Spectra of Chemical Trees

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Abstract

A method is developed for obtaining the spectra of trees of NMR and chemical interests. The characteristic polynomials of branched trees can be obtained in terms of the characteristic polynomials of unbranched trees and branches by pruning the tree at the joints. The unbranched trees can also be broken down further till we obtain a tree containing just two vertices. This effectively reduces the order of the secular determinant of the tree we started with to determinants of orders at most equal to the number of vertices in the branch containing the largest number of vertices. An illustrative example of a NMR graph is given for which the $22 \times 22$ secular determinant is reduced to determinants of orders at most $4 \times 4$ in just the second step of the algorithm. The tree pruning algorithm can be applied even to trees with no symmetry elements and such a factoring can be achieved. Methods developed here can be elegantly used to find if two trees are cospectral and to construct cospectral trees.

1. Introduction

In recent years graph theory has been found to be extremely useful in chemical applications. These applications concern representation of dynamical processes in molecules, intermolecular interactions, enumerations of structures, topological correlation of chemical properties that depend on the structure of molecules, etc. For example, thermodynamic properties of molecules can be correlated to their topologies [1]. Ever since the middle of this century chemists have recognized the intimate relation between the topology of molecules and their energy, etc. An evidence of this recognition is the valence bond method and the associated combinatorial and graph theoretical techniques [2–7]. It is well known that molecular topology can be characterized by the associated graphs but for automorphisms. However, these automorphisms can be recognized as shown by Randić [8].

The relation between the topological matrices used in Hückel theory and the adjacency matrices of the associated molecular graphs is well known [9–30]. Many quantum mechanical results can be derived or rederived using the spectral properties of the associated graphs.

The characteristic polynomials and spectra of chemical graphs have significant applications in other areas of chemical physics such as chemical kinetics [31, 32], dynamics of oscillating chemical reactions [33], solutions of Navier–Stokes equations [34], and related applications in statistical mechanics.

The spectra of graphs are important in obtaining topological indices such as Hosoya index [18, 19] which are potentially useful in the correlation of topology to thermodynamic properties of molecules.
One of the achievements of graph theory is the recognition of isospectral graphs. Isospectral graphs are graphs which can be topologically nonequivalent and yet have identical spectra. Thus isospectral molecules will have similar thermodynamic properties.

The present author [35] recently introduced the concept of nmr graphs which are diagrammatic representations of nuclear spin–spin coupling interactions. Consequently, the study of the spectra of graphs will have special significance in obtaining the spectra of nmr spin Hamiltonians within the spirit of equal coupling limit. The methods developed here can also be extended to nonequal coupling limits which makes these methods especially important in magnetic resonance. This aspect will be considered in a future publication.

The methods of simplifying spectra of graphs such as the Sach theorem [30] become quite cumbersome for graphs containing large number of vertices. Even for a graph containing 12 vertices the Sach theorem becomes quite difficult. It is possible to factor the characteristic polynomials of graphs exploiting the symmetry elements present in the graphs. Such symmetry factorings of the characteristic polynomials of graphs have been considered by King [26], D'Amata [25], and Davidson [27]. These methods naturally depend on the symmetry elements and are therefore not applicable for graphs with no symmetry elements. In this paper we develop techniques to factor the characteristic polynomials of trees even if they have no symmetry element.

The objective of this investigation is to develop elegant graph–theoretical factoring techniques for evaluating the characteristic polynomials of trees by a tree-pruning technique outlined in this paper. Tree-pruning techniques have been used by Balaban [36] and the present author [37, 38] in other applications. The motivation for the method developed in this paper takes its origin in the papers of Godsil and McKay [39], Schwenk [40], and the present author [37]. The methods developed here can considerably simplify the evaluation of spectra of chemical trees and do not depend on symmetry of the trees. For example, a 22 x 22 secular determinant of nmr interest is shown to be reducible to determinants of orders at most equal to 4 x 4. The method developed here also leads to the construction of cospectral trees. In Sec. 2 we outline these methods and in Sec. 3 we give examples to show the use of the methods developed in this paper for characterizing cospectral trees. In the Appendix an algorithm is formulated based on the techniques developed here.

