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CHEMICAL GRAPH POLYNOMIALS. PART 3.[1]

THE LAPLACIAN POLYNOMIAL OF MOLECULAR GRAPHS

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The Laplacian polynomial of molecular graphs representing saturated acyclic and cyclic hydrocarbons is investigated. The expansion of the Laplacian polynomial of an acyclic molecular graph in a series of homologous compounds is expressed in terms of the Laplacian polynomials of the precedents terms in the series, enabling the rapid computation of the polynomial for large graphs. Some expressions were derived for the Laplacian polynomial of molecular graphs representing 2-methyl, 3-methyl, and 2,2-dimethylalkanes in terms of the Laplacian polynomials of linear graphs. The existence of nonisomorphic graphs with identical Laplacian polynomial was investigated for 4-trees, representing alkanes, up to 12 vertices. Six pairs of Laplacian isospectral 4-trees were found, the smallest pair having 11 vertices.

INTRODUCTION

Graph theoretic polynomials are important molecular graph invariants,[2–4] representing a convenient way of expressing the bonding topology of a molecular graph.

By removing all hydrogen atoms from the chemical formula of a chemical compound containing covalent bonds we obtain the hydrogen-depleted graph (or molecular graph) of that compound, whose vertices correspond to non-hydrogen atoms. In the particular case of hydrocarbons the vertices of the molecular graph denote carbon atoms.

A number of useful graph definitions will be introduced. Let $G = (V, E)$ be a graph G, without loops and multiple edges. All N vertices of a graph form the vertex set $V = V(G)$, and the M edges are elements of the edge set $E = E(G)$. The adjacency matrix of the graph G, $A = A(G)$, is the square $N \times N$ symmetric matrix which contains information about the connectivity of the vertices in G. Its entries are defined as :

$$(A)_{ij} = \begin{cases} 1 \text{ if } (i, j) \in E(G) \\ 0 \text{ if } (i, j) \notin E(G) \end{cases}$$

The characteristic or spectral polynomial Ch (G, x) of the molecular graph G is the characteristic polynomial of its adjacency matrix :[2-4]

$$Ch(G, x) = \det (xI - A) \tag{1}$$

where I is the N × N unit matrix.

In the present paper we will investigate the properties and the applications of a less used graph theoretical polynomial, namely the Laplacian polynomial of a molecular graph.

THE LAPLACIAN MATRIX

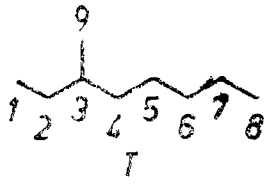
The degree deg(i) of a vertex i ∈ V(G) is the number of edges incident to i. Denote by DEG(G) the diagonal matrix with its ii-entry equal to deg(i). The matrix

$$L(G) = DEG(G) - A(G)$$

is called the Laplacian matrix.[5] The elements of the Laplacian matrix are

$$L_{ij} = \begin{cases} \deg(i) & \text{if } i = j \\ -1 & \text{if } (i, j) \in E(G) \\ 0 & \text{if } (i, j) \notin E(G) \end{cases}$$

As example, the molecular graph and the Laplacian matrix of 3-methylhexane (T) are given below. This graph is the smallest identity tree because its only symmetry operation is the identity (no vertices are equivalent) and it has the smallest number of vertices among all identity trees.



T

$$L(T) = \begin{bmatrix} 1 & -1 & 0 & 0 & 0 & 0 & 0 \\ -1 & 2 & -1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 3 & -1 & 0 & 0 & -1 \\ 0 & 0 & -1 & 2 & -1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 2 & -1 & 0 \\ 0 & 0 & 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Let us mention that the Laplacian matrix L is sometimes called the Kirchhoff matrix due to its role in the spanning tree theorem of Kirchhoff. [6-8]

Eichinger [9-14] showed that the eigenvalues of the Laplacian matrix of a molecular graph determine the distribution function of the radius of gyration of the molecule. The asymptotic behaviour of the distribution function of the radius of gyration of a molecule depends mostly upon the magnitude and multiplicity of λ_2, the second smallest Laplacian eigenvalue.

THE LAPLACIAN POLYNOMIAL

The Laplacian polynomial of the molecular graph G is the characteristic polynomial of its Laplacian matrix:

$$La(G, x) = \det(xI - L) \quad (1)$$

where I is the N × N unit matrix.

