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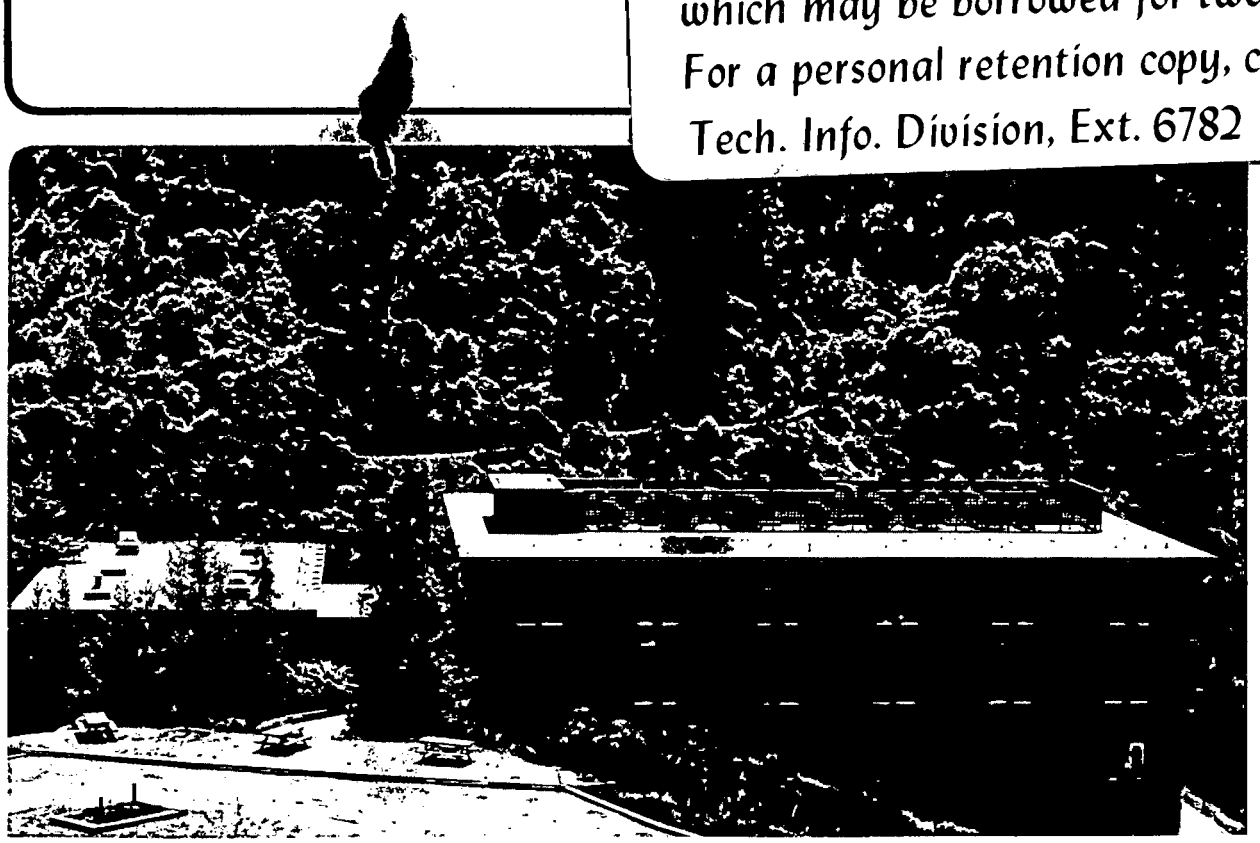

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Spectra of Chemical Trees

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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 x 22 secular determinant is reduced to determinants of orders at most 4 x 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.

I. 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, inter-molecular 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 non-equivalent 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 non-equal 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 Sach's theorem [30] becomes quite cumbersome for graphs containing large number of vertices. Even for a graph containing 12 vertices Sach's 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 polynomial 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.II we outline these methods and in Sec.III 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.