2. Spectra of Root–to–Root Products

A. Preliminaries

The adjacency matrix of a graph is defined as follows:

\[ A_{ij} = \begin{cases} 1 & \text{if the vertices } i \text{ and } j \text{ are connected,} \\ 0 & \text{otherwise.} \end{cases} \]  

The secular determinant of the adjacency matrix of a graph is known as the characteristic polynomial of the graph. The eigenvalues of the adjacency matrix
constitute the spectrum of the graph. Two graphs are said to be isospectral or cospectral if their spectra are identical. Two graphs can have identical spectra even if their adjacency matrices are not transformable into one another by any permutation of the vertices of these two graphs. If the characteristic polynomials of two graphs are identical then their spectra must be identical. Consequently, if the characteristic polynomials of two graphs are identical then they are cospectral.

Tree is a connected graph with no cycles. The vertices of a tree with degree (valence) more than 1 can be defined as the roots of the tree. Then a tree with degree (valence) more than 1 can be defined as the roots of the tree. Then a tree can be expressed as a product of a quotient tree $Q$ formed by these roots alone and the branch resulting from pruning the tree at these roots. For example, the tree $\Gamma$ in Figure 1 can be obtained by joining the black dots (roots) of $Q$ and a black dot of a copy of type $T$. Let $Y_i$ be the set of all vertices in $Q$ that have the same degree and are attached to a root of the copy of the same type $T_i$. Then the root-to-root product of $Q$ with $T_1, T_2, \ldots, T_i$ denoted as $Q \cdot (T_1, T_2, \ldots, T_i)$, is defined as the tree resulting by attaching a root in the set $Y_i$ and the root of a copy of type $T_i$. This product was introduced by the author in the context of isomer enumeration [37]. In Figure 2 we have another example of a root-to-root product. The rooted product defined by Godsil and McKay [39] is similar to root-to-root product. For example, the tree in Figure 1 can be considered as the rooted product of $Q$ with $T^{(1)}$ and $T^{(2)}$, where $T^{(1)}$ and $T^{(2)}$ are the copies of the same type $T$ shown in Figure 1. In general, rooted product of a graph $Q$ with a sequence of graphs $T^{(1)}, T^{(2)}, \ldots, T^{(n)}$, is obtained by identifying the roots of $Q$ with the roots of $T^{(1)}, T^{(2)}, \ldots, T^{(n)}$. 

Figure 1. Quotient tree $Q$ and type $T$ and their root-to-root product.

Figure 2. Branched tree on nine vertices expressed as a root-to-root product. The roots of $Q$ with the same symbol are attached to the root of a type which carries that symbol.
B. Spectra of Trees by Pruning the Trees

Any tree can be pruned at the branches successively till we obtain an unbranched tree. The characteristic polynomial of the tree we started with can be obtained in terms of the characteristic polynomials of branches and the unbranched tree as we show here.

We start with the method proposed by Godsil and McKay for the characteristic polynomials of rooted product of two graphs. Let \( H_i(x) \) be the characteristic polynomial of type \( T_i \). Let \( H'_i(x) \) denote the characteristic polynomial obtained by deleting the root of \( T_i \). Let \( q_{ij} \) be an element of the adjacency matrix of the quotient tree \( Q \). Let \( Y_i \) be the set of vertices in \( Q \) that are mapped to the same type \( T_i \). Equivalently, roots of \( T_i \) are joined to the root of a copy of the type \( T_i \) in obtaining the root-to-root product. Then define a new adjacency matrix \( A \) given as follows:

\[
A_{ij} = \begin{cases} 
H_k(x) & \text{if } i = j \text{ and } i \in Y_k, \\
-q_{ij}H_k(x) & \text{if } i \neq j \text{ and } i \in Y_k.
\end{cases}
\] (2.2)

This definition of matrix \( A \) is not identical to the definition of Godsil and McKay. However, this can be reduced to their definition. We have the following theorem:

Theorem 1 [Godsil and McKay]:

The characteristic polynomial of the root-to-root product \( Q \cdot (T_1, T_2, \ldots) \) is the determinant of the matrix \( A \) defined above. This theorem was proved by Godsil and McKay using a lemma of Schwenk stated below Lemma 1:

Lemma 1 (Schwenk):

Let \( G \) be a graph with a root \( r \), and let \( H \) be a graph with a root \( s \). Let \( G(x) \) and \( H(x) \) be the characteristic polynomials of \( G \) and \( H \), respectively. Let \( G'(x) \) and \( H'(x) \) be the characteristic polynomials of the graphs obtained by deleting the roots \( r \) and \( s \) of \( G \) and \( H \), respectively. Let \( G \cdot H \) be the graph obtained by identifying the roots \( r \) and \( s \). Then the characteristic polynomial of \( G \cdot H \), denoted by \( G \cdot H(x) \) is given as follows:

\[
G \cdot H(x) = G(x)H'(x) + G'(x)H(x) - xG'(x)H'(x). \quad (2.3)
\]

Proof of this lemma was given by Schwenk [40].

Let \( h_i \) be the characteristic polynomial of a type containing \( i \) vertices including the root. Then \( h_i \) can be seen to be equal to \( x^i - (i - 1)x^{i-2} \). Let \( h'_i \) be the characteristic polynomial of the tree obtained after deleting this root. \( h'_i \) can be seen to be \( x^{i-1} \).

Let us now illustrate Theorem 1 with the tree shown in Figure 1. In this case there is one type and one \( Y \) set. The adjacency matrices of \( Q \) and \( T \) are identical for this example and are

\[
((Q)) = ((T)) = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}.
\] (2.4)
Thus \( H(x) = h_2 \) and \( H'(x) = h_2' \). Matrix \( A \) is

\[
A = \begin{bmatrix}
    h_2 & -h_2' \\
    -h_2' & h_2
\end{bmatrix}.
\] (2.5)

By Theorem 1 the characteristic polynomial of the graph \( Q \cdot T \) is just the determinant of \( A \) which is

\[
h_2^2 - h_2'^2 = (x^2 - 1)^2 - x^2 = x^4 - 3x^2 + 1.
\] (2.6)

Incidentally, this is the characteristic polynomial of the topological matrix of butadiene. The secular determinant of butadiene which is of the order \( 4 \times 4 \) was reduced to a secular determinant of order \( 2 \times 2 \). This reduction has nothing to do with the symmetry of the molecule. It is purely graph theoretical. Thus, such a reduction is possible for molecules with no symmetry.

As a second illustrative example, consider the graph \( \Gamma \) in Figure 2. \( \Gamma \) is the root–to–root product \( Q \cdot (T_1, T_2, T_3) \) with \( Y_1 = \{1, 2\}, Y_2 = \{3\}, \) and \( Y_3 = \{4\} \). The secular determinant of order \( 9 \times 9 \) by an application of this theorem can be reduced considerably. The adjacency matrix of \( Q \) is

\[
((Q)) = \begin{bmatrix}
    0 & 0 & 0 & 1 \\
    0 & 0 & 0 & 1 \\
    0 & 0 & 0 & 1 \\
    1 & 1 & 1 & 0
\end{bmatrix}. \] (2.7)

Matrix \( A \) is

\[
((A)) = \begin{bmatrix}
    h_2 & 0 & 0 & -h_2' \\
    0 & h_2 & 0 & -h_2' \\
    0 & 0 & h_4 & -h_4' \\
    -h_1' & -h_1' & -h_1' & h_2
\end{bmatrix}.
\] (2.8)

Inserting the appropriate values of \( h_1, h_1, \) etc., in \( A \), and evaluating the secular determinant of \( A \), we obtain the characteristic polynomial of \( \Gamma \) as

\[
|((\Gamma(x)))| = x^9 - 8x^7 + 17x^5 - 10x^3.
\] (2.9)

In this case we reduced the \( 9 \times 9 \) determinant to determinants of orders atmost \( 4 \times 4 \). In many cases further reduction is possible if the quotient graph has more than one root as we show in Sect. 2.C.

