

Applications of Combinatorics and Graph Theory to Spectroscopy and Quantum Chemistry

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I. Introduction

Discrete mathematics is a branch of mathematics which deals with the properties of sets that can be mapped into a set of integers. The objects of discrete sets are countable, and they can be labeled by integers. For example, a set of apples is discrete in the sense that the apples in this set can be labeled A_1, A_2 , etc. On the contrary the set $(0, 1)$ which represents the set of real numbers in the open interval between 0 and 1 cannot be mapped into a set of integers. A few mathematicians consider discrete mathematics and combinatorics synonymous. This is not unrealistic if one defines combinatorics in such a way that it encompasses all the facets of the study of discrete structures. Even though the definition of discrete mathematics mentioned above is precise, it does not satisfactorily describe the various facets of discrete mathematics. When the new journal of discrete mathematics was established in 1971, it stated that the fields covered by the journal would include Boolean algebra and applications, coding theory, combinatorial geometries, combinatorics and combinatorial structures, computational complexity, discrete aspects of mathematical programming and operations research, discrete models in Biology, discrete probabilities, extremal set theory, finite algebras, games, graphs, hyper graphs, integer programming, logic and automata, mathematical linguistics, matrices, networks, statistical mechanics, and related topics.

Consider one of the most important branches of discrete mathematics, namely combinatorics or combinatorial mathematics. It appears that a satisfactory definition of this area is not found in the literature even though one understands what it means. Berge¹ defines



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combinatorics as a science which counts, enumerates, examines, and investigates the existence of "configurations" with certain specified properties. A configuration is defined as a mapping of objects into a finite abstract set with a given structure. For example, a permutation of n objects is a one-to-one mapping of the objects of the set to the ordered set $\{1, 2, \dots, n\}$ if there are n objects in the set under consideration. Combinatorics evolved by finding methods or algorithms for enumerating configurations (instead of executing the experiment with desired specifications by brute force). One such method is the generating function method discovered by Laplace although it appears that it was conceived by Euler earlier. The binomial expansion $(1 + x)^n$ can be thought of as a generating function for $\binom{n}{r}$ since the coefficient of x^r in $(1 + x)^n$ is $\binom{n}{r}$. Thus to obtain the number of ways of choosing r objects out of n objects, one looks at the coefficient of x^r in $(1 + x)^n$ (instead of actually choosing these objects and finding how many such ways exist). The subject evolved to a considerable extent through the problems posed by other branches of science which ask for such counting techniques. Chemistry seems to have been a fertile ground for the development of some most important combinatorial techniques. Cayley²⁻⁵ showed the correspondence between enumerating the isomers of organic molecules of the formula C_nH_{2n+2} and enumerating trees. Pólya⁶ published an important and classical paper on what is now well-known as Pólya's

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theorem which was anticipated by Redfield⁷ earlier. This theorem provides generating functions for the enumeration of configurations under group action in terms of what is known as the cycle index of a group.

Since the development of this celebrated Pólya's theorem numerous papers have appeared in both chemical and mathematical literature⁸⁻⁷⁷ which deal with several ramifications of this theorem and other methods and their applications to chemical problems. The chemical applications of Pólya's theorem include enumeration of stereoisomers, positions isomers, geometrical isomers of inorganic compounds, enumeration of labeled compounds, enumeration of NMR signals,^{56,63} enumeration of electron-rich and electron-poor Boron compounds, enumeration of electronic configurations in configuration interaction, etc.

Isomer enumeration and related topics were reviewed by Rouvray.^{28,29} We will not describe in details the various topics covered in these references. Interested readers are referred to ref 28 and 29 and some of the papers of the present author for recent developments.^{55-59,61-65}

The other important aspect of combinatorics is the problem of the existence of a configuration. It is this aspect that led to the celebrated problem of the seven bridges of the town of Königsberg which can be considered as the first pioneering problem that developed the theory of graphs. The problem was to stroll across the seven bridges connecting four land areas exactly once and return to the starting point. Euler showed that the problem is insoluble by representing each land area by a vertex of a graph and each bridge by an edge connecting the vertices. These types of investigations can be found as early as 2200 B.C., for example, in the divinatory book used in China by the lesser Taoists. This work describes two configurations, namely, the grand plan and the river map. (See Berge,¹ for more details.)

Graph theory has developed into a subject in itself with a variety of applications. A graph is simply a diagram with vertices connected by edges. If the vertices represent atoms and the edges represent chemical bonds, then the associated graph is a representation of a molecule. The use of such connection diagrams goes back to ancient chemists such as Kekulé and mathematicians like Cayley, who used trees to represent alkanes. The vertices of a graph may represent certain reactive species or isomers and the edges being possible reactions or isomerizations. Then the associated graph may be called isomerization or reaction graph. The construction of isomerization graphs, their properties, and important applications to stereochemistry have been discussed in a number of publications.⁷⁸⁻¹⁰⁵ The scope of our present review does not permit to include extensive discussions on this topic.

Graphs are representations for quantum mechanical Hamiltonians, interactions, etc. An example of such a diagram is the Feynman diagram.¹⁰⁶ A nonweighted ordinary graph is a representation of the Hückel Hamiltonian matrix of π -electronic systems.¹⁰⁷ It can be shown that the Hückel matrix can be transformed to a topological or adjacency matrix which is simply a matrix of connectivity information. The topological representation of such a matrix would be a diagram with n vertices (if n is the number of rows), and the

vertices i and j connected in the diagram if the ij th matrix element is 1. The extension of this representation to other ab initio Fock matrices would be edge-weighted diagrams with the weights of the edges representing matrix elements. The usefulness of weighted diagrams have not been explored in great depth in chemical literature. However, a number of papers have dealt with the applications of ordinary (nonweighted) graphs to Hückel theory, extended Hückel theory, electronic structure of polymers, etc. Some of these works will be reviewed in this manuscript in the section on applications to quantum chemistry.

A classical example of a problem soluble using graph theory in chemical physics is the well-known Ising problem. The problem is to obtain the partition function (and hence the thermodynamic behavior) of a lattice of interacting ferromagnets with nearest-neighbor interaction. The problem is soluble for a one-dimensional lattice, and Onsager solved the two-dimensional problem. The correspondence between the Ising problem and a graphical problem known as the dimer covering problem on a "bathroom tile lattice" is well known.^{108,109} The dimer covering problem asks for the number of ways of forming dimers on a lattice of points where a dimer is a set of two vertices connected by an edge.

The dimer covering problem has another important application in the estimation of the resonance energy of aromatic hydrocarbons. It turns out that the number of possible Kekulé structures of a polycyclic aromatic hydrocarbon is given by the number of dimers that can be formed with the molecular graph of the aromatic hydrocarbon. For an elementary review of this topic, see Herndon's paper.¹¹⁰ Numerous papers have appeared in the chemical literature that deal with graph theory, aromaticity, dimer coverings, etc.¹¹¹⁻¹⁶³ An intimately connected generating function for dimers is called matching polynomial. The coefficient of a particular term in the matching polynomial enumerates the number of ways of placing a given number of dimers on a lattice (partial covering of dimers). Methods and computer programs have been developed to construct the matching polynomials of very complicated graphs by the present investigator and co-workers.¹⁵⁹ The topic of topological approach to the chemistry of conjugated molecules was reviewed by Graovac, Gutman and Trinajstić¹³⁹ and more recently by Trinajstić.¹³⁴

Graph theory is useful in simplifying certain integrals which appear in the partition function using the Mayer-Mayer expansion.¹⁶⁴ To obtain the partition function of a system of N classical monoatomic particles in a volume V , one has to evaluate the integrals over momentum and position space. It turns out that the integrals over momentum space can be rather easily evaluated in comparison to the integrals over position variables which remain a bottleneck of many problems in statistical mechanics since the latter involve the interactions between particles i and j which depend on the separation between them. It is thus impossible to obtain the partition function exactly for these many-body systems. Nevertheless, one can classify these interactions according to certain criteria and include only those terms that are significant. Mayer and Mayer expanded the partition function as a series and each term in the series can be represented by a graph (known

as the Mayer graph). The idea is reminiscent of Feynman diagrams in the many-body perturbation theory.

Combinatorial methods have important applications in chemical kinetics. For example, combinatorial and topological methods in nonlinear chemical kinetics can be seen in the paper of Glass.¹⁶⁵ Some results of nonlinear chemical systems were derived recently by Beratta et al.¹⁶⁶ using graph theoretical methods. Graph theoretical models of finding the possible mechanisms for a given type of reaction can be seen in the paper of Sinanoğlu¹⁶⁷ and papers of Lee and Sinanoğlu.^{168,169} King¹⁷¹ has shown that graph theory can be used to determine the dynamics of complex chemical reactions such as oscillatory reactions. The use of graph theory in chemical dynamics is reviewed by Clarke.¹⁷² Combinatorial techniques such as Möbius inversion have several applications in physical sciences. A graph theoretic formulation of Ising problem, percolation, and graph coloring problems is given by Essam.¹⁷⁰ The coloring problem of all connected subgraphs which is useful in statistical mechanics was solved by Essam using the Möbius inversion technique. The chromatic polynomials thus obtained using the Möbius inversion techniques were shown to have applications in statistical mechanics.

Graph theoretical methods have been found to be successful in evaluating pressure virial coefficients of hydrocarbons, fluorocarbons, and their mixtures using the walks on chemical graphs.^{173,174} The methods seem to be successful in predicting both liquid-state properties and pressure second virial coefficients of *n*-alkanes, *n*-perfluorocarbons, and alk-1-enes. Properties of the binary mixtures can also be predicted in terms of the properties of pure compounds. Graph theory was also applied to chromatography by Randić.¹⁷⁵ Graph theory was used in fluid dynamics in solving Navier-Stoke's equation by Amit et al.¹⁷⁶ Graph theoretical methods have been applied to several other areas such as statistical mechanics of polymers and related topics,¹⁷⁷⁻¹⁷⁹ structure and bonding of inorganic clusters, etc.¹⁸⁰⁻¹⁸⁹

As one can see from the above-cited references, a significant amount of work has been done on a variety of topics dealing with applications of graph theory and combinatorics to chemical problems. While some of the topics have been reviewed, a satisfactory review of applications of combinatorics and graph theory to especially spectroscopy and quantum chemistry is timely and could be valuable. The objective of this manuscript is to review these applications to mainly spectroscopy and quantum chemistry.

II. Some Combinatorial Methods

The objective of this section is to introduce some elementary combinatorial techniques, especially the ones which we apply here to spectroscopy and related areas. Methods are illustrated with examples from chemistry.

A. Pólya's Theorem

As mentioned in the introduction Pólya developed an important procedure now well-known as Pólya's theorem which was anticipated by Redfield. We outline this

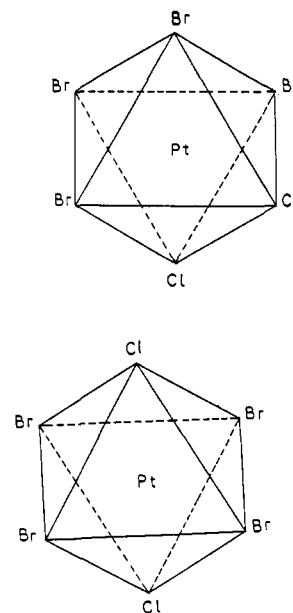


Figure 1. The two geometrical isomers of PtBr_4Cl_2 .

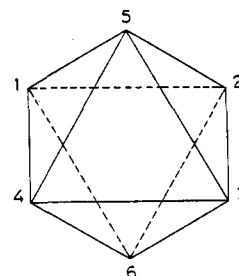


Figure 2. The molecular graph used to enumerate isomers of octahedral compounds.

technique with chemical isomers as illustrative examples.

By the term isomers one means two structures with the same molecular formula one not transformable into another by any rotation in physical space. In group theoretical terms, this would correspond to structures with the same formula one not transformable into another by the proper rotations of the corresponding point group.

We shall first take up as an illustrative example the problem of counting the number of isomers of an octahedral molecule with a metal atom in the center and formulate it in mathematical terms. PtBr_4Cl_2 , for example, is well-known to have just two isomers, namely, those shown in Figure 1.

To abstract the problem in the language of mathematics, one looks at all maps (functions) from \mathbf{D} to \mathbf{R} where \mathbf{D} is the set $\{1, 2, 3, 4, 5, 6\}$ of six vertices of the octahedron shown in Figure 2 and \mathbf{R} is the set $\{\text{Br}, \text{Cl}\}$ of atoms. Each map represents a chemical structure of an octahedral molecule containing Br and/or Cl atoms and vice versa.

For example the structures shown in Figure 1 correspond to the maps

t-map	c-map
1 → Br	1 → Br
2 → Br	2 → Br
3 → Br	3 → Cl
4 → Br	4 → Br
5 → Cl	5 → Br
6 → Cl	6 → Cl

(1)

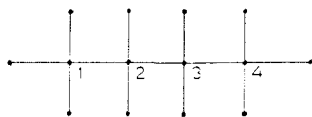


Figure 3. A molecular graph containing four carbon atoms. This is used to enumerate the isomers of polysubstituted saturated compounds containing four unbranched carbon atoms.

Another structure with the same molecular formula corresponds to a different map but is certainly obtainable (as can be verified easily) from one of the above by a permutation of the vertices induced by the rotations of the octahedron. This leads to the mathematical concept of equivalence wherein equivalent maps represent the same isomer and nonequivalent maps represent different isomers. This concept of equivalence can be abstracted and formulated mathematically. Before we do this, we shall introduce the concept of weights to take care of the fact that isomers have the same molecular formula. To each element $r \in \mathbf{R}$ let us attach a weight of $w(r)$, which may be a formal symbol for the atoms or functional groups. With every function $f(\mathbf{D} \rightarrow \mathbf{R})$ is associated a weight of $W(f)$ which is the product of the weights of all the images by f . Symbolically

$$W(f) = \prod_{d \in \mathbf{D}} w(f(d)) \quad (2)$$

To illustrate let us associate a weight \mathbf{Br} to the atom Br and a weight \mathbf{Cl} to the atom Cl. Then $W(\text{t-map}) = \mathbf{Br}^4\mathbf{Cl}^2$ and $W(\text{c-map}) = \mathbf{Br}^4\mathbf{Cl}^2$. Note, therefore, that molecules with the same atomic constituents correspond to maps with the same weight.