II. Spectra of Root-to-root Products

A. Preliminaries

The adjacency matrix of a graph is defined as follows.

$$A_{ij} = \begin{cases} 1 \text{ if the vertices i and j are connected} \\ 0 \text{ otherwise} \end{cases} \tag{2.1}$$

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 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 Γ in Fig. 1 can be obtained by joining the black dots (roots) of Q and a black dot of a copy of the 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 $T_1, T_2, \ldots, T_t$ denoted as $Q.(T_1, T_2, \ldots, T_t)$, is defined as the tree resulting by attaching a root in the set Y_i and the root of a copy of the type T_i. This product was introduced by the author in the context of isomer enumeration.[37] In Fig. 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 Fig. 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 Fig. 1. In general, rooted product of a graph Q with a sequence of graphs $T^{(1)}, T^{(2)}, \ldots$ and $T^{(n)}$, is obtained by identifying the roots of Q with the roots of $T^{(1)}, T^{(2)}, \ldots$ and $T^{(n)}$.

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 the 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 Y_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.

$$A_{ij} = \begin{cases} H_k(x) & \text{if } i=j \text{ and } i\varepsilon Y_k \\ -q_{ij}H_k'(x) & \text{if } i\neq j \text{ and } i\varepsilon Y_k \end{cases} \tag{2.2}$$

This definition of the matrix A is not identical to the definition of God$il 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.$(T_1,T_2,....)$ is the determinant of the matrix A defined above.

This theorem was proved by Godsil and McKay using a lemma of Schwenk stated below as 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.H be the graph obtained by identifying the roots r and s. Then the characteristic polynomial of G.H, denoted by G.H(x) is given as follows.

$$G.H(x) = G(x)H'(x) + G'(x)H(x) - xG'(x)H'(x) \tag{2.3}$$

The proof of this lemma was given by Schwenk [40].

Let h_i be the characteristic polynomial of a type containint 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 Fig. 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 shown below.

$$((Q))=((T)) = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \tag{2.4}$$

Thus $H(x) = h_2$ and $H'(x) = h_2'$. The matrix A is shown below.

$$A = \begin{bmatrix} h_2 & -h_2' \\ -h_2' & h_2 \end{bmatrix} \tag{2.5}$$

By theorem 1 the characteristic polynomial of the graph Q.T is just the determinant of A which is

$$h_2^2 - h_2'^2 = (x^2-1)^2-x^2 = x^4-3x^2+1 \tag{2.6}$$

Incidentally, this is the characteristic polynomial of the topological matrix of butadiene. The secular determinant of butadiene which is of the order 4 x 4 was reduced to a secular determinant of order 2 x 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 Γ in Fig. 2. Γ is the root-to-root product $Q.(T_1,T_2,T_3)$ with $Y_1 = \{1,2\}$, $Y_2 = \{3\}$, and $Y_3 = \{4\}$. The secular determinant of order 9 x 9 by an application of this theorem can be reduced considerably. The adjacency matrix of Q is shown below.

$$((Q)) = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{bmatrix} \tag{2.7}$$

The matrix A is shown below.

$$((A)) = \begin{bmatrix} h_2 & 0 & 0 & -h_2' \\ 0 & h_2 & 0 & -h_2' \\ 0 & 0 & h_4 & -h_4' \\ -h_1' & -h_1' & -h_1' & h_1 \end{bmatrix} \tag{2.8}$$

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 Γ as

$$|((\Gamma(x)))| = x^9 - 8x^7 + 17x^5 - 10x^3 \tag{2.9}$$

In this case we reduced the 9 x 9 determinant to determinants of orders at most 4 x 4. In many cases further reduction is possible if the quotient graph has more than one root as we show in the next section.

