CHEMICAL GRAPH POLYNOMIALS. PART 3\textsuperscript{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\textsuperscript{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: \( ^{2-4} \)

\[
Ch(G, x) = \det (xI - A)
\]

where \( I \) is the \( N \times N \) 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 \( \text{deg}(i) \) of a vertex \( i \in V(G) \) is the number of edges incident to \( i \). Denote by \( \text{DEG}(G) \) the diagonal matrix with its \( ii \)-entry equal to \( \text{deg}(i) \). The matrix

\[
L(G) = \text{DEG}(G) - A(G)
\]

is called the Laplacian matrix.\(^5\) The elements of the Laplacian matrix are

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

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.

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

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\textsuperscript{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 \( \lambda_2 \), the second smallest Laplacian eigenvalue.

**THE LAPLACIAN POLYNOMIAL**

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

\[
\text{La}(G, x) = \det(xI - L)
\]  

(1)

where \( I \) is the \( N \times N \) unit matrix.

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

\[
\text{La}(T) = x^7 - 12x^6 + 54x^5 - 114x^4 + 115x^3 - 50x^2 + 7x
\]

Some expressions were derived for the Laplacian polynomial of molecular graphs representing polymers.\textsuperscript{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.\textsuperscript{17–20}

Using the recurrence relationships devised for the characteristic polynomial of vertex-weighted molecular graphs,\textsuperscript{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:

\[
\begin{array}{c}
\bigcirc \rightarrow N-2 \rightarrow N-1 \rightarrow N \\
G_N \\
\end{array}
\]

\[
\text{La}(G_N) = (x - 2) \text{La}(G_{N-1}) - \text{La}(G_{N-2})
\]

The Laplacian polynomials of linear molecular graphs representing normal alkanes with up to 12 vertices are presented in Table 1. We will denote by \( \text{Li}_n = \text{Li}_n(x) \) 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 \( 2\text{-Me-C}_m \), where \( m \) takes values from 3 to 11.
Table 1

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

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Table 2

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

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The theoretic polynomial of a molecular graph is usually expressed as a function of x. An alternative representation of the characteristic polynomial was introduced, 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 Liₐ polynomials to express the Laplacian polynomials of families of structurally related graphs in terms of Liₐ.

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

\[
x = \text{Li}_1
\]

\[
x^2 = \text{Li}_2 + 2 \text{Li}_1
\]
\[ x^3 = \text{Li}_3 + 4 \text{Li}_2 + 5 \text{Li}_1 \]
\[ x^4 = \text{Li}_4 + 6 \text{Li}_3 + 14 \text{Li}_2 + 14 \text{Li}_1 \]
\[ x^5 = \text{Li}_5 + 8 \text{Li}_4 + 27 \text{Li}_3 + 48 \text{Li}_2 + 42 \text{Li}_1 \]

From the Laplacian polynomials of 2-Me-C\text{m}, presented in Table 2, we obtain the following expressions in terms of \( \text{Li}_n \):

\[
\text{La}(2\text{-Me-C}_3) = \text{Li}_4 - \text{Li}_2 - 2 \text{Li}_1 - \text{Li}_0
\]
\[
\text{La}(2\text{-Me-C}_4) = \text{Li}_5 - \text{Li}_3 - 2 \text{Li}_2 - \text{Li}_1
\]
\[
\text{La}(2\text{-Me-C}_5) = \text{Li}_6 - \text{Li}_4 - 2 \text{Li}_3 - \text{Li}_2
\]
\[
\text{La}(2\text{-Me-C}_6) = \text{Li}_7 - \text{Li}_5 - 2 \text{Li}_4 - \text{Li}_3
\]
\[
\text{La}(2\text{-Me-C}_7) = \text{Li}_8 - \text{Li}_6 - 2 \text{Li}_5 - \text{Li}_4
\]

From the above expressions we readily obtain the general formula

\[ \text{La}(2\text{-Me-C}_{\text{N}-1}) = \text{Li}_N - \text{Li}_{\text{N}-2} - 2 \text{Li}_{\text{N}-3} - \text{Li}_{\text{N}-4} \]

As is evident from the above expressions, the equivalent formulas of the Laplacian polynomials in terms of \( \text{Li}_n \) 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\text{m}, where \( m \) takes values between, 5 and 11.