We are now ready to give a precise mathematical definition of isomers. This will ultimately lead to general methods of counting of isomers. Let the chemical formula of the molecule M be given. The problem is to find the isomers of M . First we go to the graph Γ of M . The vertex set of Γ shall be partitioned into two parts, namely, (i) the set of chemically unlabeled vertices, i.e., those vertices to which the substituents are attached and (ii) the set of the remaining vertices, which may be called "chemically labeled" vertices. For example, to find the isomers of $\text{C}_4\text{H}_9\text{Br}$, one considers the graph shown in Figure 3. Here the unlabeled vertices are those where the nine Hydrogen atoms and one bromine atom can be substituted; and the vertices 1, 2, 3, and 4 are the chemically labeled ones, since they are already labeled as carbon atoms.

Let \mathbf{D} stand for the set of chemically unlabeled vertices of Γ , the graph of M . Let \mathbf{R} be the set of substituents which are used to label the vertices of \mathbf{D} . Each map $f(\mathbf{D} \rightarrow \mathbf{R})$ will now correspond uniquely to a structure of a chemical molecule with the same parent as M . With each type of substituent let us associate a weight w_i . Let the given molecule M have b_1 functional groups of the type 1, b_2 of the type 2, ..., and so on. Then the weight of the corresponding function will be $w_1^{b_1}w_2^{b_2} \dots$. Let this be shortly denoted as w_M . Consider the set \mathbf{F} of all maps from \mathbf{D} to \mathbf{R} . Let \mathbf{F}_M be a subset of \mathbf{F} consisting of those maps $\mathbf{D} \rightarrow \mathbf{R}$ with the weight w_M . Now let \mathbf{G} be a group of permutations acting on \mathbf{D} induced by the rotations in physical space which give the needed isomers of M .

In the above setting two functions f_1 and $f_2 \in \mathbf{F}$ are said to be \mathbf{G} -equivalent where \mathbf{G} is the group of 24

rotations of the octahedron acting on the vertices. The \mathbf{G} -equivalence classes of \mathbf{F}_M are said to be the isomers of M . Thus the number of isomers of M is precisely the number of \mathbf{G} -equivalence classes of \mathbf{F}_M .

Pólya's Theorem gives a formula for the number of various \mathbf{G} -equivalence classes and also a generating polynomial for the number of \mathbf{G} -equivalence classes of \mathbf{F}_M for various molecules M . Before stating the theorem, we need to know the concepts of the cycle index of a permutation group and of the pattern inventory.

Let \mathbf{G} be a permutation group. Every permutation of \mathbf{G} has a unique cycle decomposition. Let a typical permutation $g \in \mathbf{G}$ have b_1 cycles of length 1, b_2 cycles of length 2, and so on. Then $x_1^{b_1}x_2^{b_2} \dots$ is said to be the cycle representation of the permutation g . The cycle index of \mathbf{G} is defined as the sum of the cycle representations of various elements in \mathbf{G} divided by $|\mathbf{G}|$, the number of elements in \mathbf{G} . It is denoted by $P_G(x_1, x_2, \dots)$. Thus

$$P_G(x_1, x_2, \dots) = \frac{1}{|\mathbf{G}|} \sum_{g \in \mathbf{G}} x_1^{b_1} x_2^{b_2} \dots \quad (3)$$

In Pólya's terminology each \mathbf{G} -equivalence class of functions from \mathbf{D} to \mathbf{R} is called a pattern. It can be easily proved that the functions (maps) belonging to the same pattern have the same weight. Pólya defined therefore the weight of a pattern as the weight of any function belonging to it. Given a set of functions \mathbf{F} from \mathbf{D} to \mathbf{R} and a permutation group \mathbf{G} acting on \mathbf{D} , we define the pattern inventory as the sum of the weights of various patterns contained in \mathbf{F} . Let $n(\mathbf{F}_M)$ stand for the number of isomers of M . It is nothing but the number of \mathbf{G} -equivalence classes belonging to \mathbf{F}_M . Each function \mathbf{F}_M has clearly the same weight w_M by the definition of \mathbf{F}_M . Therefore the weight of each pattern (isomer) belonging to \mathbf{F}_M has the same weight w_M . Thus we can form what may be called isomer inventory as $\sum_M n(\mathbf{F}_M)w_M$ where the summation runs over all molecules M having the same graph and the same set \mathbf{D} of chemically unlabeled vertices.

Consider a set \mathbf{F} of functions from a finite set \mathbf{D} to a finite set \mathbf{R} . Let \mathbf{G} be the permutation group acting on \mathbf{D} giving rise to \mathbf{G} -equivalence classes, i.e., the patterns of \mathbf{F} . Then, by Pólya's theorem (i) the pattern inventory is given by

$$P_G(x_k \rightarrow \sum_{r \in \mathbf{R}} (w(r))^k) \quad (4)$$

In particular, (ii) the total number of patterns is given by

$$P_G(|\mathbf{R}|, |\mathbf{R}|, \dots) \quad (5)$$

Equivalently, the pattern inventory is obtained by replacing x_k by $\sum_{r \in \mathbf{R}} (w(r))^k$ in the cycle index $P_G(x_1, x_2, \dots)$. As a special case the number of patterns is obtained by letting $w(r) = 1$ for each $r \in \mathbf{R}$. This amounts to the substitution $x_k = |\mathbf{R}|$ for every k in the cycle index $P_G(x_1, x_2, \dots)$.

Let us now apply Pólya's theorem to enumerate the isomers of certain octahedral molecules. The group \mathbf{G} acting on the vertices of the octahedron will be the set of proper rotations of the point group O_h . The cycle index is easily computed by operating each of the typical element of the conjugacy class of proper rotations of O_h . The classes of rotations are shown in Figure 4.

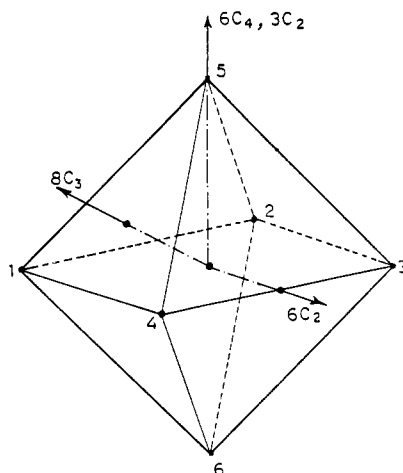


Figure 4.

A permutation representation for each rotation is obtained by considering the effect of that operation on the six vertices of octahedron. (The vertices are considered, since isomers are obtained by substituting the vertices with substituents.) For example, the effect of the C_4 operation shown in Figure 4, described as a permutation of the vertices of octahedron, would be (1234)(5)(6). Since this yields two cycles of length 1 and a cycle of length 4, the cycle representation of this permutation is $x_1^4 x_5 x_6$. The cycle index polynomial of the octahedral group is obtained by summing up the cycle representations of all elements in the O group. The resulting expression is

$$P_G(x_1, x_2, \dots, x_6) = \frac{1}{24}(x_1^6 + 6x_1^2x_4 + 3x_1^2x_2^2 + 8x_3^2 + 6x_2^3) \quad (6)$$

The Pattern inventory, which is a generating function for isomers, is obtained by replacing every x_k by $\sum_{r \in R} (w(r))^k$ and is given by

$$PI = \frac{1}{24}[(w_1 + w_2 + \dots + w_6)^6 + 6(w_1 + w_2 + \dots + w_6)^2(w_1^4 + w_2^4 + \dots + w_6^4) + 3(w_1 + w_2 + \dots + w_6)^2(w_1^2 + w_2^2 + \dots + w_6^2)^2 + 8(w_1^3 + w_2^3 + \dots + w_6^3)^2 + 6(w_1^2 + w_2^2 + \dots + w_6^2)^3] \quad (7)$$

If one identifies the weight w_1 with the Br atom and w_2 with the weight Cl, then the number of isomers of $PtBr_4Cl_2$ is given by the coefficient of $w_1^4 w_2^2$ in expression 7. It can be seen that the coefficient of $w_1^4 w_2^2$ in expression 7 is

$$\frac{1}{24} \left(\frac{6!}{4!2!} + 9 + 6 + 18 \right) = 2 \quad (8)$$

Thus, the number of isomers of $PtBr_4Cl_2$ is simply the coefficient of $w_1^4 w_2^2$ in expression 7. Expression 7 is thus a *generation function* for all possible isomers of octahedral molecules. For example, the number of isomers of $RuCl_4(H_2O)(CO)$ is given by the coefficient of $w_1^4 w_2 w_3$ in (7) which is

$$\frac{1}{24} \left[\frac{6!}{4!1!1!} + 6 \frac{2!}{1!1!} + 3 \frac{2!}{1!1!} \right] = 2 \quad (9)$$

The number of isomers of $RhCl(CH_3)CO(PPh_3)_2$ is given by the coefficient of $w_1 w_2 w_3 w_4 w_5$ shown.

$$\frac{1}{24} \left[\frac{6!}{2!1!1!1!1!} \right] = 15 \quad (10)$$

Finally, the number of isomers of octahedral $MABCDEF$, where M is the metal atom is the coefficient of $w_1 w_2 w_3 w_4 w_5 w_6$ in (7) and is given by (11).

$$\frac{1}{24} \left[\frac{6!}{1!1!1!1!1!1!} \right] = 30 \quad (11)$$

A review of simple use of Pólya's theorem for enumeration of chemical isomers and related topics can be found in references 28 and 29.

B. Group Characters and Generalized Character Cycle Indices

The ordinary cycle index defined in section IIA (used in Pólya's theorem) can be extended to any character of an irreducible representation in a group G .

Let $g \rightarrow \chi(g)$ be the character of an irreducible representation Γ in the group G . Then one can define a cycle index for each irreducible representation Γ with character χ as

$$P_G^\chi = \frac{1}{|G|} \sum_{g \in G} \chi(g) x_1^{b_1} x_2^{b_2} \dots \quad (12)$$

where $x_1^{b_1} x_2^{b_2} \dots$ has the same meaning as the cycle representation in section IIA: $\chi(g)$ is the character of the irreducible representation which corresponds to the element g in G .

Let F be a set of all maps from $D \rightarrow R$. There are $|R|^{|D|}$ such maps, where $|R|$ and $|D|$ are the number of elements in the sets R and D , respectively. Suppose $w(r)$ is simply the weight of an element $r \in R$. Then a generating function can be obtained for each irreducible representation Γ with character χ as

$$GF^\chi = P_G^\chi(x_k \rightarrow \sum_{r \in R} (w(r))^k) \quad (13)$$

Note that Pólya's theorem is just a special case of the above generating function, namely, the generating function for the totally symmetric representation. Then the generating function for the totally symmetric representation is the pattern inventory. The coefficient of a typical term $w_1^{b_1} w_2^{b_2} \dots$ in the generating function for the totally symmetric representation gives the number of totally symmetric representation in the set of functions with the weight $w_1^{b_1} w_2^{b_2} \dots$. It follows that the number of totally symmetric representations is simply the number of equivalence classes (isomers). This is, indeed, the celebrated Frobenius' theorem! Thus from expression 13 one can derive very powerful theorems such as Pólya's theorem, Frobenius' theorem, etc. This extension of Pólya's theorem to all characters was suggested by Williamson^{12,13} for characters of one-dimensional representation and by Merris¹⁴ for characters of higher dimensional representations. The present author gave a physical significance for this extension for the first time.

The present author showed that the coefficient of a typical term $w_1^{b_1} w_2^{b_2} \dots$ in the GF^χ corresponds to the number of times an irreducible representation Γ whose character is χ occurs in the (reducible) representation spanned by the set of functions from D to R with the same weight $w_1^{b_1} w_2^{b_2} \dots$. This result is very significant. It is extremely useful in several chemical areas such as

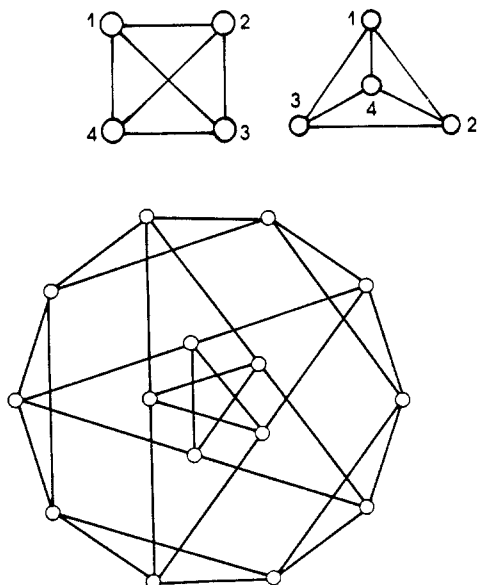


Figure 5. Examples of graphs. The first two graphs are isomorphic (see section IIC).

NMR spectroscopy, nuclear spin statistics, NQR spectroscopy, unitary group approach to electron correlation, symmetry adaptation, etc.

C. Elements of Graph Theory

There are several excellent books on graph theory and applications.^{43,134,190,191} For details on graph theory and applications the readers are referred to these books. In this section we review briefly the basic concepts of graph theory needed for the applications outlined in this review.

A graph is a diagram containing vertices and edges and the theory of graphs deals with the underlying *connectivity* relationship and their properties. In formal terms, the graph G is defined as an ordered set $(V(G), E(G))$, where $V(G)$ is the set of vertices of the graph G and $E(G)$ is the set of edges. Figure 5 shows examples of graphs. It is important to stress that a graph depicts only the connectivity information (i.e., whether two vertices in G are connected or not) and does not provide any information on the arrangement of vertices in space. The same graph can be drawn in different ways. For example, the first two graphs in Figure 5 are the same since they provide the same connectivity information. A tree is a connected graph with no cycles.

The adjacency matrix A of a graph is defined as

$$A_{ij} = \begin{cases} 1 & \text{if } i \text{ is connected to } j \\ 0 & \text{otherwise} \end{cases} \quad (14)$$

To illustrate the adjacency matrix of the first two graphs in Figure 5 is shown below.

$$\begin{bmatrix} 0 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{bmatrix} \quad 14a$$

Two graphs are said to be isomorphic if the adjacency matrix of one is obtainable from another by relabeling the vertices. A formal definition of graph isomorphism is given in text books.^{190,191}

A walk in a graph is a sequence of connected edges e_1, e_2, \dots, e_k . k is referred to as the length of a walk. A

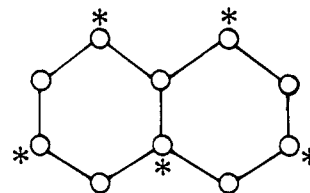


Figure 6. A bipartite graph. Molecules with bipartite molecular graphs are also known as alternant molecules.

self-returning walk is a walk in which one returns to the starting vertex by the end of walk. A self-avoiding walk is a walk in which no vertex appears more than once. The enumeration of walks on graphs is an important problem since it has several applications in diffusion, conformations of polymers, etc. Computer-assisted enumeration of walks and self-returning walks by way of obtaining generating functions (walk polynomials) was considered by the present author.¹⁹²

A graph is said to be bipartite if the vertices of this graph can be colored with say a green color such that no two connected vertices carry the green color. To illustrate, the graph in Figure 6 is bipartite. In chemical terms a molecule with a bipartite graph is called an alternant molecule. The coloring of the vertices of a graph is useful in several areas such as exact finite lattice statistics and adsorption of metals on surfaces. For details see the papers by Balasubramanian and Ramaraj¹⁹³ and Motoyama and Hosoya.¹⁹⁴

III. Applications to Spectroscopy

In this section we consider applications of techniques outlined in section II to several areas of spectroscopy such as NMR spectroscopy, dynamic NMR, molecular spectroscopy, and NQR spectroscopy of crystals exhibiting phase transition.

