(G) \Delta c(H - v) + \\
+ \Delta c(G - v_1) \Delta c(H) - (x + a) \Delta c(G - v_1) \Delta c(H - v_2) - \\
- \sum_{1}^{\sigma} (b_{ij}^2 - 1) \Delta c(G - v_1 - v_2) \Delta c(H - v_2) - \\
- \sum_{1}^{\sigma} (b_{ij}^2 - 1) \Delta c(G - v_1) \Delta c(H - v_2 - v_j)
\]

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

5. CONCLUSIONS

Several combinatorial relations between \(\mu\), 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