C. Iterative Algorithm for Evaluating the Characteristic Polynomials of Trees

The algorithm we outlined in Sec.IIB can be iterated particularly for bigger trees till the secular determinant becomes sufficiently small. Actually, the algorithm can be repeated till we obtain a tree that contains at most one root. This algorithm reduces the secular determinant of the matrix of the tree we started with to determinants of order at most 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 till 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 $t_{\ell m}^{(ij)}$ be the elements of the adjacency matrix of the type T_{ij}. Let Y_{ij} be the set of vertices in Q_i that are mapped to the same type T_{ij}. We define a matrix $D^{(ij)}$ as follows

$$D_{\ell m}^{(ij)} = \begin{cases} H_{k,j-1} \text{ if } \ell=m \text{ and } \ell \varepsilon Y_{k,j-1} \\ -H'_{k,j-1} t_{\ell m}^{(ij)} \text{ if } \ell \neq m \text{ and } \ell \varepsilon Y_{k,j-1} \end{cases} \qquad (2.10)$$

where $H_{k,j-1}$ is the secular determinant of $D^{(k,j-1)}$. $H'_{k,j-1}$ is the secular determinant of the matrix $D'^{(k,j-1)}$ which is obtained by deleting the row and column of $D^{(k,j-1)}$ that corresponds to the root in $T_{k,j-1}$. H_{kl} is the characteristic polynomial of the type T_{kl} which is h_i (defined in Sec. IIB) 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.

$$A_{\ell m} = \begin{cases} H_{kn} \text{ if } \ell=m \text{ and } \ell \varepsilon Y_{k,n} \\ -H'_{kn} q_{\ell m}^{(n)} \text{ if } \ell \neq m \text{ and } \ell \varepsilon Y_{k,n} \end{cases} \qquad (2.11)$$

where $q_{\ell m}^{(n)}$ 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 Fig. 3. This tree was used by the author in NMR application.[35] This tree can be pruned iteratively to a quotient tree containing just 2 vertices in 2 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 H_{ij}'s are shown below.

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

$$H_{31} = h_1 \quad H'_{31} = 1.$$

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

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

$$H_{12} = h_3^2 h_4 h_1 - 2h_3 h'_3 h_4 - h_3^2 h'_4$$

$$H'_{12} = h_3^2 h_4$$

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

Det $(A^{(2)}) = H_{12}^2 - H_{12}'^2$, which on simplification yields,

$$x^{10}.(x^6-10x^4+30x^2-28)^2 - x^8(x^6-7x^4+10x^2-12) \qquad (2.12)$$

Thus we reduced the 22 x 22 determinant problem in to problems involving at most 4 x 4 determinants. Further, symmetry in trees T_{21} and T_{12} can simplify the problem.

III. 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 Fig. 2 while the other is shown in Fig. 6. We now show that these two trees are cospectral i.e., they have identical spectra. The characteristic polynomial of the tree in Fig. 2 was already obtained as an illustrative example (c.f., Eq. 2.9). The quotient tree Q and the types T_1,T_2, and T_3 of Γ in Fig. 6 expressed as root-to-root product are also shown in this figure.

$$[Q.(T_1,T_2,T_3)](x) = \left|\begin{bmatrix} h_2 & -h_2' & 0 & 0 \\ -h_2' & h_2 & -h_2' & 0 \\ 0 & -h_1' & h_1 & -h_1' \\ 0 & 0 & -h_2' & h_2 \end{bmatrix}\right| \tag{3.1}$$

Substituting the expressions for h_1, h_1', etc., in 3.1 we obtain

$$[Q.(T_1,T_2,T_3)](x) = x^9 - 8x^7 + 17x^5 - 10x^3. \tag{3.2}$$

Expressions 3.2 and 2.9 are identical and thus the cospectrality of the trees in Figs 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.