A. NMR Spectroscopy

The present author showed that Pólya's theorem, generalized character cycle indices and double cosets can be applied to a number of problems in NMR.^{56,57,63,195-198} First we consider enumeration of NMR signals in the low-resolution spectrum, where the number of signals corresponds to the number of magnetically equivalence classes.

Let D be the set of the nuclei of the same kind (such as H, ^{13}C , etc.) in the molecule. For example, if ^{13}C NMR of naphthalene is under consideration, then D would be the set of 10 carbon nuclei present in the molecule. Let R be a set containing just two elements. Let G be the point group or the permutation-inversion group of the molecule. To differentiate enantiotopic protons, G should be the rotational subgroup. Since G is the set of all permutational and composite permutation-inversion operations, any $g \in G$ induces permutations on elements in D since D is just the set of nuclei of the same kind in the molecule. Consider the set F of all maps from D to R . The action of G on D can in turn be transferred to F by the following recipe. Every $g \in G$ acts on F as defined by the formula

$$gf(d) = f(g^{-1}d) \text{ for every } d \in D \quad (15)$$

Two maps f_i and $f_j \in F$ are equivalent if

$$f_i(d) = f_j(gd) \text{ for every } d \in D \quad (16)$$

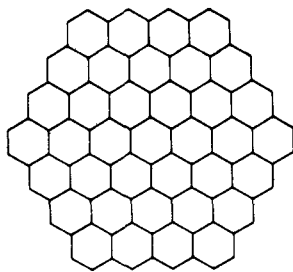


Figure 7. A pericondensed benzenoid hydrocarbon. The numbers of ^{13}C and proton NMR signals of this molecule are enumerated by using Pólya's theorem (see section IIIA).

Maps in \mathbf{F} that are equivalent can be grouped into the same equivalence class. Thus the group \mathbf{G} partitions \mathbf{F} into equivalence classes. Let us restrict ourselves to the maps in \mathbf{F} which have the following structure. Let the elements of \mathbf{R} be denoted by α_1 and α_2 . Label the elements of \mathbf{D} as d_1, d_2, \dots, d_n with $n = |\mathbf{D}|$. Then consider a subset \mathbf{F}_w of \mathbf{F} with every $f_i \in \mathbf{F}_w$ defined as

$$f_i(d_j) = \begin{cases} \alpha_1 & \text{if } i \neq j, d_j \in \mathbf{D} \\ \alpha_2 & \text{if } i = j \end{cases} \quad (17)$$

It can be seen that two nuclei d_i and d_j are magnetically equivalent if f_i is equivalent to f_j . Thus the equivalence classes of \mathbf{F}_w are the magnetic equivalence classes of nuclei in the set \mathbf{D} . Hence the number of equivalence classes gives the number of NMR signals of the molecule.

Define the weight of an element r in \mathbf{R} and that of the function \mathbf{f} as in section II. Since any $f_i \in \mathbf{F}_w$ takes all $d_j \in \mathbf{D}$ to α_1 except for $i = j$, the weight of any f_i in \mathbf{F}_w is $w = \alpha_1^{n-1}\alpha_2$ if α_1 is the weight associated with α_1 and α_2 is the weight associated to α_2 . Then a generating function can be obtained by Pólya's theorem as follows

$$\text{GF} = P_G(x_k \rightarrow \alpha_1^k + \alpha_2^k) \quad (18)$$

The coefficient of $w = \alpha_1^{n-1}\alpha_2$ in GF gives the number of magnetic equivalence classes of nuclei in \mathbf{D} or the NMR signals of nuclei in \mathbf{D} . Thus in order to enumerate the NMR signals, we need to evaluate the generating function.

Consider the molecule $\text{CH}_3\text{-CHClCH}_2\text{Cl}$. This molecule is nonrigid at room temperature. The symmetry group of this nonrigid molecule can be obtained as a generalized wreath product group. The symmetry groups of nonrigid molecules and their applications to several chemical applications have been considered by the present author in several publications.^{56,57,200-204} The generating function for $\text{CH}_3\text{-CHClCH}_2\text{Cl}$ is shown.

$$\text{GF} = \frac{1}{3}[(\alpha_1 + \alpha_2)^6 + 2(\alpha_1^3 + \alpha_2^3)(\alpha_1 + \alpha_2)^3] \quad (19)$$

The coefficient of $\alpha_1^5\alpha_2$ in the above expression is the number of proton signals at low resolution and is given by

$$\frac{1}{3}[\binom{6}{5} + 2\binom{3}{2}] = 4 \quad (20)$$

Thus there are four signals in the low-resolution NMR spectrum.

We now consider many examples of molecules whose ^{13}C and proton NMR signals will be enumerated. First, consider the polycyclic pericondensed benzenoid hydrocarbon shown in Figure 7. This molecule has 96-

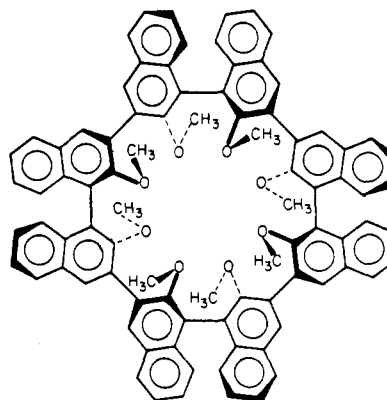


Figure 8. A chiral macrocycle. The ^{13}C and proton NMR signals of both rigid and nonrigid structures are enumerated in section IIIA.

carbon nuclei. The point group can be seen to be D_{6h} . The cycle index for these carbon nuclei is

$$P_G = \frac{1}{24}[2x_1^{96} + 4x_6^{16} + 4x_3^{32} + 8x_2^{48} + 6x_1^3x_2^{44}] \quad (21)$$

The number of ^{13}C signals is the coefficient of $\alpha_1^{95}\alpha_2$ in the appropriate generating function and can be seen to be 10. Consider the proton NMR of the same molecule. The cycle index for the transformation of protons is

$$P_G = \frac{1}{12}[x_1^{24} + 7x_2^{12} + 2x_6^4 + 2x_3^8] \quad (22)$$

The coefficient of $\alpha_1^{23}\alpha_2$ in the appropriate generating function is 2. One can immediately infer that this molecule gives rise to 10 ^{13}C resonances and two proton resonances. As another nontrivial example we consider the chiral macrocycle containing enforced cavities reported by Helgenson et al.²⁰⁵ It is shown in Figure 8. This chiral molecule possesses only a fourfold axis of rotation, and its point group can be seen to be C_4 . The cycle index for the ^{13}C NMR is

$$P_G = \frac{1}{4}[x_1^{88} + 2x_4^{22} + x_2^{44}] \quad (23)$$

From the coefficient of $\alpha_1^{87}\alpha_2$ in the generating function one infers that the low-resolution ^{13}C NMR of this molecule would contain 22 signals. This molecule has eight methyl rotors exhibiting torsion at room temperature and is thus an example of a nonrigid molecule. The symmetry of such a system can in general be described by generalized wreath product groups. The symmetry group of this nonrigid molecule is $C_4\{C_3\}$, where C_3 is the torsional group for each methyl protons. The cycle index of generalized wreath products can be obtained by using the method described elsewhere.⁵⁶ The cycle index for protons is

$$P_G = \frac{1}{4}[x_1^{40}Z_1^8 + 2x_4^{10}Z_4^2 + x_2^{20}Z_2^4] \quad (24)$$

where $Z_i = (\frac{1}{3})(x_i^3 + 2x_{3i})$. When the torsional permutations can be differentiated by NMR at feasible experimental conditions, the group becomes C_4 and the cycle index is

$$P_G = \frac{1}{4}[x_1^{64} + 2x_4^{16} + 3x_2^{32}] \quad (25)$$

The coefficients of $\alpha_1^{63}\alpha_2$ in the degenerating functions obtained from expressions 24 and 25 can be seen to be 12 and 16, indicating that the molecule would exhibit 16 proton resonances at very low temperatures in comparison to 12 resonances at high temperatures.

The generating function method outlined here can be applied to dynamic NMR spectroscopy. Consider the nonrigid PCl_5 molecule. Our method will explain the classical and well-known result that the NMR spectrum of the molecule PCl_5 contains only one signal. Even though the point group of the rigid PCl_5 molecule is D_{3h} , the rotational group of the nonrigid molecule, the nonrigidity introduced through the Berry mechanism, is S_5 . (S_5 stands for the symmetric group, containing $5!$ elements.) The coefficients of $\alpha_1^4\alpha_2$ in the NMR generating functions [26] and [27] of rigid and nonrigid molecules can be seen to be 2 and 1, respectively, explaining one NMR signal contrary to two signals.

$$\frac{1}{12}[(\alpha_1 + \alpha_2)^5 + 2(\alpha_1 + \alpha_2)^2(\alpha_1^3 + \alpha_2^3) + 3(\alpha_1 + \alpha_2) \times (\alpha_1^2 + \alpha_2^2)^2 + (\alpha_1 + \alpha_2)^3(\alpha_1^2 + \alpha_2^2) + 2(\alpha_1^2 + \alpha_2^2)(\alpha_1^3 + \alpha_2^3) + 3(\alpha_1 + \alpha_2)^3(\alpha_1^2 + \alpha_2^2)] \quad (26)$$

$$\frac{1}{120}[(\alpha_1 + \alpha_2)^5 + 10(\alpha_1 + \alpha_2)^3(\alpha_1^2 + \alpha_2^2) + 20(\alpha_1 + \alpha_2)^2(\alpha_1^3 + \alpha_2^3) + 30(\alpha_1 + \alpha_2)(\alpha_1^4 + \alpha_2^4) + 15(\alpha_1 + \alpha_2)(\alpha_1^2 + \alpha_2^2)^2 + 20(\alpha_1^2 + \alpha_2^2)(\alpha_1^3 + \alpha_2^3) + 24(\alpha_1^5 + \alpha_2^5)] \quad (27)$$

Another example exemplifying the effect of internal rotation on the NMR spectrum is propane. The symmetry groups of rigid and nonrigid molecules are C_{2v} and $C_{2v}[C_3, E]$, respectively. The NMR generating functions of the rigid and nonrigid propane are given by (28) and (29), respectively.

$$\frac{1}{4}[(\alpha_1 + \alpha_2)^8 + 2(\alpha_1 + \alpha_2)^2(\alpha_1^2 + \alpha_2^2)^3 + (\alpha_1^2 + \alpha_2^2)^4] \quad (28)$$

$$\frac{1}{36}[(\alpha_1 + \alpha_2)^8 + 4(\alpha_1 + \alpha_2)^5(\alpha_1^3 + \alpha_2^3) + 4(\alpha_1 + \alpha_2)^2(\alpha_1^3 + \alpha_2^3)^2 + 3(\alpha_1^2 + \alpha_2^2)^4 + 6(\alpha_1^2 + \alpha_2^2)(\alpha_1^6 + \alpha_2^6) + 12(\alpha_1 + \alpha_2)^2(\alpha_1^2 + \alpha_2^2)^3 + 6(\alpha_1 + \alpha_2)^2(\alpha_1^6 + \alpha_2^6)] \quad (29)$$

The coefficients of $\alpha_1^7\alpha_2$ in (28) and (29) are given by (30) and (31), respectively.

$$\frac{1}{4}[\binom{8}{1} + 2\binom{2}{1}] = 3 \quad (30)$$

$$\frac{1}{36}[\binom{8}{1} + 4\binom{5}{1} + 4\binom{2}{1} + 12\binom{2}{1} + 6\binom{2}{1}] = 2 \quad (31)$$

If one labels the two sets of methyl protons {1, 2, 3} and {6, 7, 8} and if the methylene protons are labeled 4 and 5, the eight protons are partitioned into the following three classes at very low temperatures with the convention that a σ_v plane of the C_{2v} group passes through the protons 1 and 6.

$$\{1, 6\}, \{4, 5\}, \{2, 3, 7, 8\}$$

Thus, at low temperature this method predicts three NMR signals, two due to two classes of methyl protons and one attributed to methylene proton with the intensity ratio 1:2:1. However, at high temperature the eight protons are partitioned into just two classes shown.

$$\{1, 2, 3, 6, 7, 8\}, \{4, 5\}$$

Consequently, at high temperature one observes only two signals with the intensity ratio 3:1 and the effect

of internal rotation is to coalesce the two NMR signals (1:2) due to methyl protons into one signal.

Since the barrier to rotation in propane is rather small, it is very difficult to resolve the coalesced signals at low temperature. Consider the NMR restricted to *tert*-butyl group of 3-chloro-2,2,3-trimethylpentane. Experimental dynamic NMR spectrum of this molecule was recorded by Roberts and co-workers.²⁰⁶ The symmetry group of the nonrigid molecule restricted to *tert*-butyl group at high temperature is $C_3[C_3]$. If temperature is not high enough for the molecule to tunnel through the barrier to rotation around the tertiary group, the symmetry group of the tertiary group becomes $E[C_3]$. If one considers the nine protons of tertiary group alone, the coefficient of $\alpha_1^8\alpha_2$ in the generating functions for $C_3[C_3]$ and $E[C_3]$ groups can be seen to be 1 and 3. This is in agreement with the experimentally observed spectrum²⁰⁶ of this molecule which shows three peaks at low temperature which are coalesced into one signal at high temperature.

Graph theory and combinatorics can be applied to high-resolution NMR spectra also. One needs to consider spin-spin couplings and the nature of NMR spin Hamiltonian for this problem. The present author¹⁹⁵ developed a graph theoretical method to characterize the symmetry group of NMR spin Hamiltonian and to classify the NMR spin functions. Operator methods were developed subsequently to generate NMR spin species and symmetry-adapted NMR spin functions.^{197,198} We only briefly review those methods here. For further details the readers are referred to 195, 197, and 198. The applications of group theory to simplifying NMR spin Hamiltonian were first considered by McConnell, McLean, and Reilly²⁰⁷ and Wilson.²⁰⁸ Soon after the development of symmetry groups of nonrigid molecules by Longuet-Higgins,²⁰⁹ Woodman^{210,211} showed that NMR groups of these molecules can be expressed as semidirect product groups. Flurry and Siddall²¹² developed the unitary group treatment for the NMR problem.

