GEOMETRY-DEPENDENT CHARACTERISTIC POLYNOMIALS OF MOLECULAR STRUCTURES

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A new approach is presented to characterize the topological and geometric information contained in chemical structures. Characteristic polynomials which depend on the geometries of chemical structures are proposed. It is shown that elegant computational procedures could provide geometry-dependent characteristic polynomials. The newly developed polynomials differentiate isospectral structural graphs and can be extended to encompass stereochemistry.

1. Introduction

Characteristic polynomials of chemical graphs have received considerable attention in recent years [1–19] (the references in ref. [3] give a good review of the characteristic polynomials) since they have many chemical applications. In summary, characteristic polynomials are useful in chemical kinetics, dynamics of oscillatory reactions [12,13], NMR spin eigenvalue problems [19,20], isomerization reactions, reaction networks, fluid dynamics [21] and in characterization of molecules themselves. A possible solution to the graph isomorphism problem as well as computer differentiation of molecules could be obtained through the characteristic polynomials. However, it has been shown that characteristic polynomials are not unique structural invariants since there could be two non-isomorphic graphs with the same characteristic polynomial [22,23]. This is one of the limitations in using characteristic polynomials as structural invariants or in discriminating the topological information in a molecule.

Topological indices have been proposed based on characteristic and related polynomials [24]. They too suffer from the same criticism that characteristic polynomials are not unique and furthermore, the connectivity matrix of the graph does not take into account the geometric information in a molecule. This is because the ordinary characteristic polynomials proposed up to now are based purely on the connectivity of the vertices and do not take into account the geometric information in the molecules which they represent. Yet many physical properties are based more on the overall geometries of molecules. Randić [25,26] has used intramolecular distances to generate topographic or geometric matrices to discriminate some stereoisomers and to characterize three-dimensional structures.

The objective of this study is to propose a new class of structural invariants which we call geometry-dependent characteristic polynomials. We show that these polynomials could be easily obtained through computational techniques proposed before. It is exemplified that the geometry-dependent characteristic polynomials can discriminate isospectral graphs, provide a solution to the structural isomorphism problem and finally can be extended to include the stereochemical information in a molecule. Section 2 describes geometry-dependent characteristic polynomials and a simple computational technique to obtain these. Section 3 comprises results and discussion.

2. Geometry-dependent characteristic polynomials

The ordinary characteristic polynomial of a graph is defined as the secular determinant

\[ \det(A - \lambda I) = 0 \]

Camille and Henry Dreyfus Teacher–Scholar.
where $A$ is the adjacency matrix (connectivity matrix) of a graph. It can be easily shown that the above polynomial is invariant for labelling of vertices of the graph and hence it was thought that characteristic polynomials characterize the connectivity information in the structure without any dependence on labelling. However, it was shown that two different structures could have the same characteristic polynomials, thereby eliminating the possibility of using characteristic polynomials as unique structural invariants.

Consider a two-dimensional geometric embedding of a molecular graph. If it is a molecular graph then we use the natural geometry information contained in the molecule, namely bond lengths and bond angles. For a molecular chemical graph since bond angles are often available we shall use this information to embed the graph. Let $D$ be a matrix of shortest geometrical distances of vertices in the graph. That is, $D$ is defined as

$$D_{ij} = \begin{cases} 0, & \text{if } i=j, \\ d_{ij}, & \text{if } i \neq j, \end{cases}$$

where $d_{ij}$ is the shortest Cartesian distance between the vertices $i$ and $j$ in arbitrary units. Then the geometry-dependent characteristic polynomial is defined as

$$|D - \lambda I|.$$

Consider the carbon skeleton in butadine. The $D$ matrix can be easily seen to be given as follows if the distance between the adjacent carbon atoms is defined as unity,

$$D = \begin{bmatrix} 0 & 1 & \sqrt{3} & 2 \\ 1 & 0 & 1 & \sqrt{3} \\ \sqrt{3} & 1 & 0 & 1 \\ 2 & \sqrt{3} & 1 & 0 \end{bmatrix}.$$

The eigenvalues of the $D$ matrix are given by $-2 - \sqrt{2}, -1.162278, -0.5857864$ and $5.162278$. The ordinary characteristic polynomial of butadiene is

$$\lambda^4 - 3\lambda^2 + 1.$$

If the distance between C-C atoms is taken as unity (where the unit value is approximately 1.40 Å) the $D$ matrix for the benzene graph is given by

$$D = \begin{bmatrix} 0 & 1 & \sqrt{3} & 2 & \sqrt{3} & 1 \\ 1 & 0 & 1 & \sqrt{3} & 2 & \sqrt{3} \\ \sqrt{3} & 1 & 0 & 1 & \sqrt{3} \\ 2 & \sqrt{3} & 1 & 0 & 1 \\ \sqrt{3} & 2 & \sqrt{3} & 1 & 0 \\ 1 & \sqrt{3} & 2 & \sqrt{3} & 1 & 0 \end{bmatrix}.$$