Acknowledgments

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Bibliography

1. M. Randić, J. Am. Chem. Soc., 97, 6609 (1975).
2. M. Gordon and W. H. T. Davidson, J. Chem. Phys., 20, 428 (1952).
3. M. Randić, Molecular Physics, 34, 849 (1977).
4. M. Randić, Tetrahedron, 33, 1905 (1977).
5. M. Randić, Chem. Phys. Lett., 38, 68 (1977).
6. I. Gutman and M. Randić, Chem. Phys., 41, 265 (1979).
7. W. C. Herndon, J. Chem. Educ. 51, 10 (1974).
8. M. Randić, J. Chem. Phys., 60, 3920 (1974).
9. E. Heilbronner, Hel. Chim. Acta, 37, 921 (1954).
10. A. Graovac, I. Gutman, N. Trinajstić, and T. Zinković, Theor. Chim. Acta, 26, 67 (1972).
11. I. Gutman, Theor. Chim. Acta, 45, 79 (1977).
12. I. Gutman and N. Trinajstić, Topics current Chem., 42, 49 (1973).
13. I. Gutman, N. Trinajstić and T. Zinković, Chem. Phys. Lett. 14, 342 (1972).
14. I. Gutman, Theor. Chim. Acta, 50, 287 (1979).
15. M. Randić, G. M. Brissey, R. B. Spencer, and C. L. Wilkins, Computers and Chemistry, 3, 5 (1979).
16. M. Randić, J. Computational Chem. 1, 386 (1980).
17. M. Randić, Match, 5, 135 (1979).
18. H. Hosoya and T. Yamaguchi, Tetrahedron Lett. 4659 (1975).
19. H. Hosoya, Bull Chem. Soc. Japan, 44, 2332 (1971).
20. W. C. Herndon, Tetrahedron Lett. 671 (1974).
21. W. C. Herndon and M. L. Ellzey, Jr., Tetrahedron, 31, 99 (1973).
22. Hs. H. Gunthard and H. Primas, Hel. Chim. Acta, 39, 1645 (1956).
23. W. C. Herndon and M. L. Ellzey, Jr., J. Am. Chem. Soc., 96, 6631 (1974).

24. A. J. Schwenk, W. C. Herndon, and M. L. Ellzey, Jr., Annal N.Y. Acad. Aci., 319, 490 (1979).

25. S. S. D'Amata, Theor. Chim. Acta, 53, 319 (1979); Molecular Phys. 37, 1363 (1979).

26. R. B. King, Theor. Chim. Acta, 44, 223 (1977).

27. R. A. Davidson, Ibid., 58, 193 (1981).

28. T. Au-chin and K. Yuan-sun, Scientia Sinica, 1, 49 (1976); 3, 218 (1977).

29. R. B. Mallion and D. H. Rouvray, Molecular Physics, 36, 125 (1978).

30. D. H. Rouvray in "Chemical Applications of Graph Theory" (Editor: A. T. Balaban), Academic, 1976.

31. J. Dugundji, P. Gillespie, D. Marquarding, I. Ugi and F. Ramirez, in "Chemical Applications of Graph Theory" Academic, NY, 1976.

32. L. Glass, J. Chem. Phys. 63, 1325 (1975).

33. R. B. King, Theor. Chim. Acta, 56, 269 (1980).

34. R. Amit, C. A. Hall and T. A. Porsching, J. Computational Phys., 40, 183 (1981).

35. K. Balasubramanian, J. Chem. Phys. 73, 3321 (1980).

36. A. T. Balaban, Theor. Chim. Acta, 53, 355 (1979).

37. K. Balasubramanian, Ibid., 51, 37 (1979).

38. K. Balasubramanian, International J. Quantum Chemistry (in press).

39. C. D. Godsil and B. D. McKay, Bull. Australian Math. Soc., 18, 21 (1978).

40. A. J. Schwenk, Lecture Notes in Mathematics, 406, 153 (1973).

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) $h_i \leftarrow x^i - (i-1)\, x^{i-2}$

$h_i' \leftarrow x^{i-1}$

$H_{kl} \leftarrow h_i$ if there are i vertices in the type T_{kl}.

$H_{kl}' \leftarrow h_i'$.