The NMR spin Hamiltonian can be defined as

$$\mathbf{H}_{\text{NMR}} = \sum_i \nu_i I_{z_i} + \sum_i \sum_{j < i} J_{ij} \vec{I}_i \cdot \vec{I}_j \quad (32)$$

where ν_i is the chemical shift of the *i*th nucleus and J_{ij} is the coupling constant between the nuclei *i* and *j*. The NMR group is defined as the set of permutations of nuclei that leave the NMR spin Hamiltonian invariant. In symbols, a permutation of the nuclei is in the NMR group if the corresponding permutation matrix \mathbf{P} satisfies

$$\mathbf{P}\mathbf{H}_{\text{NMR}}\mathbf{P}^{-1} = \mathbf{H}_{\text{NMR}} \quad (33)$$

The present author¹⁹⁵ showed that a diagrammatic representation of \mathbf{H}_{NMR} can be obtained by representing nuclei as vertices and edges by the coupling constants. Such a diagram is shown in Figure 9 for propane. The NMR graph in Figure 9 can be expressed as a composition of the graphs \mathbf{Q} and \mathbf{T}_1 and \mathbf{T}_2 shown in Figure 10. The graph in Figure 9 can be obtained by replacing vertices 1 and 3 of \mathbf{Q} in Figure 10 by a copy of \mathbf{T}_1 and the vertex 2 by a copy of \mathbf{T}_2 . Consequently, the NMR group of propane is expressible as a generalized wreath product. This group is $S_2[S_3, S_2]$. For details see ref 195.

One can use GCCI's for classifying NMR spin species.^{197,198} We review this here. Table I shows all the

TABLE I. GCCI's of $S_2[S_3, S_2]$: NMR Group of Butane

	x_1^{10}	$x_1^8 x_2$	$x_1^6 x_2^2$	$x_1^4 x_2^3$	$x_1^7 x_3$	$x_1^6 x_2 x_3$	$x_1^3 x_2^2 x_3$	$x_1^2 x_2^4$	$x_1 x_2^3 x_3$	$x_1^4 x_3^2$	$x_1^2 x_2 x_3^2$	$x_2^2 x_3^2$	x_2^5	$x_2^3 x_4$	$x_2^2 x_6$	$x_2 x_4^2$	$x_4 x_6$
A ₁	1	8	22	24	4	20	28	9	12	4	8	4	12	48	24	36	24
A ₂	1	8	22	24	4	20	28	9	12	4	8	4	-12	-48	-24	-36	-24
A ₃	1	4	-2	-12	4	4	-20	9	12	4	-8	4	12	24	24	-36	-24
A ₄	1	4	-2	-12	4	4	-20	9	12	4	-8	4	-12	-24	-24	36	24
A ₅	1	-4	-2	12	4	-4	-20	9	-12	4	8	4	12	-24	24	-36	24
A ₆	1	-4	-2	12	4	-4	-20	9	-12	4	8	4	-12	24	-24	36	-24
A ₇	1	-8	22	-24	4	-20	28	9	-12	4	-8	4	12	-48	24	36	-24
A ₈	1	-8	22	-24	4	-20	28	9	-12	4	-8	4	-12	48	-24	-36	24
E ₁	2	12	16	-12	8	24	-8	-18	-24	8	0	-8	0	0	0	0	0
E ₂	2	4	-16	-36	8	16	8	-18	0	8	16	8	0	0	0	0	0
E ₃	2	0	-20	0	8	0	-8	18	0	8	0	-8	0	0	0	0	0
E ₅	2	-4	-16	36	8	-16	8	-18	0	8	-16	8	0	0	0	0	0
E ₆	2	-12	16	12	8	-24	-8	-18	24	8	0	-8	0	0	0	0	0
G ₁	4	20	28	12	4	-4	-20	0	-12	-8	-16	-8	0	0	0	0	0
G ₂	4	12	-4	-12	4	-12	-4	0	12	-8	0	8	0	0	0	0	0
G ₄	4	4	-20	12	4	-20	28	0	-12	-8	16	-8	0	0	0	0	0
G ₅	4	8	4	0	-8	-16	-8	0	0	4	8	4	24	24	-24	0	-24
G ₆	4	8	4	0	-8	-16	-8	0	0	4	8	4	-24	-24	24	0	24
G ₇	4	-8	4	0	-8	16	-8	0	0	4	-8	4	24	-24	-24	0	24
G ₈	4	-8	4	0	-8	16	-8	0	0	4	-8	4	-24	24	24	0	-24
G ₉	4	-4	-20	-12	4	20	28	0	12	-8	-16	-8	0	0	0	0	0
G ₁₀	4	-12	-4	12	4	12	-4	0	-12	-8	0	8	0	0	0	0	0
G ₁₂	4	-20	28	-12	4	4	-20	0	12	-8	16	-8	0	0	0	0	0
K ₁	8	0	-8	0	-16	0	16	0	0	8	0	-8	0	0	0	0	0

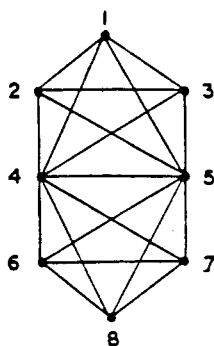


Figure 9. NMR graph of propane.

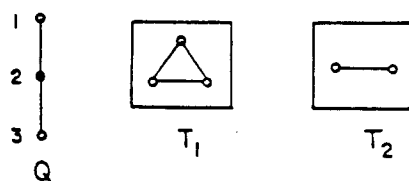
GCCI's of the NMR group of the butane molecule which is $S_2[S_3, S_2]$, a group of order 288. Note that GCCI's of the representation pairs (E_3, E_4), (G_2, G_3), and (G_{10}, G_{11}) are the same. Table I lists only the unique GCCI's. If one replaces every x_k in the GCCI's of butane by $\alpha^k + \beta^k$, one obtains the NMR spin species of butane. Consider the GCCI of G_1 representation in Table I. To obtain the proton spin multiplets of the nonrigid butane corresponding to G_1 , we replace every x_k by $\alpha^k + \beta^k$ in the GCCI of G_1 . This results in

$$\begin{aligned}
 GF^{G_1} = & \frac{1}{288} [4(\alpha + \beta)^{10} + 20(\alpha + \beta)^8(\alpha^2 + \beta^2) + \\
 & 28(\alpha + \beta)^6(\alpha^2 + \beta^2)^2 + 12(\alpha + \beta)^2(\alpha^2 + \beta^2)^3 + 4(\alpha + \\
 & \beta)^7(\alpha^3 + \beta^3) - 4(\alpha + \beta)^5(\alpha^2 + \beta^2)(\alpha^3 + \beta^3) - \\
 & 20(\alpha + \beta)^3(\alpha^2 + \beta^2)^2(\alpha^3 + \beta^3) - \\
 & 12(\alpha + \beta)(\alpha^2 + \beta^2)^3(\alpha^3 + \beta^3) - 8(\alpha + \beta)^4(\alpha^3 + \beta^3)^2 - \\
 & 16(\alpha + \beta)^2(\alpha^2 + \beta^2)(\alpha^3 + \beta^3)^2 - 8(\alpha^2 + \beta^2)^2(\alpha^3 + \beta^3)^2] \quad (34)
 \end{aligned}$$

The above expression upon simplification yields

$$GF^{G_1} = \alpha^9 \beta + 4\alpha^8 \beta^2 + 9\alpha^7 \beta^3 + 14\alpha^6 \beta^4 + 16\alpha^5 \beta^5 + 14\alpha^4 \beta^6 + 9\alpha^3 \beta^7 + 4\alpha^2 \beta^8 + \alpha \beta^9 \quad (35)$$

Thus there is $1G_1$ representation in the set of spin functions that have 9α 's and 1β , $4G_1$'s in the set of spin functions containing 8α 's and 2β 's, and $9G_1$'s in the set containing 7α 's and 3β 's, etc. The coefficient of $\alpha^{n_1}\beta^{n_2}$ generates number of times G_1 occurs in the set of spin

Figure 10. NMR graph of propane expressed as generalized composition of the graph Q with T_1 and T_2 .TABLE II. Proton NMR Species of Butane^a

Γ^{2S+1}	1	3	5	7	9	11
A ₁	0	5	3	4	1	1
A ₂	3	2	5	2	2	0
A ₃	0	1	0	1	0	0
A ₄	1	0	1	0	0	0
A ₅	0	0	0	0	0	0
A ₆	0	0	0	0	0	0
A ₇	0	0	0	0	0	0
A ₈	0	0	0	0	0	0
E ₁	1	3	3	2	1	0
E ₂	0	0	0	0	0	0
E ₃	0	0	0	0	0	0
E ₄	0	0	0	0	0	0
E ₅	0	0	0	0	0	0
E ₆	0	0	0	0	0	0
G ₁	2	5	5	3	1	0
G ₂	1	2	2	1	0	0
G ₃	1	2	2	1	0	0
G ₄	0	1	1	0	0	0
G ₅	0	3	1	1	0	0
G ₆	2	1	2	0	0	0
G ₇	0	1	0	0	0	0
G ₈	1	0	0	0	0	0
G ₉	0	0	0	0	0	0
G ₁₀	0	0	0	0	0	0
G ₁₁	0	0	0	0	0	0
G ₁₂	0	0	0	0	0	0
K ₁	1	2	1	0	0	0

^aNumbers are the frequencies of that spin species.

functions containing $n_1\alpha$'s and $n_2\beta$'s. Note that the term $\alpha^{n_1}\beta^{n_2}$ corresponds to the total two-component spin quantum number $M_F = (n_1 - n_2)/2$ so that if the coefficients in GF's are sorted in accordance to their M_F values, one obtains the proton NMR G_1 species as

$${}^1G_1(2), {}^3G_1(5), {}^5G_1(5), {}^7G_1(3), {}^9G_1(1)$$

TABLE III. $48P_G^x$ for Various Irreducible Representations in the Group O_h

irreducible representation	$48P_G^x$
A_{1g}	$x_1^6 + 8x_2^3 + 7x_3^3 + 6x_4^2x_4 + 9x_1^2x_2^2 + 6x_2x_4 + 8x_6 + 3x_1^4x_2$
A_{2g}	$x_1^6 + 8x_2^3 - 5x_3^3 - 6x_1^2x_4 - 3x_1^2x_2^2 - 6x_2x_4 + 8x_6 + 3x_1^4x_2$
E_g	$2x_1^6 - 8x_2^3 + 6x_1^2x_2^2 + 2x_3^3 - 8x_6 + 6x_1^4x_2$
T_{1g}	$3x_1^6 - 3x_2^3 + 6x_1^2x_4 - 9x_1^2x_2^2 + 6x_2x_4 - 3x_1^4x_2$
T_{2g}	$3x_1^6 + 9x_2^3 - 6x_1^2x_4 + 3x_1^2x_2^2 - 6x_2x_4 - 3x_1^4x_2$
A_{1u}	$x_1^6 + 8x_2^3 + 5x_3^3 + 6x_1^2x_4 - 3x_1^2x_2^2 - 6x_2x_4 - 8x_6 - 3x_1^4x_2$
A_{2u}	$x_1^6 + 8x_2^3 - 7x_3^3 - 6x_1^2x_4 + 9x_1^2x_2^2 + 6x_2x_4 - 8x_6 - 3x_1^4x_2$
E_u	$2x_1^6 - 8x_2^3 + 6x_1^2x_2^2 - 2x_3^3 + 8x_6 - 6x_1^4x_2$
T_{1u}	$3x_1^6 - 9x_2^3 + 3x_1^2x_2^2 + 6x_1^2x_4 - 6x_2x_4 + 3x_1^4x_2$
T_{2u}	$3x_1^6 + 3x_2^3 - 9x_1^2x_2^2 - 6x_1^2x_4 + 6x_2x_4 + 3x_1^4x_2$

The numbers in parentheses give the number of G_1 multiplets of the appropriate multiplicity. This can be briefly summarized in Table II where we give all the proton NMR multiplets of nonrigid butane obtained by using the GCCIs. If one is interested in the effect of nonrigidity on these spin species, one can construct the spin species in the NMR group of the rigid molecule and correlate the rigid and nonrigid species. Such a correlation can be easily obtained in the total representation as shown by the author in an earlier paper where he called the resulting diagram a coalescence diagram.¹⁹⁵

If one needs to obtain the deuterium NMR spin species of butane, all that one needs to do is to replace every x_k in the GCCIs in Table I by $\lambda^k + \mu^k + \nu^k$, where λ , μ , and ν are the weights corresponding to $m_f = -1$, 0, and 1, respectively, of the \mathbf{D} nucleus. One can then easily sort the coefficients in the generating function in accordance to their total M_F values and thus generate the multiplets.

The NMR spin Hamiltonian matrix can be blocked into a block-diagonal form if one constructs symmetry-adapted NMR spin functions in the NMR group. This aspect was considered by the present author.^{195,197,198} The readers are referred to these references for further details.

The use of GCCIs to enumerate the number of multiple quantum NMR signals is being considered by Balasubramanian and Pines.²¹³ One can differentiate dipolar couplings by orienting the molecule in liquid-crystal media and study its multiple quantum spectrum. Such spectra can reveal detailed information on the structure and can be much simpler for higher quantum spectra.