The characteristic polynomial of the above matrix is

$$\lambda^6 - 36\lambda^4 - 124.71\lambda^3 - 156\lambda^2 - 83.14\lambda - 16,$$

where we show only the first and second decimal points for convenience. The eigenvalues of the $D$ matrix of benzene are $-(1+\sqrt{3}), -(1+\sqrt{3}), -\sqrt{3}+1, -\sqrt{3}+1, -4+2\sqrt{3}$ and $2\sqrt{3}+4$. Note that the $D$ matrix is superior to the adjacency matrix of a graph in that it not only contains the simple neighborhood information (unit matrix elements imply that the corresponding vertices are neighbors) but also the geometry information.

The $D$ matrix may not appear to be as straightforward to generate as the $A$ matrix. However, once the coordinates of various centers in the defined units are generated it is trivial to generate this matrix. Generation of coordinates of various centers from the geometry information is quite routine in molecular quantum chemical programs. We have interfaced such codes with codes developed by us to generate the $D$ matrix from coordinates.

The $D$ matrix can also be redefined in terms of reciprocals of distances rather than the actual distances between two points. An advantage of the reciprocal distance matrix approach is that if the distances were to represent interactions then the matrix elements go to zero as the distances approach infinity. Hence for such applications where distances represent interactions, the reciprocal distance matrix would be more suitable.

The characteristic polynomial of the $D$ matrix is
obtained using a numerical procedure called Frame's method by the author [3] in an earlier investigation. The codes developed before [4] were extended and interfaced with the $D$-matrix generator. In addition a scaling procedure was also implemented for larger graphs since geometry-dependent characteristic polynomials grow more rapidly compared to ordinary characteristic polynomials. The scaling procedure simply scales the $D$ matrix by an input factor (usually an integer such as 2, 3, 4, 6, etc.). The effect of such a scaling procedure is simply to divide the eigenvalues by the same factor and the coefficient of a term $\lambda^k$ is reduced by the polynomial $s^{n-k}$, if $s$ is the scaling factor and $n$ is the number of atoms. For many practical applications since one would actually use the ratios of the coefficients of the characteristic polynomial the scaling procedure is quite advantageous.

The only disadvantage in applying the procedure described here to ordinary graphs (which are not molecular graphs) is that the $D$ matrix depends only on the geometry and not on the connectivity of a graph. For example, the $D$ matrix of $C_4$ and $K_4$ graphs will be the same if they are both embedded in a square geometry. Consequently, the most natural use of the polynomials proposed here are for geometrical characterization of molecular structures that are invariant to labellings and yet most probably unique for a given geometry. If stereochemistry is also taken into consideration through three-dimensional embeddings then the geometry-dependent polynomials can differentiate stereoisomers except optical isomers.

3. Results and discussion

The geometry dependent characteristic polynomials of a few $L_n$ graphs, where $L_n$ denotes a linear chain containing $n$ vertices, are shown in table 1. For example, $L_4$ could represent butadiene while $L_6$ could represent octatetraene. Table 2 shows the geometry-dependent characteristic polynomials of linear polyacenes simplest of which are benzene and naphthalene. As seen from tables 1 and 2, the coefficients of geometry-dependent polynomials increase more rapidly compared to the ordinary characteristic polynomials of the adjacency matrices. This is expected since the distance between various atoms increases as the number of atoms increases. To circumvent this rapid growth we introduced a scaling technique described in section 2. For example, if one scales the $D$ matrix of butadiene by a factor of 2 the polynomial becomes

$$\lambda^4 - 5\lambda^2 - 4\lambda + 1.$$ 

One powerful application of the geometry-dependent characteristic polynomials is to discriminate isospectral graphs [22]. A simple embedding of two isospectral graphs is shown in fig. 1. Note that we use this embedding for convenience although if these graphs represented molecules, the coordinates of the branch atoms would depend on bond angles. The ge-

