The Characteristic Polynomial Does Not Uniquely Determine the Topology of a Molecule *

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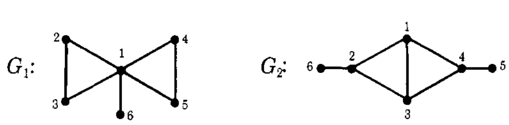
The necessity of a computer-oriented information storage system for chemical compounds has led to approaches based either on coding conventions or on the topology of the molecule. The latter, more promising, approach assimilates a covalently-bonded molecule with a graph whose vertices (points) are the atoms and whose edges (lines) are the covalent bonds. The structure or topology of the molecule is then uniquely encoded in the adjacency matrix of its graph.[5] By definition, the *adjacency matrix* $A = [a_{ij}]$ of a graph G with p points $v_1, v_2, \ldots, v_p$ is the binary matrix in which $a_{ij} = 1$ when v_i and v_j are adjacent (bonded in chemical terminology) and $a_{ij} = 0$ otherwise, including the main diagonal elements.

A different but related matrix which also encodes uniquely the structure of the molecule is the atom connectivity matrix.[8-10] This matrix differs from the adjacency matrix in two respects: On the main diagonal, the chemical elements are displayed instead of zeros which contain no information; and off the main diagonal, bond orders 1,2,3 or fractional ones are displayed, whenever the corresponding atoms have a single, double, triple or fractional chemical bond between them.

Spialter conjectured in 1963–1964[8-10] that the characteristic polynomials obtained from the adjacency or atom connectivity matrices were uniquely related to the structure of a molecule. He also devised ways of determining the coefficients of the characteristic polynomial without expanding the determinant of the matrix $A - xI$, where A is the adjacency matrix, I is the identity matrix, and x is a variable. This result is paralleled by independent work of Collatz and Sinogowitz[1] and Sachs.[7]

One of us[4] had in an opening footnote independently made the same erroneous conjecture. It was observed in the same paper that this conjecture is false because of the existence of two nonisomorphic graphs with the same eigenvalue spectrum. Detailed mathematical demonstrations of the smallest possible examples are provided in a recent paper.[6] There it is demonstrated that the smallest connected counter example to this ill-fated conjecture is given by the following pair of nonisomorphic connected graphs with the same characteristic polynomial:



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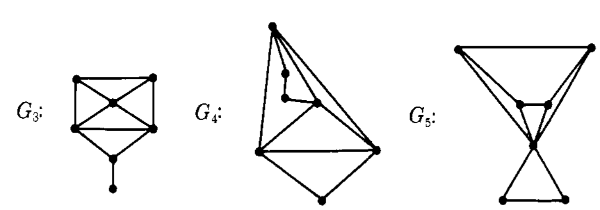
Obviously G_1 and G_2 are not isomorphic since G_1 has just one endpoint (the monovalent vertex numbered 6) while G_2 has two such points, 5 and 6.

The adjacency matrices A_1 and A_2 of these two graphs G_1 and G_2 are:

$$A_1 = \begin{array}{c} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{array} \begin{array}{c} \begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 & 6 \end{array} \\ \begin{bmatrix} 0 & 1 & 1 & 1 & 1 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \end{array} \qquad A_2 = \begin{array}{c} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{array} \begin{array}{c} \begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 & 6 \end{array} \\ \begin{bmatrix} 0 & 1 & 1 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 1 \\ 1 & 1 & 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix} \end{array}$$

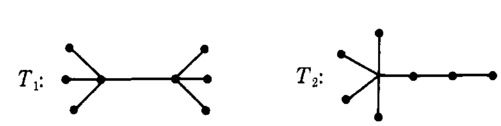
Let $\phi(A)$ be the characteristic polynomial of a square matrix A. Then for these two matrices we have $\phi(A_1) = \phi(A_2) = x^6 - 7x^4 - 4x^3 - 7x^2 + 4x - 1$.

The smallest triple of cospectral[6] nonisomorphic graphs (with the same characteristic polynomial) is presented below. The first two of these have no points with degrees (valencies) greater than 4, and hence might be taken to represent organic compounds if steric strain were ignored.



The common characteristic polynomial of the above graphs is $\phi(A_3) = \phi(A_4) = \phi(A_5) = x^7 - 11x^5 - 10x^4 - 16x^3 + 16x^2$.

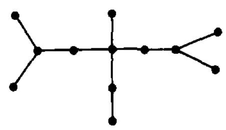
Collatz and Sinogowitz[1] had already provided in 1957 the earliest recorded discovery of a pair T_1 and T_2 of cospectral nonisomorphic graphs. They also proved by exhaustion that these are the smallest possible such *trees* (connected graphs with no cycles).



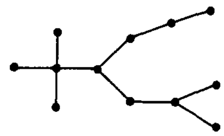
Their common characteristic polynomial is $\phi(T_1) = \phi(T_2) = x^8 - 7x^6 + 9x^4$.

Another pair of cospectral trees which have no points of degree (valency) higher than 4 and might therefore represent hydrocarbons, is provided[6] by T_3 and T_4.

T_3:



T_4:



Here $\phi(T_3) = \phi(T_4) = x^{12} - 11x^{10} + 40x^8 - 55x^6 + 21x^4$.

Since these two trees also have the same partition—i.e., they have the same number of points with the same degrees—they correspond to isomeric structures even if some of the points represent other atoms than carbon. It has just been shown that other such *cospectral isomeric trees* with $8 < p < 12$ exist. Fisher[2] published in 1966 the first example of two cospectral isomeric graphs, having 15 points and 27 lines with no end points or cut points.

Up till now no simple reduced form of the adjacency matrix can characterize the topology of a molecule—i.e., can characterize a graph up to isomorphism. Therefore, chemical documentation systems[3] or attempts to use matrices for encoding the structure of molecules[11] should be aware of the pitfalls provided by characteristic polynomials.

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