B. Molecular Spectroscopy

In this section, we show that the GCCIs defined in section IIB are useful in generating the nuclear spin statistical weights of the rovibronic levels. The methods reviewed in this section were developed in the present author's papers.^{214,215} Application of GCCIs to nuclear spin statistics of weakly bound van der Waals complexes was considered by Balasubramanian and Dyke.²¹⁶ Using these methods nuclear spin statistical weights of other complicated molecules like cubane (both normal and deuterated) and icosahedral borohydride ions were obtained by Balasubramanian, Pitzer, and Strauss.²¹⁷ Algorithms and computer programs for computing nuclear spin statistical weights, nuclear spin species were developed by the present investigator.^{218,219} The use of unitary group approach to study the hyperfine and superfine structure in the molecular spectra of mole-

cules such as SF_6 was considered by Harter and co-workers.^{220,221}

Almost any theory or experiment in molecular spectroscopy is concerned with the selection rules for rovibronic levels and the statistical weights of these levels which in turn yield information on the possible spectral lines and their intensities.^{222,223} The usual approach for finding the statistical weights of rovibronic levels is to find the character of the representation spanned by the nuclear spin species of the nuclei in the molecule and then take the inner product of the rovibronic species and nuclear spin species and see if this contains the species of the overall internal function which must obey the Pauli exclusion principle. For a molecule containing b_1 nuclei of the type 1, b_2 nuclei of the type 2, etc. with their possible number of spin states being a_1, a_2 , etc., there are $a_1^{b_1}a_2^{b_2}\dots$ spin functions. Even for a simple molecule like triphenylene there are 4096 spin functions. Consequently, to find the irreducible representations that these spin functions span, if one has to enumerate all the 4096 functions, look at their transformation properties, then get their characters and break them into irreducible representations, then this problem will probably remain unsolved for complex polyatomics. However, GCCIs are useful in generating the irreducible representations in a straightforward manner. For the problem of nuclear spin statistics, \mathbf{D} is the set of nuclei and \mathbf{R} is the set of possible spin states of the nuclei in \mathbf{D} . For a set of spin $1/2$ nuclei, \mathbf{R} would be a set consisting of two elements which can be denoted by α (spin up) and β (spin down). The image of \mathbf{F} is the set of spin functions. For example, the map f_1 from a set \mathbf{D} , consisting of four nuclei, labeled 1, 2, 3, and 4, to \mathbf{R} , which consists of the spin states α and β , is shown.

$$\begin{aligned} f_1(1) &= \alpha & f_1(2) &= \beta & f_1(3) &= \beta \\ f_1(4) &= \alpha \end{aligned} \quad (36)$$

Then the spin function generated by f_1 is $\alpha\beta\beta\alpha$. \mathbf{G} acts on the elements of \mathbf{F} by the procedure shown.

$$g(f(i)) = f(g^{-1}i) \text{ for every } i \in \mathbf{D}$$

To illustrate if we take g to be the permutation (1234), then $g^{-1} = (1432)$. Thus for the map f_1 shown above

$$\begin{aligned} gf_1(1) &= f_1(g^{-1}1) = f_1(4) = \alpha \\ gf_1(2) &= f_1(g^{-1}2) = f_1(1) = \alpha \\ gf_1(3) &= f_1(g^{-1}3) = f_1(2) = \beta \\ gf_1(4) &= f_1(g^{-1}4) = f_1(3) = \beta \end{aligned} \quad (37)$$

Thus by the action of the permutation (1234) on f_1 , the spin function $\alpha\beta\beta\alpha$ gets permuted to $\alpha\alpha\beta\beta$. Two functions f_i and f_j in \mathbf{F} are equivalent if there is a g in \mathbf{G} such that

$$f_i(d) = f_j(gd) \text{ for every } d \in \mathbf{D} \quad (38)$$

All equivalent maps can be grouped together, and they form an equivalence class which is called a pattern. Then \mathbf{G} divides \mathbf{F} into patterns.

If one associates a weight α to the spin state α and a weight β to the spin state β , then the generating function corresponding to the irreducible representation Γ with character χ is given by

$$GF^x = P_G^x(x_k \rightarrow \alpha^k + \beta^k) \quad (39)$$

TABLE IV. Generating Functions of Fluorine Species of SF₆

irreducible representation	GF
A _{1g}	$\alpha^6 + \alpha^5\beta + 2\alpha^4\beta^2 + 2\alpha^3\beta^3 + 2\alpha^2\beta^4 + \alpha\beta^5 + \beta^6$
A _{2g}	$\alpha^3\beta^3$
E _g	$\alpha^5\beta + 2\alpha^4\beta^2 + 2\alpha^3\beta^3 + 2\alpha^2\beta^4 + \alpha\beta^5$
T _{1g}	0
T _{2g}	$\alpha^4\beta^2 + \alpha^3\beta^3 + \alpha^2\beta^4$
A _{1u}	0
A _{2u}	$\alpha^3\beta^3$
E _u	0
T _{1u}	$\alpha^5\beta + \alpha^4\beta^2 + 2\alpha^3\beta^3 + \alpha^2\beta^4 + \alpha\beta^5$
T _{2u}	$\alpha^4\beta^2 + \alpha^3\beta^3 + \alpha^2\beta^4$

The coefficient of a typical term $\alpha^{a_1}\beta^{a_2}$ gives the number of times the irreducible representation Γ occurs in the reducible representation spanned by spin functions containing $a_1\alpha$'s and $a_2\beta$'s. In particular, the number of times the irreducible representation Γ occurs in the set of all spin functions is given by

$$n_{\Gamma} = P_G^x(x_k \rightarrow |\mathbf{R}|) \quad (40)$$

where $|\mathbf{R}|$ is the number of elements in one set \mathbf{R} .

Consider the ³³SF₆ molecule as an example. The set \mathbf{D} is the set of ¹⁹F nuclei. The set \mathbf{R} for F nuclei contains two elements since ¹⁹F is a spin $1/2$ nucleus and hence can take two possible spin states. We may associate the weights α and β to these states. To illustrate, consider the species E_g of the O_h group. The nuclear species which belong to this species can be obtained by replacing every x_k by $(\alpha^k + \beta^k)$ in the corresponding P_G^x . The result of this substitution is shown.

$$P_G^{E_g} = \frac{1}{48} [2x_1^6 - 8x_3^2 + 6x_1^2x_2^2 + 2x_2^3 - 8x_6 + 6x_1^4x_2] \quad (41)$$

Thus

$$GF^{E_g} = \frac{1}{48} [2(\alpha + \beta)^6 - 8(\alpha^3 + \beta^3)^2 + 6(\alpha + \beta)^2(\alpha^2 + \beta^2)^2 + 2(\alpha^2 + \beta^2)^3 - 8(\alpha^6 + \beta^6) + 6(\alpha + \beta)^4(\alpha^2 + \beta^2)] \quad (42)$$

The above expression on simplification yields

$$\alpha^5\beta + 2\alpha^4\beta^2 + 2\alpha^3\beta^3 + 2\alpha^2\beta^4 + \alpha\beta^5 \quad (43)$$

Thus there is one E_g in the reducible representation spanned by spin functions containing 5 α 's and 1 β , 2E_g in the reducible representation spanned by spin functions containing 4 α 's and 2 β 's, and so on. The generating functions thus obtained for the fluorine species are shown in Table IV. One can obtain the nuclear spin species by a simple examination of the generating functions. The coefficient of a typical term $\alpha^{a_1}\beta^{b_1}$ in a generating function corresponding to the species Γ gives the number of functions belonging to the species Γ with the spin quantum number $m_z = (a_1 - b_1)/2$. When these species are arranged according to their m_z values, they separate into spin multiplets with m_z varying from $-S$ to S . For example, the generating function which corresponds to A_{1g} gives rise to species ⁷A_{1g} and ³A_{1g}. In this manner when one groups the spin species into multiplets as obtained from their generating functions one obtains the fluorine species as ⁷A_{1g}, ³A_{1g}, ⁵E_g, ³E_g, ³T_{2g}, ¹A_{2u}, ⁵T_{1u}, ¹T_{1u}, and ³T_{2u}. The spin species of the ³³S nucleus is easily obtained as ⁴A_{1g} since the spin of ³³S nucleus is $3/2$. The overall spin species is the direct

product of sulfur and fluorine species. A typical direct product of the species $\mathbf{D}_i^{s_1}$ and $\mathbf{D}_j^{s_2}$, $\mathbf{D}_i^{s_1} \times \mathbf{D}_j^{s_2}$, decomposes into a Clebsch-Gordan series³⁵

$$\mathbf{D}_i^{s_1} \times \mathbf{D}_j^{s_2} = \sum_k \sum_{s=|s_1-s_2|}^{s_1+s_2} \mathbf{D}_k^s \quad (44)$$

where

$$\mathbf{D}_i \times \mathbf{D}_j = \sum_k \mathbf{D}_k \quad (45)$$

the direct sum of irreducible representations \mathbf{D}_k 's contained in $\mathbf{D}_i \times \mathbf{D}_j$. This way we obtain the overall spin species as ¹⁰A_{1g}, ⁶A_{1g}(2), ⁴A_{1g}(2), ²A_{1g}, ⁴A_{2g}, ⁸E_g, ⁶E_g(2), ⁴E_g(2), ²E_g(2), ⁶T_{2g}, ⁴T_{2g}, ²T_{2g}, ⁴A_{2u}, ⁸T_{1u}, ⁶T_{1u}, ⁴T_{1u}(2), ²T_{1u}, ⁶T_{2u}, ⁴T_{2u}, and ²T_{2u}. All these spin species span a reducible representation which is decomposed into the irreducible representations of O_h by adding all the multiplicities times the frequency of the same species. The result is shown.

$$\Gamma^{\text{spin}}(\text{SF}_6) = 40A_{1g} + 4A_{2g} + 32E_g + 12T_{2g} + 4A_{2u} + 24T_{1u} + 12T_{2u} \quad (46)$$

If one is interested in obtaining Γ^{spin} instead of the actual spin multiplets, then this can be generated directly by expression 40 without generating the nuclear spin multiplets. For the purpose of statistical weights of rovibronic levels, we need Γ^{spin} only rather than the whole spin multiplet pattern.

This method can be applied easily to complex polyatomic molecules. Consider triphenylene in two forms as examples of such molecules. The point group of triphenylene can be easily seen to be D_{3h} whose character table can be readily obtained. We now consider [¹²C]triphenylene. In this molecule only the 12 protons possess nuclear spin, and hence we consider \mathbf{D} as just the set of these protons. The various cycle indices for these protons are shown.

$$P^{A_1'} = \frac{1}{12} (2x_1^{12} + 4x_3^4 + 6x_2^6) \quad (47)$$

$$P^{A_2'} = \frac{1}{12} (2x_1^{12} + 4x_3^4 - 6x_2^6) \quad (48)$$

$$P^{E'} = \frac{1}{12} (4x_1^{12} - 4x_3^4) \quad (49)$$

All the other cycle indices are zero. The number of A₁'s, A₂'s, and E's in Γ_H^{spin} are shown.

$$N(A_1') = \frac{1}{6} (2^{12} + 2 \cdot 2^4 + 3 \cdot 2^6) = 720 \quad (50)$$

$$N(A_2') = \frac{1}{6} (2^{12} + 2 \cdot 2^4 - 3 \cdot 2^6) = 656 \quad (51)$$

$$N(E') = \frac{1}{6} (2 \cdot 2^{12} - 2 \cdot 2^4) = 1360 \quad (52)$$

Thus

$$\Gamma_H^{\text{spin}} = 720A_1' + 656A_2' + 1360E' \quad (53)$$

When all the ¹²C carbon nuclei are replaced by ¹³C carbon nuclei, then we have to consider the set of 18 carbon atoms to obtain Γ^{spin} . We now let \mathbf{D} be the set of ¹³C carbon nuclei and \mathbf{R} as their spin states. Then the various cycle indices are as follows

$$P^{A_1'} = \frac{1}{6} [x_1^{18} + 2x_3^6 + 3x_2^9] \quad (54)$$

$$P^{A_2'} = \frac{1}{6} [x_1^{18} + 2x_3^6 - 3x_2^9] \quad (55)$$

$$P^{E'} = \frac{1}{6} [2x_1^{18} - 2x_3^6] \quad (56)$$

TABLE V. Proton Species of Benzene Dimer

Γ	spin species
A ₁	¹³ A ₁ (1), ⁹ A ₁ (3), ⁷ A ₁ (2), ⁵ A ₁ (6), ³ A ₁ (1), ¹ A ₁ (4)
A ₂	¹¹ A ₂ (1), ⁹ A ₂ (2), ⁷ A ₂ (3), ⁵ A ₂ (3), ³ A ₂ (4), ¹ A ₂ (1)
A ₃	¹ A ₃ (1)
A ₄	none
A ₅	⁵ A ₅ (1), ¹ A ₅ (1)
A ₆	³ A ₆ (1)
A ₇	⁹ A ₇ (1), ⁵ A ₇ (3), ¹ A ₇ (4)
A ₈	⁷ A ₈ (1), ⁵ A ₈ (2), ³ A ₈ (1), ¹ A ₈ (1)
E ₁	⁷ E ₁ (1), ³ E ₁ (2)
E ₂	⁹ E ₂ (1), ⁷ E ₂ (1), ⁵ E ₂ (3), ³ E ₂ (2), ¹ E ₂ (2)
E ₃	¹¹ E ₃ (1), ⁹ E ₃ (1), ⁷ E ₃ (5), ⁵ E ₃ (3), ³ E ₃ (7)
E ₄	³ E ₄ (1)
E ₅	⁵ E ₅ (1), ¹ E ₅ (2)
E ₆	⁷ E ₆ (1), ⁵ E ₆ (1), ³ E ₆ (3)
G ₁	¹¹ G ₁ (1), ⁹ G ₁ (2), ⁷ G ₁ (5), ⁵ G ₁ (6), ³ G ₁ (7), ¹ G ₁ (2)
G ₂	¹¹ G ₂ (1), ⁹ G ₂ (3), ⁷ G ₂ (5), ⁵ G ₂ (9), ³ G ₂ (7), ¹ G ₂ (4)
G ₃	⁵ G ₃ (1), ³ G ₃ (1), ¹ G ₃ (1)
G ₄	⁵ G ₄ (1), ³ G ₄ (2)
G ₅	⁷ G ₅ (1), ⁵ G ₅ (2), ³ G ₅ (3), ¹ G ₅ (1)
G ₆	⁷ G ₆ (1), ⁵ G ₆ (3), ³ G ₆ (3), ¹ G ₆ (2)
G ₇	⁹ G ₇ (1), ⁷ G ₇ (2), ⁵ G ₇ (5), ³ G ₇ (4), ¹ G ₇ (3)
G ₈	⁹ G ₈ (1), ⁷ G ₈ (3), ⁵ G ₈ (5), ³ G ₈ (7), ¹ G ₈ (1)
G ₉	⁹ G ₉ (1), ⁷ G ₉ (1), ⁵ G ₉ (4), ³ G ₉ (2), ¹ G ₉ (3)
G ₁₀	⁷ G ₁₀ (2), ⁵ G ₁₀ (2), ³ G ₁₀ (4)
G ₁₁	⁹ G ₁₁ (1), ⁷ G ₁₁ (2), ⁵ G ₁₁ (6), ³ G ₁₁ (3), ¹ G ₁₁ (4)
G ₁₂	⁷ G ₁₂ (3), ⁵ G ₁₂ (3), ³ G ₁₂ (6), ¹ G ₁₂ (1)
K	⁹ K(1), ⁷ K(4), ⁵ K(7), ³ K(8), ¹ K(3)

The other cycle indices are zeros. Thus $N(A_1')$, $N(A_2')$, and $N(E')$ for carbon species are shown.

$$N(A_1') = \frac{1}{6}(2^{18} + 2 \cdot 2^6 + 3 \cdot 2^9) = 43\,968 \quad (57)$$

$$N(A_2') = \frac{1}{6}(2^{18} + 2 \cdot 2^6 - 3 \cdot 2^9) = 43\,456 \quad (58)$$

$$N(E') = \frac{1}{6}(2 \cdot 2^{18} - 2 \cdot 2^6) = 87\,360 \quad (59)$$

Hence

$$\Gamma_C^{\text{spin}} = 43\,968 A_1' + 43\,456 A_2' + 87\,360 E' \quad (60)$$

The overall species, $\Gamma^{\text{spin}} = \Gamma_C^{\text{spin}} \times \Gamma_H^{\text{spin}}$, is given by (61).

$$\Gamma^{\text{spin}} = 178\,973\,696 A_1' + 178\,940\,928 A_2' + 357\,913\,600 E' \quad (61)$$

One can obtain the statistical weights from Γ^{spin} easily. This is done by stipulating that $\Gamma^{\text{spin}} \times \Gamma^{\text{rve}}$ should contain Γ^{int} , where Γ^{rve} is the rovibronic species and Γ^{int} is the species of the overall internal wave function. By the Pauli exclusion principle Γ^{int} must be antisymmetric and hence the character of Γ^{int} must be -1 with respect to permutations for fermions. For bosons it must be $+1$. Since 18 ¹³C nuclei of [¹³C]triphenylene transform as χ_2^9 under the operation c_2 and since they are fermions, Γ^{int} is A_2' or A_2'' . Thus the statistical weights are as follows:

$$A_1'(178\,940\,928), A_2'(178\,973\,696), E'(357\,913\,600), \\ A_1''(178\,940\,928), A_2''(178\,973\,696), E''(357\,913\,600)$$

The method of GCCI's can be applied to nonrigid molecules also. The readers are referred to ref 215 for applications to nonrigid molecules.