<table>
<thead>
<tr>
<th>$n$</th>
<th>Polynomial</th>
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<tbody>
<tr>
<td>4</td>
<td>$\lambda^4 - 20\lambda^2 - 32\lambda - 12$</td>
</tr>
<tr>
<td>6</td>
<td>$\lambda^6 - 105\lambda^4 - 448\lambda^2 - 384\lambda - 80$</td>
</tr>
<tr>
<td>8</td>
<td>$\lambda^8 - 336\lambda^6 - 2688\lambda^4 - 7920\lambda^2 - 11264\lambda - 3072\lambda - 448$</td>
</tr>
<tr>
<td>10</td>
<td>$\lambda^{10} - 825\lambda^8 - 10560\lambda^6 - 51480\lambda^4 - 128128\lambda^2 - 182000\lambda^4 - 182000\lambda^6 - 182000\lambda^8 - 182000\lambda^{10}$</td>
</tr>
<tr>
<td>12</td>
<td>$\lambda^{12} - 1716\lambda^{10} - 32032\lambda^8 - 231660\lambda^6 - 787392\lambda^4 - 1980160\lambda^2 - 2340960\lambda^6 - 182000\lambda^8 - 2340960\lambda^{10} - 2340960\lambda^{12} - 182000\lambda^{14} - 182000\lambda^{16}$</td>
</tr>
<tr>
<td>14</td>
<td>$\lambda^{14} - 3185\lambda^{12} - 81536\lambda^{10} - 81536\lambda^8 - 1410864\lambda^6 - 2856288\lambda^4 - 6306528\lambda^2 - 1318912\lambda^6 - 1318912\lambda^{10} - 1318912\lambda^{12} - 1318912\lambda^{14} - 1318912\lambda^{16}$</td>
</tr>
<tr>
<td>16</td>
<td>$\lambda^{16} - 5540\lambda^{14} - 182784\lambda^{12} - 2418624\lambda^{10} - 7119104\lambda^8 - 75246080\lambda^6 - 43932000\lambda^4 - 630060192\lambda^2 - 652861440\lambda^6 - 489988160\lambda^{10} - 263577600\lambda^{14} - 99090432\lambda^{16} - 24707072\lambda^{18} - 36700161\lambda^{20} - 245760$</td>
</tr>
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Table 2
Geometry-dependent characteristic polynomials of linear polyacenes containing n rings

<table>
<thead>
<tr>
<th>n</th>
<th>Polynomial</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>( \lambda^8 - 36\lambda^6 - 124.7\lambda^4 - 156\lambda^2 - 83.14\lambda - 16 )</td>
</tr>
<tr>
<td>2</td>
<td>( \lambda^{10} - 205\lambda^8 - 1806.6\lambda^6 - 6865.6\lambda^4 - 14225.2\lambda^2 - 17543.97\lambda^0 - 13232.72 )</td>
</tr>
<tr>
<td>3</td>
<td>( \lambda^{14} - 825.65\lambda^{12} - 14396.32\lambda^{10} - 112350.97\lambda^8 - 50892.81\lambda^6 - 1440619.12\lambda^4 - 277831.51\lambda^2 - 5177.72 )</td>
</tr>
<tr>
<td>4</td>
<td>( \lambda^{18} - 1809\lambda^{16} - 43878.41\lambda^{14} - 481912.51\lambda^{12} - 3117353.12\lambda^{10} - 13278763.62\lambda^8 - 6058046.72\lambda^6 - 161209039.6\lambda^4 - 1397467926.2\lambda^2 - 66509421970.4 )</td>
</tr>
</tbody>
</table>

Fig. 1. Two isospectral graphs. Note that their geometry-dependent characteristic polynomials are different although their ordinary characteristic polynomials are identical.

The geometry-dependent characteristic polynomial of the first graph in fig. 1 is

\[
\lambda^9 - 198\lambda^7 - 1615.9\lambda^5 - 5548.2\lambda^3 - 10021.3\lambda^1 - 10253.9\lambda^1 - 5973.99\lambda^1 - 1846.4\lambda - 234.84 .
\]

The geometry-dependent polynomial of the second graph is given by

\[
\lambda^9 - 166\lambda^7 - 1259.48\lambda^5 - 4052.05\lambda^3 - 6945.28\lambda^1 - 6819.52\lambda^1 - 3845.69\lambda^1 - 1157.91\lambda - 144.16 .
\]

Note that the geometry-dependent characteristic polynomials of the two graphs in fig. 1 are substantially different although their ordinary characteristic polynomials are the same, given by

\[
\lambda^9 - 9\lambda^7 + 25\lambda^5 - 25\lambda^3 + 8\lambda .
\]

Although a particular arbitrary geometry was assumed for the two isospectral graphs, a practical method would be to use the actual coordinates of the various centers if these graphs represented molecules. It is interesting to note that topologically it is possible to deform isospectral graphs such that various centers may have the same coordinates thus leading to the same geometry-dependent characteristic polynomials. However, such a deformation may produce an unrealistic molecular structure. Consequently, the question of differentiation of realistic molecular structures through geometry-dependent characteristic polynomials is resolvable for many cases. For chemical applications it would be meaningful to embed the two isospectral graphs in fig. 1 on a graphite lattice.