**Table 3**

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Using the same procedure to translate the Laplacian polynomial in terms of \( \text{Li}_n \), we have obtained the following expressions for the 3-Me-C\text{m} molecular graphs:

\[
\text{La}(3\text{-Me-C}_5) = \text{Li}_6 - \text{Li}_4 - 2 \text{Li}_3 - 2 \text{Li}_2 - 2 \text{Li}_1 - \text{Li}_0
\]
\[
\text{La}(3\text{-Me-C}_6) = \text{Li}_7 - \text{Li}_5 - 2 \text{Li}_4 - 2 \text{Li}_3 - 2 \text{Li}_2 - \text{Li}_1
\]
\[ \text{La}(3\text{-Me-C}_7) = \text{Li}_8 - \text{Li}_6 - 2 \text{Li}_5 - 2 \text{Li}_4 - 2 \text{Li}_3 - \text{Li}_2 \]
\[ \text{La}(3\text{-Me-C}_8) = \text{Li}_9 - \text{Li}_7 - 2 \text{Li}_6 - 2 \text{Li}_5 - 2 \text{Li}_4 - \text{Li}_3 \]
\[ \text{La}(3\text{-Me-C}_9) = \text{Li}_{10} - \text{Li}_8 - 2 \text{Li}_7 - 2 \text{Li}_6 - 2 \text{Li}_5 - \text{Li}_4 \]

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

\[ \text{La}(3\text{-Me-C}_{N-1}) = \text{Li}_N - \text{Li}_{N-2} - 2 \text{Li}_{N-3} - 2 \text{Li}_{N-4} - 2 \text{Li}_{N-5} - \text{Li}_{N-6} \]

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-\text{Me}_2\text{-C}_m, \text{ where } m \text{ takes values between 3 and 10.} \]

**Table 4**

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<td>3587</td>
<td>-1094</td>
<td>207</td>
<td>-22</td>
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</tr>
</tbody>
</table>

For this more branched molecular graphs, the expressions obtained using \( \text{Li}_n \) contain more terms:

\[ \text{La}(2,2\text{-Me}_2\text{-C}_3) = \text{Li}_5 - 3 \text{Li}_3 - 8 \text{Li}_2 - 7 \text{Li}_1 \]
\[ \text{La}(2,2\text{-Me}_2\text{-C}_4) = \text{Li}_6 - 3 \text{Li}_4 - 8 \text{Li}_3 - 9 \text{Li}_2 - 6 \text{Li}_1 \]
\[ \text{La}(2,2\text{-Me}_2\text{-C}_5) = \text{Li}_7 - 3 \text{Li}_5 - 8 \text{Li}_4 - 9 \text{Li}_3 - 6 \text{Li}_2 - 2 \text{Li}_1 \]
\[ \text{La}(2,2\text{-Me}_2\text{-C}_6) = \text{Li}_8 - 3 \text{Li}_6 - 8 \text{Li}_5 - 9 \text{Li}_4 - 6 \text{Li}_3 - 2 \text{Li}_2 \]
\[ \text{La}(2,2\text{-Me}_2\text{-C}_7) = \text{Li}_9 - 3 \text{Li}_7 - 8 \text{Li}_6 - 9 \text{Li}_5 - 6 \text{Li}_4 - 2 \text{Li}_3 \]
\[ \text{La}(2,2\text{-Me}_2\text{-C}_8) = \text{Li}_{10} - 3 \text{Li}_8 - 8 \text{Li}_7 - 9 \text{Li}_6 - 6 \text{Li}_5 - 2 \text{Li}_4 \]
\[ \text{La}(2,2\text{-Me}_2\text{-C}_9) = \text{Li}_{11} - 3 \text{Li}_9 - 8 \text{Li}_8 - 9 \text{Li}_7 - 6 \text{Li}_6 - 2 \text{Li}_5 \]