Balasubramanian and Dyke²¹⁶ have considered very recently, applications of GCCI's and other group theoretical techniques to obtain correlation tables, nuclear spin statistical weights, and nuclear spin species of weakly bound van der Waals complexes such as benzene dimer, synthesized in a supersonic beam. We show the

TABLE VI. Correlation Table for (C₆H₆)₂ and (C₆D₆)₂

	C_2	$S_2[D_6] \times I$
(C ₆ H ₆) ₂ A ₁ [±] (1984)		A ₁ [±] (28) + A ₂ [±] (21) + A ₅ [±] (1) + A ₆ [±] (0) E ₁ [±] (21) + E ₃ [±] (91) + E ₄ [±] (3) + 2E ₅ [±] (39) + E ₆ [±] (13) + G ₁ [±] (77) + 3G ₂ [±] (63) + 3G ₃ [±] (33) + G ₄ [±] (27) + 3G ₅ [±] (11) + G ₆ [±] (9) + G ₇ [±] (143) + 3G ₈ [±] (117) + 2G ₉ [±] (66) + 2G ₁₀ [±] (55) + 2G ₁₁ [±] (45) + 2G ₁₂ [±] (36) + 4K [±] (99)
(C ₆ D ₆) ₂ A ₁ [±] (266814)		A ₁ [±] (4278) + A ₂ [±] (4186) + A ₅ [±] (1081) + A ₆ [±] (1035) + E ₁ [±] (3496) + E ₃ [±] (6716) + E ₄ [±] (1748) + 2E ₅ [±] (2774) + E ₆ [±] (3358) + G ₁ [±] (10672) + 3G ₂ [±] (11408) + 3G ₃ [±] (4408) + G ₄ [±] (4712) + 3G ₅ [±] (5336) + G ₆ [±] (5704) + G ₇ [±] (8468) + 3G ₈ [±] (9052) + 2G ₉ [±] (6786) + 2G ₁₀ [±] (6670) + 2G ₁₁ [±] (7750) + 2G ₁₂ [±] (7626) + 4K [±] (14384)
(C ₆ H ₆) ₂ A ₂ [±] (2112)		A ₃ [±] (6) + A ₄ [±] (3) + A ₇ [±] (91) + A ₈ [±] (78) + E ₁ [±] (21) + 2E ₂ [±] (7) + E ₃ [±] (91) + E ₄ [±] (3) + E ₆ [±] (13) + 3G ₂ [±] (77) + G ₂ [±] (63) + G ₃ [±] (33) + 3G ₄ [±] (27) + G ₅ [±] (11) + 3G ₆ [±] (9) + 3G ₇ [±] (143) + G ₈ [±] (117) + 2G ₉ [±] (66) + 2G ₁₀ [±] (55) + 2G ₁₁ [±] (45) + 2G ₁₂ [±] (36) + 4K [±] (99)
(C ₆ D ₆) ₂ A ₂ [±] (264627)		A ₃ [±] (741) + A ₄ [±] (703) + A ₇ [±] (2701) + A ₈ [±] (2628) + E ₁ [±] (3496) + 2E ₂ [±] (4232) + E ₃ [±] (6716) + E ₄ [±] (1748) + E ₆ [±] (3358) + 3G ₁ [±] (10672) + G ₂ [±] (11408) + G ₃ [±] (4408) + 3G ₄ [±] (4712) + G ₅ [±] (5336) + 3G ₆ [±] (5704) + 3G ₇ [±] (8468) + G ₈ [±] (9052) + 2G ₉ [±] (6786) + 2G ₁₀ [±] (6670) + 2G ₁₁ [±] (7750) + 2G ₁₂ [±] (7626) + 4K [±] (14384)

nuclear spin species for benzene dimer in Table V and the rovibronic correlation table including the spin statistical weights in Table VI. In Table VI, the equilibrium geometry of the benzene dimer is assumed to be T-shaped.

C. NQR Spectra of Crystals

NQR spectroscopy of crystals uses a quadrupolar nucleus as a probe to detect and estimate electric field gradients in crystals.²²⁴⁻²²⁵ A problem in interpreting complex NQR spectra of crystals is to theoretically obtain these NQR spectral patterns which should include the number of NQR lines and their intensity ratios in a given crystalline environment. NQR frequency is quite sensitive to minute differences in electric field gradients, and thus this method is very useful in investigating crystals exhibiting phase transition. At the critical temperature the symmetry of the crystal usually changes. This is in turn reflected in their NQR spectra. Sutton and Armstrong²²⁶ have recently studied the NQR spectra of antiferroite crystals in various phases. It would be valuable to have an easy theoretical method to obtain NQR spectral patterns so that given the symmetry of the unit cell of the crystal under consideration, one can predict the NQR spectral patterns. Conversely, this method would be of immense use in assigning the symmetries of the various phases. This method was recently developed by the present author.²²⁷

Let \mathbf{G} be the point group corresponding to the space group of the crystal. Let \mathbf{D} be the set of nuclei. Then each operation $g \in \mathbf{G}$ can be considered as a permutation or permutation-inversion operation on \mathbf{D} . Let \mathbf{R} be a set containing just two elements denoted by α_1 and α_2 . Let f_i be a map from \mathbf{D} to \mathbf{R} defined as follows

$$f_i(d_j) = \begin{cases} \alpha_1 & \text{if } i \neq j, d_j \in \mathbf{D} \\ \alpha_2 & \text{if } i = j \end{cases} \quad (62)$$

Two maps f_i and f_j ($i \neq j$) are equivalent if there is a $g \in \mathbf{G}$ such that

$$f_i(gd) = f_j(d) \text{ for every } d \in \mathbf{D} \quad (63)$$

The above relation divides the set \mathbf{F} of all maps from \mathbf{D} to \mathbf{R} into equivalence classes. It can be easily seen that the equivalence classes of \mathbf{F} are the equivalence classes of nuclei. This is because if f_i and f_j are equivalent, then the nuclei d_i and d_j are also equivalent. With each $r \in \mathbf{R}$ let us associate a weight $w(r)$. For example, with α_1 associate a weight α_1 and with α_2 associate a weight α_2 . Define the weight of any $f \in \mathbf{F}$ as in section II of this review. The weight of any map f_i is $\alpha_1^{N-1}\alpha_2$ if N is the number of nuclei in \mathbf{D} . Pólya's theorem gives a generating function for the equivalence classes of maps by the following substitution in the cycle index.

$$\text{GF} = P_{\mathbf{G}}[x_k \rightarrow \sum_{r \in \mathbf{R}} w(r)^k] \quad (64)$$

The coefficient of $\alpha_1^{N-1}\alpha_2$ (N being the total number of nuclei) gives the number of equivalence classes of nuclei under the action of \mathbf{G} .

This can be illustrated with the example of fluorine NQR spectrum of antiferroite crystals with O_h symmetry. If one replaces every x_k in the cycle index of P_{O_h} by $\alpha_1^k + \alpha_2^k$, one obtains

$$\begin{aligned} \text{GF}_{O_h} = & \frac{1}{48}[(\alpha_1 + \alpha_2)^6 + 8(\alpha_1^3 + \alpha_2^3)^2 + 9(\alpha_1 + \alpha_2)^2(\alpha_1^2 \\ & + \alpha_2^2)^2 + 6(\alpha_1 + \alpha_2)^2(\alpha_1^4 + \alpha_2^4) + 7(\alpha_1^2 + \alpha_2^2)^3 + 8(\alpha_1^6 \\ & + \alpha_2^6) + 3(\alpha_1 + \alpha_2)^4(\alpha_2^2 + \alpha_1^2) + 6(\alpha_1^2 + \alpha_2^2)(\alpha_1^4 + \alpha_2^4)] \end{aligned} \quad (65)$$

The coefficient of $\alpha_1^5\alpha_2$ in the above expression is 1, indicating that all the nuclei are equivalent under the O_h symmetry. Consider the same crystal with distortions which correspond to C_{4h} and C_i subgroups of the O_h group. The cycle indices for C_{4h} and C_i are

$$P_{C_{4h}} = \frac{1}{8}[x_1^6 + 2x_1^2x_4 + x_1^2x_2^2 + x_1^4x_2 + 2x_2x_4 + x_2^3] \quad (66)$$

$$P_{C_i} = \frac{1}{2}[x_1^6 + x_2^3] \quad (67)$$

The corresponding generating functions are

$$\begin{aligned} \text{GF}_{C_{4h}} = & \frac{1}{8}[(\alpha_1 + \alpha_2)^6 + 2(\alpha_1 + \alpha_2)^2(\alpha_1^4 + \alpha_2^4) + (\alpha_1 + \\ & \alpha_2)^2(\alpha_1^2 + \alpha_2^2)^2 + (\alpha_1 + \alpha_2)^4(\alpha_1^2 + \alpha_2^2) + 2(\alpha_1^2 + \\ & \alpha_2^2)(\alpha_1^4 + \alpha_2^4) + (\alpha_1^2 + \alpha_2^2)^3] \end{aligned} \quad (68)$$

$$\text{GF}_{C_i} = \frac{1}{2}[(\alpha_1 + \alpha_2)^6 + (\alpha_1^2 + \alpha_2^2)^3] \quad (69)$$

The coefficient of $\alpha_1^5\alpha_2$ in these generating functions are 2 and 3, indicating 2 and 3 equivalence classes under the action of C_{4h} and C_i symmetries. Thus a single fluorine NQR line of an antiferroite crystal splits into two lines for a distorted crystal with C_{4h} symmetry and three lines for a crystal with C_i symmetry. This is consistent with the observation of Sutton and Armstrong.²²⁶

V. Applications to Quantum Chemistry

In this section, we review some of the important developments in the applications of graph theoretical and combinatorial techniques to quantum chemistry. Although, this review will focus on applications to secular equations, symmetry-adaptation and CI calculations,

we first review other important applications which have been considered in some depth elsewhere.

Sinanoglu²²⁸⁻²³¹ has recently given algebraic and graph theoretical formulation of structure of quantum chemistry and kinetics. In this formalism molecules are classified into equivalence classes (L-equivalence classes) by introducing an equivalence relation (L) using a set of nonunitary transformations belonging to several linear groups. Molecules in the same class have the same energy level patterns thereby facilitating a technique to arrive at energy level patterns based on L equivalences. Sinanoglu has derived simple qualitative rules for electronic properties such as reactivity, rough energetics, etc. For details of the topological and graph theoretical techniques used for these problems, the readers are referred to ref 228-231.

Mezey²³²⁻²⁴⁶ has formulated a new framework called "reaction topology". This enables description of molecular structure, conformational changes, and reaction mechanism. In the last few years, Mezey has published well over 40 publications in this area. Since molecules are best described by quantum mechanical probability distributions, a mathematical framework of topology is better suited to describe molecules and chemical reactions than their associated geometries. The concept of nuclear position is then best described with the quantum-topological concept of "open set" which describes a distribution of nuclear positions rather than a deterministic value for the nuclear position. Mezey has shown that topological framework is extremely useful in answering several practical chemical questions related to the enumeration of possible chemical species and chemical reactions for a given collection of nuclei and a fixed number of electrons. Mezey defined a topological matrix called "reachability matrix" on reaction networks. Several graph theoretical matrices such as adjacency matrix, distance matrix, etc. have close ties with reaction topology and are extremely useful in conventional synthesis planning. For further details on this topic the readers are referred to ref 244 and 245.

Bader and co-workers²⁴⁷⁻²⁵¹ have shown that the gradient of charge density and the associated diagrams are extremely useful in formulating a new theory of molecular structure. The investigation of the topological properties of the molecular charge distribution leads to prediction of structural stability. The mechanisms of structural changes can be discussed by using Rene Thom's theory of catastrophes. Bader²⁴⁹ has shown, for example, the formation and destruction of a cage structure in the molecule C_5H_6 ([1.1.1]propellane) can be explained through a function known as the unfolding of elliptic umbilic. One can formulate a molecular graph based on the charge density gradient diagrams. The properties of the graph and the associated critical points are then shown to be useful in predicting structural stabilities.²⁴⁹ This topic was reviewed by Bader and co-workers.^{247,249} The readers are directed to these reviews for further details.

In the ensuing subsections, we review some other applications of graph theory and combinatorics to quantum chemistry.