For j = 2,n do

A.2 Find S_j

A.3 $Q_j \leftarrow Q_{j-1} - S_j$

A.4 $D_{\ell m}^{(ij)} \leftarrow H_{k,j-1}$ if $\ell=m$ and $\ell \varepsilon Y_{k,j-1}$

$D_{\ell m}^{(ij)} \leftarrow -H_{k,j-1}'\, t_{\ell m}^{(ij)}$ if $\ell \neq m$ and $\ell \varepsilon Y_{k,j-1}$

A.5 $H_{ij} = \det (D^{(ij)})$

A.6 $A_{\ell m} \leftarrow H_{kn}$ if $\ell=m$ and $\ell \varepsilon Y_{k,n}$

$A_{\ell m} \leftarrow -H_{kn}'\, q_{\ell m}^{(n)}$ if $\ell \neq m$ and $\ell \varepsilon Y_{k,n}$

A.6 Char $\leftarrow$ det (A).

Final exit.

Char is the characteristic polynomial of the tree we started with.

Figure Captions

Figure 1. A quotient tree Q and a type T and their root-to-root product.

Figure 2. A branched tree on 9 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.

Figure 3. A NMR tree containing 22 vertices.

Figure 4. The tree Q_1 and the types T_{11}, T_{21}, and T_{31} which result on the application of the pruning algorithm to the tree in Fig. 3.

Figure 5. The tree Q_2 and the type T_{12} are generated by pruning the tree in Fig. 4.

Figure 6. A tree which is iso-spectral with the tree in Fig. 2. Iso-specricity of these two trees is established by pruning process outlined in this paper.