The general expression has the following form:

\[ \text{La}(2,2\text{-Me-C}_{N-2}) = \text{Li}_N - 3 \text{Li}_{N-2} - 8 \text{Li}_{N-3} - 9 \text{Li}_{N-4} - 6 \text{Li}_{N-5} - 2 \text{Li}_{N-6} \]
When the Laplacian polynomial is expressed in terms of $L_i^n$, 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 $L_i^n$ 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

<table>
<thead>
<tr>
<th>$N$</th>
<th>$x^0$</th>
<th>$x^1$</th>
<th>$x^2$</th>
<th>$x^3$</th>
<th>$x^4$</th>
<th>$x^5$</th>
<th>$x^6$</th>
<th>$x^7$</th>
<th>$x^8$</th>
<th>$x^9$</th>
<th>$x^{10}$</th>
<th>$x^{11}$</th>
<th>$x^{12}$</th>
</tr>
</thead>
<tbody>
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<td>3</td>
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<td>1</td>
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<td></td>
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<td>26</td>
<td>-8</td>
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<td></td>
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<tr>
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<td>-50</td>
<td>35</td>
<td>-10</td>
<td>1</td>
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<td></td>
</tr>
<tr>
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<td>0</td>
<td>-36</td>
<td>105</td>
<td>-112</td>
<td>54</td>
<td>-12</td>
<td>1</td>
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<td>-1782</td>
<td>1287</td>
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<td>4719</td>
<td>-9438</td>
<td>11011</td>
<td>-8008</td>
<td>3740</td>
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<td>209</td>
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<tr>
<td>12</td>
<td>0</td>
<td>-144</td>
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<td>19305</td>
<td>-27456</td>
<td>24752</td>
<td>-14688</td>
<td>5814</td>
<td>-1520</td>
<td>252</td>
<td>-24</td>
<td>1</td>
</tr>
</tbody>
</table>

For rings, no simple expression in terms of $L_i^n$ was obtained.

As is apparent from the above expressions in terms of $L_i^n$, 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. 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.

![Diagram of 4-trees](image)

**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

<table>
<thead>
<tr>
<th>Isospectral pair</th>
<th>$x^0$</th>
<th>$x^1$</th>
<th>$x^2$</th>
<th>$x^3$</th>
<th>$x^4$</th>
<th>$x^5$</th>
<th>$x^6$</th>
<th>$x^7$</th>
<th>$x^8$</th>
<th>$x^9$</th>
<th>$x^{10}$</th>
<th>$x^{11}$</th>
<th>$x^{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1, T_2$</td>
<td>0</td>
<td>11</td>
<td>-188</td>
<td>1051</td>
<td>-2383</td>
<td>4295</td>
<td>-3916</td>
<td>2223</td>
<td>-788</td>
<td>169</td>
<td>-20</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$T_3, T_4$</td>
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<td>-2804</td>
<td>4271</td>
<td>-3908</td>
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<tr>
<td>$T_5, T_6$</td>
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<td>3525</td>
<td>-3368</td>
<td>2014</td>
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<td>1</td>
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</tr>
<tr>
<td>$T_7, T_8$</td>
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<td>-12</td>
<td>222</td>
<td>4846</td>
<td>-8932</td>
<td>10193</td>
<td>-7472</td>
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<td>$T_9, T_{10}$</td>
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<td>207</td>
<td>4159</td>
<td>-7784</td>
<td>9114</td>
<td>-6884</td>
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<tr>
<td>$T_{11}, T_{12}$</td>
<td>0</td>
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</tbody>
</table>

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 expressions were derived for the Laplacian polynomial of molecular graphs representing 2-methyl, 3-methyl, and 2,2-dimethyl alkanes in terms of the Laplacian polynomials of linear graphs with n vertices, denoted by $L_n$. Mathematically the two forms of the Laplacian polynomial, one expressed in powers of $x$ and the other expressed in terms of $L_n$ 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.

REFERENCES