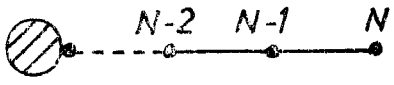
The Laplacian polynomial of the molecular graph T is equal to:

$$La(T) = x^7 - 12x^6 + 54x^5 - 114x^4 + 115x^3 - 50x^2 + 7x$$

Some expressions were derived for the Laplacian polynomial of molecular graphs representing polymers.[15,16]

In the present investigation, all computations of the Laplacian polynomial were done using a very efficient algorithm devised for the computation of the characteristic polynomial, namely Le Verrier-Fadeev-Frame algorithm.[17-20]

Using the recurrence relationships devised for the characteristic polynomial of vertex-weighted molecular graphs,[21] the expansion of the Laplacian polynomial of an acyclic molecular graph in a series of homologous compounds is expressed in terms of the Laplacian polynomials of the precedent terms in the series, enabling the rapid computation of the polynomial for large graphs. If G_N is an acyclic graph with N vertices, then its Laplacian polynomial may be expressed in terms of the polynomials of its two precedent graphs G_{N-1} and G_{N-2} by the following equation:



G_N

$$La(G_N) = (x - 2)\,La(G_{N-1}) - La(G_{N-2})$$

The Laplacian polinomials of linear molecular graphs representing normal alkanes with up to 12 vertices are presented in Table 1. We will denote by $Li_n = Li_n(x)$ the Laplacian polynomial of a linear chain consisting of n vertices.

Table 2 presents the Laplacian polynomials of molecular graphs representing 2-methyl substituted alkanes, denoted as 2-Me-C_m, where m takes values from 3 to 11.

Table 1

Laplacian polynomial of molecular graphs representing linear alkanes consisting of N carbon atoms

N	x^0	x^1	x^2	x^3	x^4	x^5	x^6	x^7	x^8	x^9	x^{10}	x^{11}	x^{12}
2	0	−2	1										
3	0	3	−4	1									
4	0	−4	10	−6	1								
5	0	5	−20	21	−8	1							
6	0	−6	35	−56	36	−10	1						
7	0	7	−56	126	−120	55	−12	1					
8	0	−8	84	−252	330	−220	78	−14	1				
9	0	9	−120	462	−792	715	−364	105	−16	1			
10	0	−10	165	−792	1716	−2002	1365	−560	136	−18	1		
11	0	11	−220	1287	−3432	5005	−4368	2380	−816	171	−20	1	
12	0	−12	286	−2002	6435	−11440	12376	−8568	3876	−1140	210	−22	1

Table 2

Laplacian polynomial of molecular graphs representing 2-Me-C_m alkanes

m	x^0	x^1	x^2	x^3	x^4	x^5	x^6	x^7	x^8	x^9	x^{10}	x^{11}	x^{12}
3	0	−4	9	−6	1								
4	0	5	−18	20	−8	1							
5	0	−6	32	−52	35	−10	1						
6	0	7	−52	116	−114	54	−12	1					
7	0	−8	79	−232	309	−212	77	−14	1				
8	0	9	−114	427	−736	679	−354	104	−16	1			
9	0	−10	158	−736	1590	−1882	1310	−548	135	−18	1		
10	0	11	−212	1203	−3180	4675	−4148	2302	−802	170	−20	1	
11	0	−12	277	−1882	5973	−10648	11661	−8204	3771	−1124	209	−22	1

The theoretic polynomial of a molecular graph is usually expressed as a function of x. An alternative representation of the characteristic polynomial was introduced,[22,23] expressing it in terms of the characteristic polynomial of linear graphs. In a series of homologous molecular graphs, the linear graph representation is mathematically equivalent to the representation in x, but appears to reflect better structural similarities in the series.

We will explore the use of Li_n polynomials to express the Laplacian polynomials of families of structurally related graphs in terms of Li_n.

One can derive the equivalent forms of the Laplacian polynomial expresed in terms of Li_n by first expressing the powers of x in terms of Li_n and then make a substitution in the corresponding polynomial expressed in powers of x. For example, the first powers of x are expressed as :

$$x = Li_1$$

$$x^2 = Li_2 + 2\,Li_1$$

$$x^3 = Li_3 + 4\,Li_2 + 5\,Li_1$$

$$x^4 = Li_4 + 6\,Li_3 + 14\,Li_2 + 14\,Li_1$$

$$x^5 = Li_5 + 8\,Li_4 + 27\,Li_3 + 48\,Li_2 + 42\,Li_1$$

From the Laplacian polynomials of 2-Me-C_m, presented in Table 2, we obtain the following expressions in terms of Li_n:

$$La(2\text{-Me-}C_3) = Li_4 - Li_2 - 2\,Li_1 - Li_0$$

$$La(2\text{-Me-}C_4) = Li_5 - Li_3 - 2\,Li_2 - Li_1$$

$$La(2\text{-Me-}C_5) = Li_6 - Li_4 - 2\,Li_3 - Li_2$$

$$La(2\text{-Me-}C_6) = Li_7 - Li_5 - 2\,Li_4 - Li_3$$

$$La(2\text{-Me-}C_7) = Li_8 - Li_6 - 2\,Li_5 - Li_4$$

From the above expressions we readily obtain the general formula

$$La(2\text{-Me-}C_{N-1}) = Li_N - Li_{N-2} - 2\,Li_{N-3} - Li_{N-4}$$

As is evident from the above expressions, the equivalent formulas of the Laplacian polynomials in terms of Li_n are more simpler than their expressions in terms of x.

In Table 3 we have collected Laplacian polynomials expressed in terms of x for the homologous series of 3-methyl substituted alkanes, denoted for brevity by 3-Me-C_m, where m takes values between, 5 and 11.

Table 3

Laplacian polynomial of molecular graphs representing 3-Me-C alkanes

m	x^0	x^1	x^2	x^3	x^4	x^5	x^6	x^7	x^8	x^9	x^{10}	x^{11}	x^{12}
5	0	−6	31	−52	35	−10	1						
6	0	7	−50	115	−114	54	−12	1					
7	0	−8	76	−228	308	−212	77	−14	1				
8	0	9	−110	417	−730	678	−354	104	−16	1			
9	0	−10	153	−716	1569	−1874	1309	−548	135	−18	1		
10	0	11	−206	1168	−3124	4639	−4138	2301	−802	170	−20	1	
11	0	−12	270	−1826	5847	−10528	11606	−8192	3770	−1124	209	−22	1

Using the same procedure to translate the Laplacian polynomial in terms of Li_n, we have obtained the following expressions for the 3-Me-C_m molecular graphs:

$$La(3\text{-Me-}C_5) = Li_6 - Li_4 - 2\,Li_3 - 2\,Li_2 - 2\,Li_1 - Li_0$$

$$La(3\text{-Me-}C_6) = L_7 - Li_5 - 2\,Li_4 - 2\,Li_3 - 2\,Li_2 - Li_1$$

$$La(3\text{-}Me\text{-}C_7) = Li_8 - Li_6 - 2\,Li_5 - 2\,Li_4 - 2\,Li_3 - Li_2$$
$$La(3\text{-}Me\text{-}C_8) = Li_9 - Li_7 - 2\,Li_6 - 2\,Li_5 - 2\,Li_4 - Li_3$$
$$La(3\text{-}Me\text{-}C_9) = Li_{10} - Li_8 - 2\,Li_7 - 2\,Li_6 - 2\,Li_5 - Li_4$$

The above expressions are leading us to derive the general form :

$$La(3\text{-}Me\text{-}C_{N-1}) = Li_N - Li_{N-2} - 2\,Li_{N-3} - 2\,L_{N-4} - 2\,Li_{N-5} - Li_{N-6}$$

In Table 4 we present the Laplacian polynomials expressed in terms of x for the homologous series of 2,2-dimethyl substituted alkanes, denoted for brevity by 2,2-Me_2-C_m, where m takes values between 3 and 10.

Table 4

Laplacian polynomial of molecular graphs representing 2,2-Me_2-C alkanes

m	x^0	x^1	x^2	x^3	x^4	x^5	x^6	x^7	x^8	x^9	x^{10}	x^{11}	x^{12}
3	0	5	−16	18	−8	1							
4	0	−6	28	−46	33	−10	1						
5	0	7	−46	102	−104	52	−12	1					
6	0	−8	71	−204	277	−198	75	−14	1				
7	0	9	−104	377	−654	621	−336	102	−16	1			
8	0	−10	146	−654	1408	−1698	1218	−526	133	−18	1		
9	0	11	−198	1077	−2816	4183	−3798	2168	−776	168	−20	1	
10	0	−12	261	−1698	5301	−9484	10561	−7608	3587	−1094	207	−22	1