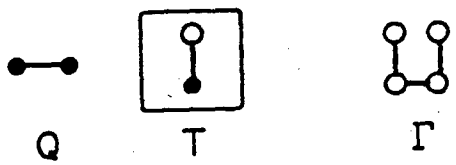

Figure 1

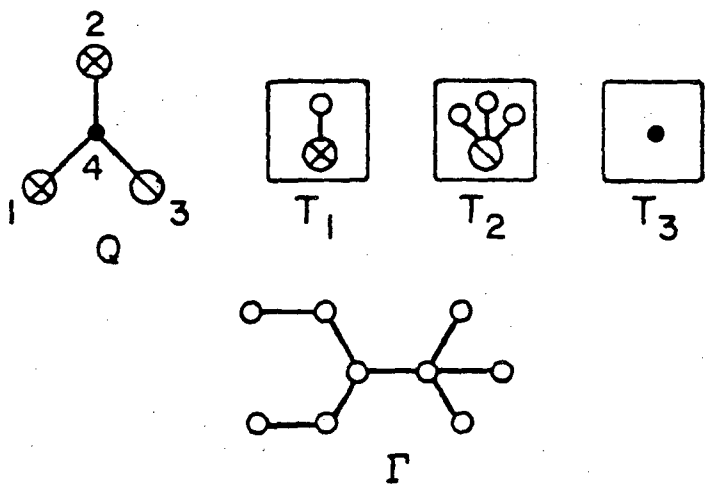

Figure 2

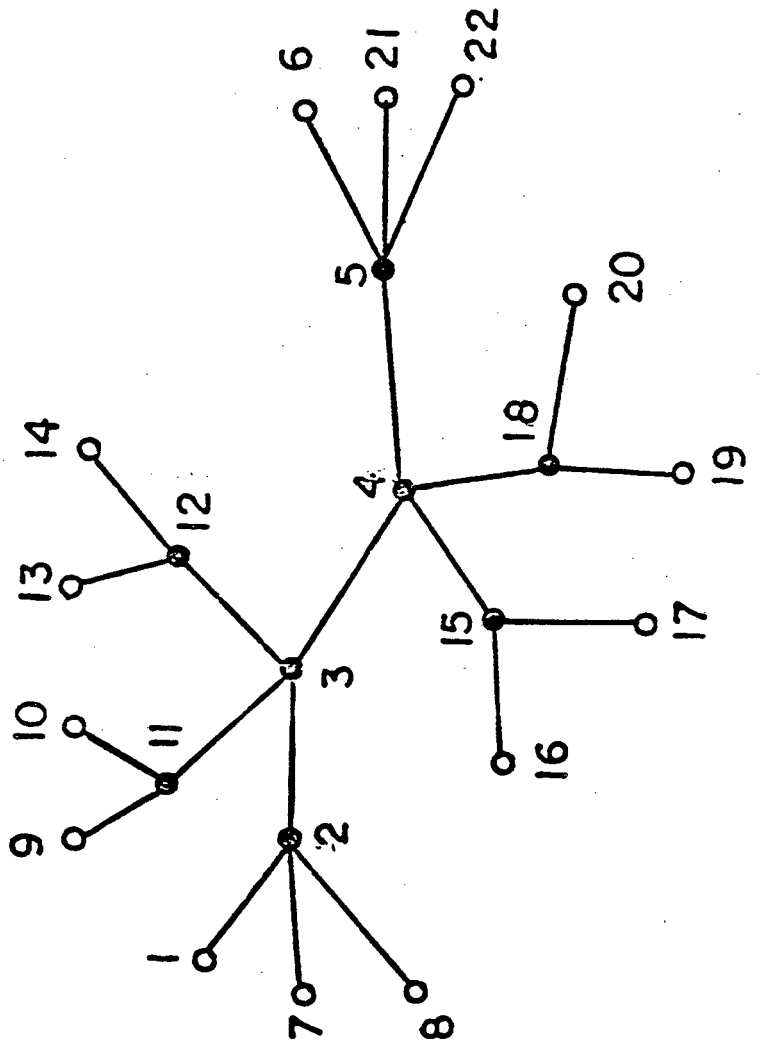

Figure 3

Q

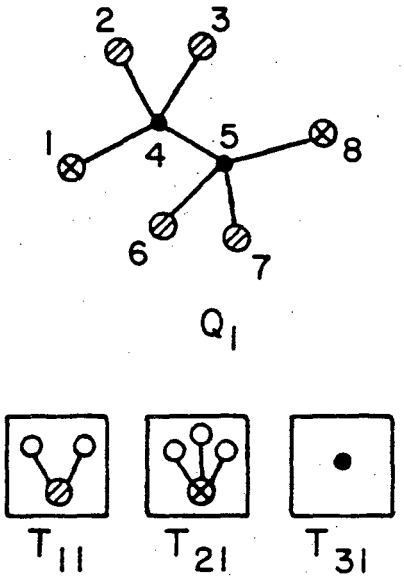

Figure 4

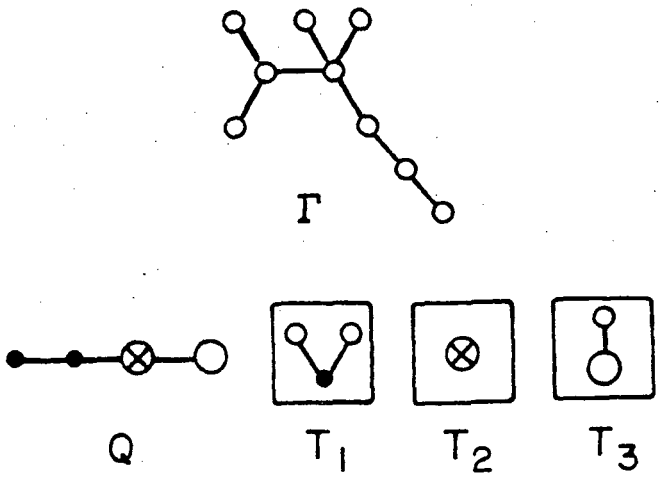

Figure 5

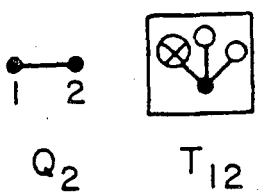

Figure 6

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