A. Characteristic Polynomials of Graphs

Characteristic polynomials of graphs are structural invariants and have several important applications to

chemical problems.²⁵²⁻²⁹⁷ (Also see ref 111-163 in relationship to applications to aromaticity and topological properties of conjugated systems.) The relationship between the adjacency matrix of a graph defined in section IIC and the Hückel matrix in the theory of π electrons is well-known. Chemists have recognized this intimate relationship and have used graph theoretical techniques to derive or rederive many of the quantum chemical results for the π -electrons. A number of papers have appeared in the chemical and mathematical literature dealing with characteristic polynomials and their applications. Since the present review is more broad, we have only cited some of the references in the literature. We review here only some of the recent developments in this area. The authors are referred to the articles by Rouvray¹⁰⁷ and Rouvray and Balaban²⁸⁴ for some of the earlier developments such as the use of Sach's theorem to derive the characteristic polynomials.

Characteristic polynomials are useful in discussing the electronic properties of polymers and periodic structures.^{291,296} They are useful in determining the stability of conjugated systems.²⁹⁶ The present author²⁹¹ recently showed that characteristic polynomials of very large periodic networks and organic polymers can be very easily derived and are extremely useful in electronic structure calculations of these systems.

Characteristic polynomials are the generators for the number of ways dimers can be placed on tree lattices and Bethe lattices since the coefficients of various terms in the polynomial generate the number of ways of placing a given set of disjoint dimers on the corresponding lattice. Exact finite lattice statistics is a useful way of obtaining the grand canonical partition function of a lattice gas. Thus characteristic polynomials and the associated acyclic or matching polynomials have potential applications in statistical mechanics.

Characteristic polynomials find applications in other areas of chemical physics such as chemical kinetics, dynamics of oscillatory chemical reactions, and fluid mechanics (in solving Navier-Stokes equation).

The coefficients in the characteristic polynomials of graphs are useful in the formulation of topological indices such as Hosoya index which are useful in correlating the physical (thermodynamic) properties of molecules with their topological properties. The interested readers are also referred to the recent book by Bonchev²⁹⁸ for further information on this topic.

The characteristic polynomial of a graph is defined as the secular determinant of the adjacency matrix of the graph, where the adjacency matrix was defined in section IIC. In symbols

$$P_G(\lambda) = |\mathbf{A} - \lambda\mathbf{I}|$$

where \mathbf{I} is the identity matrix of the same order as \mathbf{A} . The direct evaluation of this polynomial involves determinant expansion. Since determinant expansion is a computationally tedious problem, it is not suitable for large graphs. Thus the evaluation of characteristic polynomials of graphs containing a large number of vertices is a very difficult problem because of the above-mentioned combinatorial complexity. In recent years, several imaginative methods have been developed to evaluate the characteristic polynomials.

The present author²⁶⁸ developed a tree-pruning method to generate the characteristic polynomial of trees. In this method, the tree whose polynomial is in question

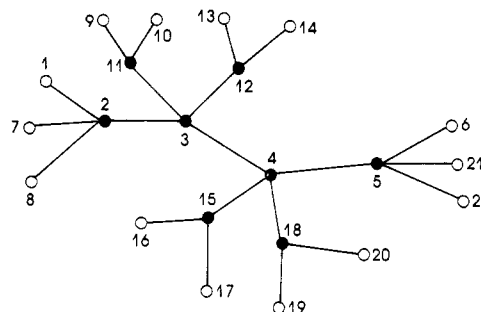


Figure 11. A tree containing 22 vertices. The characteristic polynomial of this tree can be obtained by pruning this tree. See section IVA.

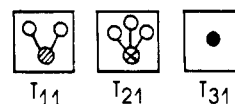
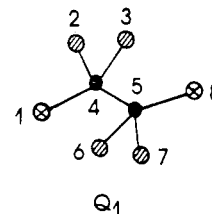


Figure 12. Q_1 is obtained by pruning the tree in Figure 11. T_{11} , T_{21} , and T_{31} are the typical fragments resulting in the process of pruning.

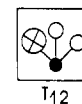
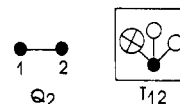


Figure 13. Q_2 is the tree obtained by pruning the tree Q_1 in Figure 12. T_{12} is a typical fragment.

is pruned at branches and simplified to smaller trees and fragments resulting in the process of pruning. We briefly review this method here. The vertices of a tree with degree (valence) 1 can be defined as the roots or joints of a tree. The joint and the leaves connected to this joint together constitute a branch. Any tree can be pruned at such joints resulting in a smaller tree and the branches or fragments. To illustrate, consider the tree Γ in Figure 11. The vertices 1, 6, 7, 8, 9, 10, 13, 14, 16, 17, 19, 20, 21, and 22 are the leaves and the vertices 2, 3, 4, 5, 11, 12, 15, and 18 are the roots and joints. When the tree in Figure 11 is pruned at the joints 2, 3, 4, 5, 11, 12, 15, and 18, one obtains a smaller tree Q_1 shown in Figure 12 and the fragments T_{11} , T_{21} , and T_{31} . Note that all the similar fragments have been grouped together in a box. Equivalently, the tree in Figure 11 can be obtained by attaching the roots 1 and 8 of Q_1 in Figure 12 to the root of a copy of T_{11} , the roots 2, 3, 6, and 7 to the root of a copy of T_{21} , and roots 4 and 5 to the root of T_{31} . This product was formulated by Balasubramanian⁵⁶ and was referred to as root-to-root product. This pruning process has brought the tree in Figure 11 to a much smaller tree in Figure 12 and the fragments resulting from the pruning process. The advantage of this pruning procedure is that several graph-theoretical properties of a bigger tree can be obtained in terms of the corresponding properties of the pruned tree and smaller fragments. The pruning pro-

cess can be iterated until one obtains a very simple tree whose characteristic polynomial can be obtained easily. Consider, for example, the tree in Figure 12. This tree can be pruned further to the tree Q_2 in Figure 13 and the fragment T_{12} . The tree Q_2 in Figure 12 has only two vertices, and thus the properties of Q_2 and T_{12} can be obtained very easily.

Let Q be the tree generated in the process of pruning and T_i 's be the corresponding fragments. Let H_i be the characteristic polynomial of the type T_i . Let H'_i be the characteristic polynomial of the fragment T_i with the root of T_i deleted. Let the vertices of Q be partitioned into the sets Y_1, Y_2, \dots such that all the vertices in Y_i when attached to a copy of the same fragment generates the original tree. Define a matrix A as follows

$$A_{ij} = \begin{cases} H_k & \text{if } i = j \text{ and } i \in Y_k \\ -H'_{kq_{ij}} & \text{if } i \neq j \text{ and } i \in Y_k \end{cases} \quad (70)$$

The determinant of the matrix A is the characteristic polynomial of the original tree. The advantage of this method is that it provides for the characteristic polynomial of a big tree in terms of the characteristic polynomials of smaller trees.

The process outlined above can be iterated until one obtains a sufficiently small tree so that its characteristic polynomial can be easily determined. Let Q_j be the tree generated in the j th iteration. Let T_{ij} be a fragment type obtained in the j th iteration. Let the vertices of Q_j be partitioned into sets Y_{ij} 's such that all the vertices in a set Y_{ij} are attached to a copy of the same fragment type T_{ij} . Let a matrix element of the adjacency matrix of T_i be $t_{lm}^{(ij)}$. Then define a matrix $D^{(i,j)}$ as follows

$$D^{(i,j)} = \begin{cases} H_{k,j-1} & \text{if } l = m \text{ and } l \in Y_{k,j-1} \\ -H'_{k,j-1} t_{lm}^{(ij)} & \text{if } l \neq m \text{ and } l \in Y_{k,j-1} \end{cases} \quad (71)$$

where $H_{k,j-1}$ is the secular determinant of the matrix $D^{(k,j-1)}$ and $H'_{k,j-1}$ is the secular determinant of the matrix $D^{(k,j-1)}$ which is obtained by deleting the row and column in the matrix $D^{(k,j-1)}$ corresponding to the root of $T_{k,j-1}$. H_{kl} is simply the characteristic polynomial of the type T_{kl} . If the type T_{kl} contains i vertices, this characteristic polynomial will be denoted as h_i and the polynomial obtained by deleting the root of T_{kl} is h'_i . Note that in general $h_i = x^i - (i-1)x^{i-2}$ and $h'_i = x^{i-1}$.

Suppose n is the last step of pruning. Then define a matrix A as follows

$$A_{lm} = \begin{cases} H_{k,n} & \text{if } l = m \text{ and } l \in Y_{k,n} \\ -H'_{k,n} q_{lm}^{(n)} & \text{if } l \neq m \text{ and } l \in Y_{k,n} \end{cases} \quad (72)$$

where $q_{lm}^{(n)}$ is an element of the adjacency matrix of the tree Q_n generated in the final iteration. The determinant of the matrix A defined above is the characteristic polynomial of the tree we started with.

Let us now illustrate this procedure with the example of the tree in Figure 11. The tree in Figure 11 is pruned to the tree in Figure 12, finally to the tree in Figure 13 in the second step of the iteration. All the relevant matrices and characteristic polynomials are shown.

$$H_{11} = h_3, H'_{11} = h'_3, H_{21} = h_4, H'_{21} = h'_4, H_{31} = h_1, \text{ and } H'_{31} = 1 \quad (73)$$

$$D^{(12)} = \begin{bmatrix} h_4 & 0 & 0 & -h'_4 \\ 0 & h_3 & 0 & -h'_3 \\ 0 & 0 & h_3 & -h'_3 \\ -1 & -1 & -1 & h_1 \end{bmatrix} \quad (74)$$

$$D^{(12)} = \begin{bmatrix} h_4 & 0 & 0 \\ 0 & h_3 & 0 \\ 0 & 0 & h_3 \end{bmatrix} \quad (75)$$

$$H_{12} = h_3^2 h_4 h_1 - 2h_3 h'_3 h_4 - h_3^2 h'_4 \quad (76)$$

$$H'_{12} = h_3^2 h_4 \quad (77)$$

$$A^{(2)} = \begin{bmatrix} H_{12} & -H'_{12} \\ -H'_{12} & H_{12} \end{bmatrix} \quad (78)$$

$$\det(A^{(2)}) = H_{12}^2 - H_{12}'^2 \quad (79)$$

By substituting $h_i = x^i - (i-1)x^{i-2}$ and $h'_i = x^{i-1}$, we obtain the following expression for the characteristic polynomial of the tree in Figure 11.

$$x^{10}(x^6 - 10x^4 + 30x^2 - 28)^2 - x^8(x^6 - 7x^4 + 10x^2 - 12) \quad (80)$$

Thus the characteristic polynomial of a tree of 22 vertices was easily obtained by this method.

The present author²⁸⁸ recently showed that an algebraic method which was attributed by Dwyer²⁹⁹ to Frame³⁰⁰ (Frame's method) is potentially useful in generating the characteristic polynomials of graphs containing a very large number of vertices. A computer program was developed by the present investigator²⁸⁹ based on the above method. Krivka, Jericevič, and Trinajstić³⁰¹ have recently shown that the Frame's method outlined in the present author's paper is the same as the Le Verrier-Faddeev's method for the characteristic polynomials. Other manifestations of Frame's method could also be found in the literature.³⁰² We briefly review this method here since characteristic polynomials of very many complicated graphs and more recently of organic polymers and periodic structures have been obtained by this method.²⁹¹

Let A be the adjacency matrix of a graph. Define the set of matrices B_k 's recursively by the following recipe.

$$C_1 = \text{trace } A \quad (81)$$

$$B_1 = A(A - C_1 I) \quad (82)$$

$$C_2 = (1/2)\text{trace } B_1 \quad (83)$$

$$B_2 = A(B_1 - C_2 I) \quad (84)$$

$$C_3 = (1/3)\text{trace } B_2 \quad (85)$$

...

$$B_{n-1} = A(B_{n-2} - C_{n-1} I) \quad (86)$$

$$C_n = (1/n)\text{trace } B_{n-1} \quad (87)$$

The characteristic polynomial of the graph whose adjacency matrix is A is given by

$$\lambda^n - C_1 \lambda^{n-1} - C_2 \lambda^{n-2} \dots - C_{n-1} \lambda - C_n \quad (88)$$

Thus, the coefficients C_1, C_2, \dots are generated as traces of matrices obtained in the above recursive matrix product. Hence the Frame method provides a very efficient algorithm for the generation of coefficients $C_1,$

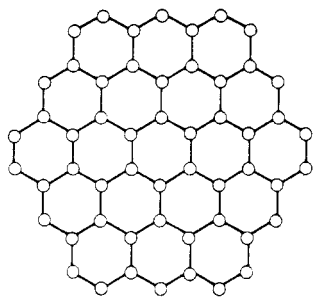


Figure 14. A honeycomb lattice graph containing 54 vertices. The characteristic polynomial of this graph can be obtained by using Frame's method (see section IVA).

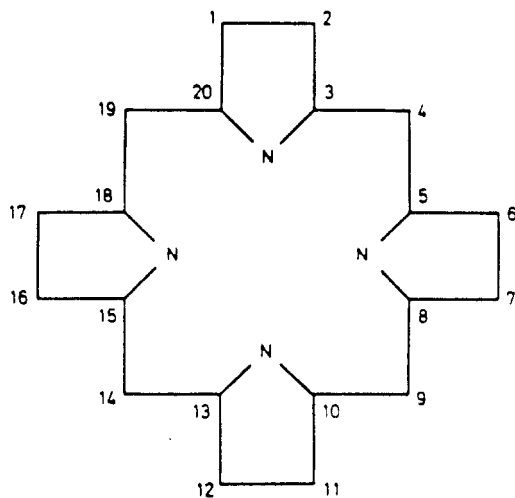


Figure 15. Porphine dianion. The SALC's of the p_z orbitals can be constructed by using combinatorial methods (see Section IVB).

C_2 , etc. and, consequently, the characteristic polynomial.