### C. Iterative Algorithm for Evaluating the Characteristic Polynomials of Trees

The algorithm we outlined in Sec. 2.B can be iterated particularly for bigger trees till the secular determinant becomes sufficiently small. Actually, the algorithm can be repeated until we obtain a tree that contains atmost one root. This algorithm reduces the secular determinant of the matrix of the tree we started with to determinants of order atmost equal to the maximum number of vertices in any type generated in all iterations. Even then, the secular determinant
of any type can be factored further if there is any symmetry element in the type. This simplification will be considered in a future paper which will incorporate the symmetry groups of graphs in this algorithm. The algorithm is outlined below.

The tree we start with is pruned at joints. Pruning is continued until we obtain a tree with no branches. This tree can also be broken down further by a rooted product. Let \( Q_j \) be the quotient tree generated at the \( j \)th iteration. Let \( T_{ij} \) be a type generated in the \( j \)th iteration. Let \( t_{im}^{(j)} \) be the elements of the adjacency matrix of the type \( T_{ij} \). Let \( Y_{ij} \) be the set of vertices in \( Q_j \) that are mapped to the same type \( T_{ij} \). We define a matrix \( D^{(ij)} \) as follows:

\[
D_{lm}^{(ij)} = \begin{cases} 
H_{k,l-1} & \text{if } l = m \text{ and } l \in Y_{k,i-1}, \\
-H_{k,l-1}^{(ij)} & \text{if } l \neq m \text{ and } l \in Y_{k,i-1}, 
\end{cases}
\]

where \( H_{k,l-1} \) is the secular determinant of \( D^{(k,i-1)} \). \( H_{k,l-1}^{(ij)} \) is the secular determinant of the matrix \( D^{(k,i-1)} \) which is obtained by deleting the row and column that corresponds to the root in \( T_{k,l-1} \). \( H_{k} \) is the characteristic polynomial of the type \( T_{k} \) which is \( h_1 \) (defined in Sec. 2.B) if this type contains \( i \) vertices. Then we have the following theorem:

**Theorem 2:** The characteristic polynomial of the tree we started with is the secular determinant of the matrix defined below:

\[
A_{lm} = \begin{cases} 
H_{k,n} & \text{if } l = m \text{ and } l \in Y_{k,n}, \\
-H_{k,n}^{(n)} & \text{if } l \neq m \text{ and } l \in Y_{k,n}, 
\end{cases}
\]

where \( q_{lm}^{(n)} \) is a typical element of the adjacency matrix of the quotient graph \( Q_n \) generated in the \( n \)th iteration. Theorem 2 can be proved easily by repeated applications of Theorem 1 at every iteration of the algorithm.

As an example to illustrate this procedure consider the tree shown in Figure 3. This tree was used by the author in NMR applications [35]. This tree can be pruned iteratively to a quotient tree containing just two vertices in two successive iterations. The quotient tree and the types generated in the first and second iterations are shown in Figures 4 and 5, respectively. The matrices \( D^{(ij)} \) and
Figure 4. Tree $Q_1$ and types $T_{11}$, $T_{21}$, and $T_{31}$ which result on the application of the pruning algorithm to the tree in Figure 3.

$H_{ij}$'s are

\[ H_{11} = h_3, \quad H'_{11} = h'_3, \quad H_{21} = h_4, \quad H'_{21} = h'_4, \]

\[ H_{31} = h_1, \quad H'_{31} = 1: \]

\[
D^{(12)} = \begin{bmatrix}
  h_4 & 0 & 0 & -h'_4 \\
  0 & h_3 & 0 & -h'_3 \\
  0 & 0 & h_3 & -h'_3 \\
  -1 & -1 & -1 & h_1
\end{bmatrix}
\]

\[
D'^{(12)} = \begin{bmatrix}
  h_4 & 0 & 0 \\
  0 & h_3 & 0 \\
  0 & 0 & h_3
\end{bmatrix}
\]

\[ H_{12} = h_3^2 h_4 h_1 - 2 h_3 h_3' h_4 - h_3^2 h_4, \]

\[ H'_{12} = h_3^2 h_4, \]

\[ A^{(2)} = \begin{bmatrix}
  H_{12} & -H'_{12} \\
  -H'_{12} & H_{12}
\end{bmatrix}. \]

\[ \det(A^{(2)}) = H_{12}^2 - H'_{12}^2, \] which on simplification yields

\[ x^{10} \cdot (x^6 - 10x^4 + 30x^2 - 28)^2 - x^8(x^6 - 7x^4 + 10x^2 - 12). \quad (2.12) \]