For this more branched molecular graphs, the expressions obtained using Li_n contain more terms :

$$La(2,2\text{-}Me_2\text{-}C_3) = Li_5 - 3\,Li_3 - 8\,Li_2 - 7\,Li_1$$
$$La(2,2\text{-}Me_2\text{-}C_4) = Li_6 - 3\,Li_4 - 8\,Li_3 - 9\,Li_2 - 6\,Li_1$$
$$La(2,2\text{-}Me_2\text{-}C_5) = Li_7 - 3\,Li_5 - 8\,Li_4 - 9\,Li_3 - 6\,Li_2 - 2\,Li_1$$
$$La(2,2\text{-}Me_2\text{-}C_6) = Li_8 - 3\,Li_6 - 8\,Li_5 - 9\,Li_4 - 6\,Li_3 - 2\,Li_2$$
$$La(2,2\text{-}Me_2\text{-}C_7) = Li_9 - 3\,Li_7 - 8\,Li_6 - 9\,Li_5 - 6\,Li_4 - 2\,Li_3$$
$$La(2,2\text{-}Me_2\text{-}C_8) = Li_{10} - 3\,Li_8 - 8\,Li_7 - 9\,Li_6 - 6\,Li_5 - 2\,Li_4$$
$$La(2,2\text{-}Me_2\text{-}C_9) = Li_{11} - 3\,Li_9 - 8\,Li_8 - 9\,Li_7 - 6\,Li_6 - 2\,Li_5$$

The general expression has the following form :

$$La(2,2\text{-}Me\text{-}C_{N-2}) = Li_N - 3\,Li_{N-2} - 8\,Li_{N-3} -$$
$$- 9\,Li_{N-4} - 6\,Li_{N-5} - 2\,Li_{N-6}$$

When the Laplacian polynomial is expressed in terms of Li_n the resulting expressions are much simpler and allow one to derive the general expression after obtaining first few members of the series. We expect that for highly branched homologous series the expressions in terms of Li_n will contain much more terms and will be harder to derive by inspecting the first terms of the series.

We include in Table 5 the Laplacian polynomials expressed in terms of x for the homologous series of cycloalkanes with N carbon atoms, where N takes values between 3 and 12.

Table 5

Laplacian polynomial of molecular graphs representing cycloalkanes consisting of N carbon atoms

N	x^0	x^1	x^2	x^3	x^4	x^5	x^6	x^7	x^8	x^9	x^{10}	x^{11}	x^{12}
3	0	9	−6	1									
4	0	−16	20	−8	1								
5	0	25	−50	35	−10	1							
6	0	−36	105	−112	54	−12	1						
7	0	49	−196	294	−210	77	−14	1					
8	0	−64	336	−672	660	−352	104	−16	1				
9	0	81	−540	1386	−1782	1287	−546	135	−18	1			
10	0	−100	825	−2640	4290	−4004	2275	−800	170	−20	1		
11	0	121	−1210	4719	−9438	11011	−8008	3740	−1122	209	−22	1	
12	0	−144	1716	−8008	19305	−27456	24752	−14688	5814	−1520	252	−24	1

For rings, no simple expression in terms of Li_n was obtained.

As is apparent from the above expressions in terms of Li_n, they show more visibly the structural similarities on comparison of structurally related systems than the classical expressions in terms of powers of x, and therefore open a route to general expression for the Laplacian polynomials for a homologous series of molecules.

ISOSPECTRAL LAPLACIAN POLYNOMIALS

The spectrum, $X(G) = (x_i,\ i = 1, 2, \ldots, N)$, of the adjacency matrix A(G) of an arbitrary, simple graph G, is an isomorphism invariant, i.e. X(G) remains unchanged under all permutations which cause the N vertices of G to be relabelled. For a long time, it was thought that X(G) formed a complete set of isomorphism invariants, i.e. that X(G) uniquely determined G up to isomorphism, until it was discovered that there exists non-isomorphic graphs with identical spectra, hence identical characteristic polynomials.[24] The smallest pair of alkane molecular graphs exhibiting identical characteristic polynomial has 9 carbon atoms (vertices).

We have investigated the existence of isospectral Laplacian polynomials for non-isomorphic graphs for a set consisting of 661 4-trees representing alkanes with 4 to 12 vertices.

Six pairs of Laplacian isospectral nonisomorphic 4-trees were found, presented in Figure 1. Their Laplacian polynomials are collected in Table 6. No structural determination of the degeneracy of the Laplacian polynomial was discovered, but work is in progress in this direction.