The computer program based on the above method was used to evaluate the characteristic polynomials of several graphs. To illustrate, consider the honeycomb lattice graph in Figure 14. The characteristic polynomial of this graph is given by expression 89.

$$\begin{aligned} &\lambda^{54} - 72\lambda^{52} + 2430\lambda^{50} - 51152\lambda^{48} + 753867\lambda^{46} - \\ &8227552\lambda^{44} + 70356380\lambda^{42} - 474823692\lambda^{40} + \\ &2589615333\lambda^{38} - 11556300564\lambda^{36} + \\ &42569538372\lambda^{34} - 130222865528\lambda^{32} + \\ &332069146453\lambda^{30} - 707192500956\lambda^{28} + \\ &1257989284\lambda^{26} - 1866287443412\lambda^{24} + \\ &2301545596335\lambda^{22} - 2347222219224\lambda^{20} + \\ &1965105361102\lambda^{18} - 1337106330756\lambda^{16} + \\ &729597602706\lambda^{14} - 313604239964\lambda^{12} + \\ &103654073940\lambda^{10} - 25479629340\lambda^8 + \\ &4438832481\lambda^6 - 508728588\lambda^4 + 33696516\lambda^2 - \\ &960400 \quad (89) \end{aligned}$$

B. Symmetry Adaptation

In this section we review the use of GCCI's for the construction of symmetry-adapted linear combination of orbitals (referred to as SALC's by Cotton³⁰³) used in quantum calculations of symmetric molecules. The present author³⁰⁴ showed that GCCI's could be used to construct SALC's. Consider the p_z orbitals perpendicular to the plane of the molecule in Figure 15. All 20 carbon p_z orbitals do not mix in any of the SALC's. The problem is to construct the SALC's for the por-

phine dianion. The above problem first reduces to finding the equivalence class of 20 nuclei such that only those p_z orbitals centered on the nuclei in a class mix to form a SALC. The solution for this problem is obtained by setting χ to be the character of the identity representation in the GCCI's. Let \mathbf{D} be the set of 20 carbon nuclei. Let \mathbf{R} be a set containing two elements. Let α_1 and α_2 be the weights of elements in \mathbf{R} . Then for this case

$$\begin{aligned} \text{GF} = & \frac{1}{16} [2(\alpha_1 + \alpha_2)^{20} + 4(\alpha_1^4 + \alpha_2^4)^5 + 6(\alpha_1^2 + \alpha_2^2)^{10} + \\ & 4(\alpha_1 + \alpha_2)^2(\alpha_1^2 + \alpha_2^2)^9] \quad (90) \end{aligned}$$

The coefficient of $\alpha_1^{19}\alpha_2$ in the above expression gives the number of patterns or the number of identity representations in each pattern. This is equal to

$$\frac{2}{16} [(20) + 2(2)] = 3 \quad (91)$$

The classes of nuclei are

$$C_1 = \{1, 2, 6, 7, 11, 12, 16, 17\}$$

$$C_2 = \{3, 5, 8, 10, 13, 15, 18, 20\} \quad (92)$$

$$C_3 = \{4, 9, 14, 19\}$$

To construct the SALC's one looks at the transformation properties of vectors perpendicular to the plane of the molecule belonging to a class. A generating function for the irreducible representations in the class C_i can be obtained by finding the generating function restricted to C_i , with the following definition of P_G^x . Let d_i denote a vector centered on the atom d_i perpendicular to the plane of the paper. Then define

$$P_G^x[C_j] = \frac{1}{|\mathbf{G}|} \sum_{g \in \mathbf{G}} \epsilon_g \chi(g) x_1^{b_1} x_2^{b_2} \dots \quad (93)$$

where

$$\epsilon_g = \begin{cases} -1 & \text{if } gd_i = d_k \text{ for some } k \\ 1 & \text{otherwise} \end{cases} \quad (94)$$

C_j denotes the set of vectors centered on the nuclei in the class C_j . The generating function for the class C_j is given by

$$\text{GF}^{C_j}(\Gamma_i) = P_G^x[C_j](x_k \rightarrow \sum_l \alpha_l^k) \quad (95)$$

where χ is the character of the irreducible representation Γ_i . Expressions thus obtained for all irreducible representations of D_{4h} and for each equivalence class are shown in Table VII. The coefficient of $\alpha_1^{m-1}\alpha_2$ in each expression, where $m = |C_j|$ gives the number of times the irreducible representation Γ_i occurs in the set C_j . They are indicated in the last column of Table VII. The complete set of generating functions for all f 's in \mathbf{F} is shown in Table VII, even though for the present problem only the coefficient of $\alpha_1^{m-1}\alpha_2$ is significant. However, the other coefficients do have combinatorial significance, viz., a typical coefficient $\alpha_1^{m_1}\alpha_2^{m_2}$ in the generating function which corresponds to the irreducible representation Γ and the class C_j represents the number of colorings of vectors with m_1 colors of the type 1 and m_2 colors of the type 2 that transform as the irreducible representation Γ and the class C_j . The projection operator which corresponds to each irredu-

TABLE VII. The Combinatorics of Symmetry Adaptation

	irreducible representation	class	GF	freq of occurrence
1	A _{1g}	C ₁ ,C ₂	0	0
2	A _{2g}	C ₁ ,C ₂	0	0
3	B _{1g}	C ₁ ,C ₂	0	0
4	B _{2g}	C ₁ ,C ₂	0	0
5	E _g	C ₁ ,C ₂	2α ₁ ⁷ α ₂ + 6α ₁ ⁶ α ₂ ² + 14α ₁ ⁵ α ₂ ³ + 16α ₁ ⁴ α ₂ ⁴ + 14α ₁ ³ α ₂ ⁵ + 6α ₁ ² α ₂ ⁶ + 2α ₁ α ₂ ⁷	2
6	A _{1u}	C ₁ ,C ₂	α ₁ ⁷ α ₂ + 2α ₁ ⁶ α ₂ ² + 7α ₁ ⁵ α ₂ ³ + 7α ₁ ⁴ α ₂ ⁴ + 7α ₁ ³ α ₂ ⁵ + 2α ₁ ² α ₂ ⁶ + α ₁ α ₂ ⁷	1
7	A _{2u}	C ₁ ,C ₂	α ₁ ⁸ + α ₁ ⁷ α ₂ + 6α ₁ ⁶ α ₂ ² + 7α ₁ ⁵ α ₂ ³ + 13α ₁ ⁴ α ₂ ⁴ + 7α ₁ ³ α ₂ ⁵ + 6α ₁ ² α ₂ ⁶ + α ₁ α ₂ ⁷ + α ₂ ⁸	1
8	B _{1u}	C ₁ ,C ₂	α ₁ ⁷ α ₂ + 4α ₁ ⁶ α ₂ ² + 7α ₁ ⁵ α ₂ ³ + 9α ₁ ⁴ α ₂ ⁴ + 7α ₁ ³ α ₂ ⁵ + 4α ₁ ² α ₂ ⁶ + α ₁ α ₂ ⁷	1
9	B _{2u}	C ₁ ,C ₂	α ₁ ⁷ α ₂ + 4α ₁ ⁶ α ₂ ² + 7α ₁ ⁵ α ₂ ³ + 9α ₁ ⁴ α ₂ ⁴ + 7α ₁ ³ α ₂ ⁵ + 4α ₁ ² α ₂ ⁶ + α ₁ α ₂ ⁷	1
10	E _u	C ₁ ,C ₂	0	0
11	A _{1g}	C ₃	0	0
12	A _{2g}	C ₃	0	0
13	B _{1g}	C ₃	0	0
14	B _{2g}	C ₃	0	0
15	E _g	C ₃	α ₁ ³ α ₂ + α ₁ ² α ₂ ² + α ₁ α ₂ ³	1
16	A _{1u}	C ₃	0	0
17	A _{2u}	C ₃	α ₁ ⁴ + α ₁ ³ α ₂ + 2α ₁ ² α ₂ ² + α ₁ α ₂ ³ + α ₂ ⁴	1
18	B _{1u}	C ₃	α ₁ ³ α ₂ + α ₁ ² α ₂ ² + α ₁ α ₂ ³	1
19	B _{2u}	C ₃	α ₁ ³ α ₂	0
20	E ₁	C ₃	0	0

cible representation of p orbitals is applied on that class to obtain an orthogonal set of symmetry-adapted orbitals.

C. Configuration Interaction Calculations

In recent years graph theoretical and combinatorial techniques have made significant impact on large scale configuration interaction calculations. One of the major developments in this area is the graphical unitary group approach to many electron correlation.³⁰⁵⁻³¹⁸ Paludus³⁰⁵⁻³¹⁰ showed that the unitary group approach to electron correlation introduces significant simplifications in the configuration interaction calculations and this approach speeds up the evaluation of symbolic formulas for CI matrix elements. Further, using the unitary group generators, the matrix elements can be constructed directly, thereby cutting down computationally expensive step of constructing symbolic CI formulas. Shavitt^{311,312,317} has further expounded on the unitary group approach and developed the graphical unitary group method which can be applied to direct configuration interaction calculations (direct CI).

The graphical unitary group approach (GUGA) is based on the notion of distinct row table (DRT) and its graph theoretical representation. Graph theory is also extremely useful here in pictorial visualization of matrix elements and computational techniques.

Schaefer and co-workers^{318,319} have developed computer programs based on GUGA which enable CI calculations involving a very large number of configurations. Schaefer's³²⁰ loop-driven GUGA programs can handle up to 1 million configurations.

The bases of unitary group are known as Gel'fand states and have also been used by Matsen³¹³ independently in spin-free quantum chemistry. The usual

genealogical construction of spin functions³²¹ can also be achieved by using Gel'fand states.

The present author³¹⁵ showed that GCCI's can be used to enumerate and construct Gel'fand states. We briefly review this here.

As a result of the correspondence between the unitary group U(n) and the symmetric group S_n, for a n particle problem one may use the symmetric group S_n. Consider **D** as the set of these n particles and **R** as the possible spin states. Then each spin configuration of n particles can be considered as a map from **D** to **R**. The group S_n divides the set of all maps from **D** to **R** into patterns. Each pattern contains exactly one identity representation of S_n. The spin configurations contained in each pattern form a reducible representation of S_n which decomposes into irreducible representations of S_n. These irreducible representations are precisely the generalized Young tableau or Gel'fand states formed by the possible spin states of the particles. This can be seen from the correspondence of unitary groups and symmetric groups. Consequently, Gel'fand states contained in each pattern can be generated by GCCI's.

Let G be the symmetric group S_n. Let w(r)'s be the weights of spin states in the set **R**. Then GF^x with the character χ generates the Gel'fand states formed by the spin states with the Young diagram associated with the irreducible representation whose character is χ.

Let us illustrate with an example. Consider the Gel'fand states associated with four particles which possess three spin states corresponding to the partition (3,1). The GCCI is given as

$$P_G^{[3,1]} = \frac{1}{24} [3x_1^4 + 6x_1^2x_2 - 6x_4 - 3x_2^2] \quad (96)$$

If α₁, α₂, and α₃ are the weights of three spin states, then GF is given by

$$GF^{[3,1]} = \frac{1}{24} [3(\alpha_1 + \alpha_2 + \alpha_3)^4 + 6(\alpha_1 + \alpha_2 + \alpha_3)^2(\alpha_1^2 + \alpha_2^2 + \alpha_3^2) - 6(\alpha_1^4 + \alpha_2^4 + \alpha_3^4) - 3(\alpha_1^2 + \alpha_2^2 + \alpha_3^2)^2] \quad (97)$$

This on simplification yields

$$\alpha_1^3\alpha_2 + \alpha_1^2\alpha_3 + \alpha_1\alpha_2^2 + \alpha_2^3\alpha_3 + \alpha_1\alpha_3^2 + \alpha_2\alpha_3^2 + \alpha_1^2\alpha_2^2 + \alpha_1\alpha_2\alpha_3^2 + \alpha_2^2\alpha_3^2 + 2\alpha_1^2\alpha_2\alpha_3 + 2\alpha_1\alpha_2^2\alpha_3 + 2\alpha_1\alpha_2\alpha_3^2 \quad (98)$$

The total number of tableaux can also be obtained by replacing every x_k by |R| in the cycle index of G with the appropriate character. In this case it is

$$\frac{1}{24} [3 \cdot 3^4 + 6 \cdot 3^2 \cdot 3 - 6 \cdot 3 - 3 \cdot 3^2] = 15 \quad (99)$$

The Gel'fand states thus generated are shown in Figure 16.

The present author³²² showed that generating functions can be obtained to generate and enumerate configurations themselves. It was further shown in ref 322 that symmetry simplifications can be introduced in CI calculations induced by orbital degeneracies. The readers are referred to ref 322 for further details on this topic.

V. Conclusion

In this manuscript we reviewed applications of combinatorics and graph theory to spectroscopy and quantum chemistry. The topics we reviewed include

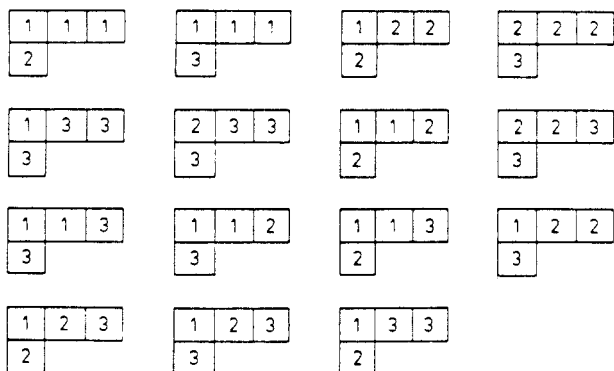


Figure 16. The 15 Gel'fand states corresponding to the irreducible representation $[3,1]$ of four particles possessing three spin states. The Gel'fand states are enumerated by using the combinatorial method outlined in section IVC.

applications to NMR, molecular spectroscopy, microwave and electric deflection experiments of weakly bound van der Waals complexes synthesized in molecular beam, NQR spectra of crystals exhibiting phase transitions, reaction topology, graph theoretical formulation of the structure of quantum chemistry, graph theory of gradient of nuclear charge densities, characteristic polynomials of graphs, graphical symmetry adaptation and graph theory, and CI calculations. Yet a variety of applications of graph theory to other areas of chemistry could not be reviewed because of the space limitation. Some of these applications include applications to stereochemistry, molecular rearrangements and dynamical processes, chemical kinetics, logical structure of chemistry, statistical thermodynamics, computer-assisted structure elucidation, logic of organic synthesis and computer-assisted organic synthesis, electronic properties of inorganic cluster compounds, conjugated compounds, topological and other information indices, chemical nomenclature and notation, etc. Balasubramanian and co-workers³²³ showed that a combinatorial problem known as the cell-growth problem has potential applications in the enumeration of carcinogenic benzenoid hydrocarbons and in the construction of potentially carcinogenic bay regions (see also ref 324). Many of these applications have been already reviewed before, although the latest developments on this topic are yet to be reviewed. Ugi and co-workers³²⁵ have recently reviewed the use of group theory and related topics in stereochemistry. Bader³²⁶ has recently provided a concise review of applications of topology to molecular structure. Kerber and James³²⁷ have reviewed the methods of representation theory of symmetry groups which has a number of chemical applications. Combinatorial matrices known as Hadamard matrices find important applications in Hadamard transform spectroscopy.³²⁸ Numerous papers have appeared on these and related topics in the chemical literature. This area provides significant opportunities for further investigations. There are many problems in this area which are yet to be solved. It is hoped that this review would attract many new investigators into this relatively new branch of mathematical chemistry.

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