Figure 5. Tree $Q_2$ and type $T_{12}$ are generated by pruning the tree in Figure 4.
Thus we reduced the $22 \times 22$ determinant problem into problems involving at most $4 \times 4$ determinants. Further, symmetry in trees $T_{21}$ and $T_{12}$ can simplify the problem.

3. Cospectral Trees

It is possible to determine elegantly if two trees are cospectral with the methods developed in Sec. 2. To illustrate consider the trees shown in the paper of Randić et al. [15]. One of them is shown in Figure 2, while the other is shown in Figure 6. We now show that these two trees are cospectral i.e., they have identical spectra. The characteristic polynomial of the tree in Figure 2 was already obtained as an illustrative example [cf. Eq. (2.9)]. The quotient tree $Q$ and the types $T_1$, $T_2$, and $T_3$ of $\Gamma$ in Figure 6 expressed as root-to-root are also shown in this figure:

$$
[Q \cdot (T_1, T_2, T_3)](x) = \begin{pmatrix}
    h_3 & -h'_3 & 0 & 0 \\
   -h'_3 & h_3 & -h'_2 & 0 \\
   0 & -h'_1 & h_1 & -h'_1 \\
   0 & 0 & -h'_2 & h_2
\end{pmatrix}.
$$

Substituting the expressions for $h_1, h'_1$, etc., in (3.1), we obtain

$$
[Q \cdot (T_1, T_2, T_3)](x) = x^9 - 8x^7 + 17x^5 - 10x^3.
$$

Expressions (3.2) and (2.9) are identical and thus the cospectrality of the trees in Figures 2 and 6 is established.

The pruning technique outlined in Sec. 2 paves the way for constructing cospectral trees. From the pruned tree one can construct several trees by attaching to the same vertex isospectral fragments. The resulting trees will be cospectral. These applications will be considered in future publications.

Appendix

The algorithm for characteristic polynomials of trees. For the explanation of notations see the text of the paper. Let $n$ be the last iteration and let $S_j$ be the set of terminal vertices (vertices of degree 1).
A.1 (Initialize):

\[ Q_i \leftarrow \begin{bmatrix} h_i \leftarrow x^i - (i-1)x^{i-2}, \\
                     h'_i \leftarrow x^{i-1}, \\
                     H_{k_i} \leftarrow h_i \text{ if there are } i \text{ vertices in the type } T_{k_i}; \\
                     H'_{k_i} \leftarrow h'_i. \end{bmatrix} \]

\[ \text{For } j = 2, n \text{ do} \]
A.2 Find \( S_j \).
A.3 \( Q_j \leftarrow Q_{j-1} - S_j \).
A.4 \( D^{(j)}_{(l)} \leftarrow H_{k_{j-1}} \text{ if } l = m \text{ and } l \in Y_{k_{j-1}}, \)
\( D^{(j)}_{(l)} \leftarrow -H'_{k_{j-1}} \text{ if } l \neq m \text{ and } l \in Y_{k_{j-1}}. \)
A.5 \( H_{ij} = \det (D^{(j)}) \).
A.6 \( A_{lm} \leftarrow H_{kn} \text{ if } l = m \text{ and } l \in Y_{k,n}, \)
\( A_{lm} \leftarrow -H'_{k,lm} \text{ if } l \neq m \text{ and } l \in Y_{k,n}. \)
A.7 \( \text{Char} \leftarrow \det (A); \)
final exit;
\( \text{Char} \) is the characteristic polynomial of the tree with which we started.

Acknowledgments

The author thanks Professor Kenneth S. Pitzer for his encouragement. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

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Received January 29, 1981
Accepted for publication June 24, 1981