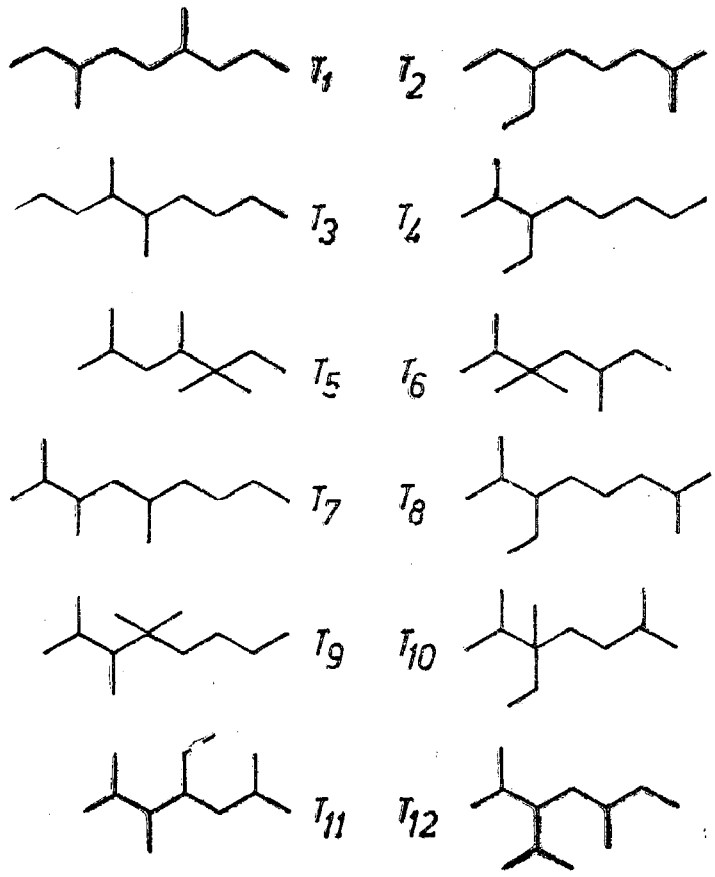


Fig. 1. — Six pairs of nonisomorphic 4-trees with identical Laplacian polynomials. Their Laplacian polynomials are presented in Table 6.

Table 6

Laplacian polynomial of isospectral molecular graphs from Figure 1

Isospectral pair	x^0	x^1	x^2	x^3	x^4	x^5	x^6	x^7	x^8	x^9	x^{10}	x^{11}	x^{12}
T_1 T_2	0	11	−188	1051	−2838	4295	−3916	2223	−788	169	−20	1	
T_3 T_4	0	11	−182	1028	−2804	4271	−3908	2222	−788	169	−20	1	
T_5 T_6	0	11	−160	843	−2264	3525	−3368	2014	−748	166	−20	1	
T_7 T_8	0	−12	232	−1510	4846	−8932	10193	−7472	3561	−1092	207	−22	1
T_9 T_{10}	0	−12	207	−1300	4159	−7784	9114	−6884	3378	−1062	205	−22	1
T_{11} T_{12}	0	−12	207	−1330	4322	−8132	9495	−7116	3457	−1076	206	−22	1

As is apparent from Table 6, the smallest pair of non-isomorphic pair of alkane molecular graphs with identical Laplacian polynomials has 11 vertices. This finding indicates, when compared with the degeneracy of the characteristic polynomial, that the Laplacian matrix, as a modified adjacency matrix, is able to generate less degenerate graph invariants.

The question of whether by a modification of the adjacency matrix (in particular by adding a constant, or variable quantity, along the principal diagonal) one can arrive at a complete graph-invariant remains an open one.

CONCLUSIONS

The Laplacian polynomial of molecular graphs representing saturated acyclic and cyclic alkanes was investigated. The expansion of the Laplacian polynomial of an acyclic molecular graph from a homologous series of compounds was expressed in terms of the Laplacian polynomials of the precedents terms in the series, enabling the rapid computation of the polynomial for large graphs.

Some expsessions were derived for the Laplacian polynomial of molecular graphs representing 2-methyl, 3-methyl, and 2,2-dimethylalkanes in terms of the Laplacian polynomials of linear graphs with n vertices, denoted by Li_n. Mathematically the two forms of the Laplacian polynomial, one expressed in powers of x and the other expressed in terms of Li_n polynomials are equivalent, but the later forms show more visibly the structural similarities in a series of homologous molecular graphs.

The existence of non-isomorphic graphs with identical Laplacian polynomial was investigated for 4-trees, representing alkanes, up to 12 vertices. Six pairs of Laplacian isospectral non-isomorphic alkane molecular graphs were found, the smallest pair having 11 vertices.

The advantage of using the Laplacian polynomial for the quantitatively characterization of the molecular structure lies in its conceptual simplicity and in its easy computation using available algorithms for the computation of the characteristic polynomial.

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