The newly developed polynomials can be easily obtained for even complicated and realistic graphs. The geometry-dependent characteristic polynomial of the graph in fig. 2 with a scaling factor of 3 is shown in table 3. (This means the weight of the nearest-neighbor is 1/3.)

An interesting observation we make is that there is only one positive eigenvalue for the geometric matrix of a molecular structure.
Table 3
Geometry-dependent characteristic polynomial and eigenvalues of the structure in fig. 2 with a scaling factor of 3

\[ \lambda^{24} - 3042^{22} - 3668.06 \lambda^{21} - 20395.29 \lambda^{20} - 68204.78 \lambda^{19} \\
- 153903.13 \lambda^{18} - 250187.62 \lambda^{17} - 305612.26 \lambda^{16} - 288750.13 \lambda^{15} \\
- 215393.11 \lambda^{14} - 128724.89 \lambda^{13} - 62268.23 \lambda^{12} - 24544.51 \lambda^{11} \\
- 7914.71 \lambda^{10} - 215393.11 \lambda^{9} - 128724.89 \lambda^{8} - 62268.23 \lambda^{7} - 24544.51 \lambda^{6} \\
- 7914.71 \lambda^{5} - 215393.11 \lambda^{4} - 128724.89 \lambda^{3} - 62268.23 \lambda^{2} - 24544.51 \lambda^{1} \\
- 7914.71 \lambda^{0} - 215393.11 \lambda^{1} - 128724.89 \lambda^{2} - 62268.23 \lambda^{3} - 24544.51 \lambda^{4} \\
- 7914.71 \lambda^{5} - 215393.11 \lambda^{6} - 128724.89 \lambda^{7} - 62268.23 \lambda^{8} - 24544.51 \lambda^{9} \\
- 7914.71 \lambda^{10} - 215393.11 \lambda^{11} - 128724.89 \lambda^{12} - 62268.23 \lambda^{13} - 24544.51 \lambda^{14} \\
- 7914.71 \lambda^{15} - 215393.11 \lambda^{16} - 128724.89 \lambda^{17} - 62268.23 \lambda^{18} - 24544.51 \lambda^{19} \\
- 7914.71 \lambda^{20} - 215393.11 \lambda^{21} - 128724.89 \lambda^{22} - 62268.23 \lambda^{23} - 24544.51 \lambda^{24} \]

The eigenvalues of the scaled $D$ matrix of coronene (fig. 2) are

-6.6372, -6.6372, -1.5648, -1.2665, -1.2665, \\
-0.6034, -0.5251, -0.4783, -0.4783, -0.3593, \\
-0.3593, -0.2448, -0.2448, -0.2296, -0.2296, \\
-0.2265, -0.2147, -0.1984, -0.1907, -0.1907, \\
-0.1907, -0.1679, -0.1542, 22.6355

The newly developed polynomials will find many applications. First, these polynomials are more structure-dependent than ordinary characteristic polynomials. Thus we believe that they should be useful in computer discrimination of different structures and could provide computer solutions to the graph isomorphism problem provided the graph in question is embedded in a lattice in accordance to a prescribed procedure. The geometry-dependent characteristic polynomials can be easily extended to include the stereochemistry in molecules. For example, the geometry-dependent characteristic polynomials of cis and trans isomers are different.

Although the geometry-dependent characteristic polynomials of optical stereoisomers (dR pairs) would be the same, introduction of chirality through the chirality polynomials discussed by King [27,28] could possibly provide geometry and stereoisomer dependent polynomials. Finally, most of the topological indices based on connectivity information alone suffer from the criticism that they are not geometry-dependent. For example, Hosoya’s z-index does not contain any geometry information. The same way Wiener index depends only on the connectivity and walks. The coefficients of geometry-dependent polynomials could be used to derive new indices which contain geometric information of a molecule including its stereochemistry thereby facilitating discrimination of stereoisomers such as geometrical isomers and some stereo and conformational isomers.

References