Applications of Combinatorics and Graph Theory to Spectroscopy and Quantum Chemistry

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Contents

I. Introduction 599
II. Some Combinatorial Methods 601
   A. Pólya’s Theorem 601
   B. Group Characters and Generalized Character Cycle Indices 603
   C. Elements of Graph Theory 604
III. Applications to Spectroscopy 604
   A. NMR Spectroscopy 604
   B. Molecular Spectroscopy 608
   C. NQR Spectra of Crystals 610
IV. Applications to Quantum Chemistry 611
   A. Characteristic Polynomials of Graphs 611
   B. Symmetry Adaptation 614
   C. Configuration Interaction Calculations 615
V. Conclusion 615

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 by integers. Two 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 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, ..., 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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with a cycle index of a group. 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. 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. Numerous papers have appeared in the chemical literature that deal with graph theory, aromaticity, dimer coverings, etc. 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. The topic of topological approach to the chemistry of conjugated molecules was reviewed by Graovac, Gutman and Trinajstić and more recently by Trinajstić.

Graph theory is useful in simplifying certain integrals which appear in the partition function using the Mayer–Mayer expansion. 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
Applications of Combinatorics and Graph Theory

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. Some results of nonlinear chemical systems were derived recently by Beratta et al. 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 Sinanoğlu and papers of Lee and Sinanoğlu. King 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. 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. 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. 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. Graph theory was used in fluid dynamics in solving Navier-Stoke's equation by Amit et al. Graph theoretical methods have been applied to several other areas such as statistical mechanics of polymers and related topics, structure and bonding of inorganic clusters, etc.

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 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. PtBr₄Cl₂, 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 D to R where D is the set \{1, 2, 3, 4, 5, 6\} of six vertices of the octahedron shown in Figure 2 and R is the set \{Br, 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

\[
\begin{align*}
t\text{-map} & & c\text{-map} \\
1 &\rightarrow Br & 1 &\rightarrow Br \\
2 &\rightarrow Br & 2 &\rightarrow Br \\
3 &\rightarrow Br & 3 &\rightarrow Cl \\
4 &\rightarrow Br & 4 &\rightarrow Br \\
5 &\rightarrow Cl & 5 &\rightarrow Br \\
6 &\rightarrow Cl & 6 &\rightarrow Cl \\
\end{align*}
\]
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 \( r \in \mathbb{R} \) let us attach a weight of \( w(r) \), which may be a formal symbol for the atoms or functional groups. With every function \( f(\mathbb{D} \rightarrow \mathbb{R}) \) is associated a weight of \( W(f) \) which is the product of the weights of all the images by \( f \). Symbolically

\[
W(f) = \prod_{d \in \mathbb{D}} w(f(d))
\]

To illustrate let us associate a weight \( \text{Br} \) to the atom \( \text{Br} \) and a weight \( \text{Cl} \) to the atom \( \text{Cl} \). Then \( W(\text{t-map}) = \text{BrCl}^2 \) and \( W(\text{c-map}) = \text{BrCl}^2 \). 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 the the graph \( \Gamma \) of \( M \). The vertex set of \( \Gamma \) 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 remaining vertices, which may be called "chemically labeled" vertices. For example, to find the isomers of \( \text{C}_6\text{H}_4\text{Br} \), 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 \( \mathbb{D} \) stand for the set of chemically unlabeled vertices of \( \Gamma \), the graph of \( M \). Let \( \mathbb{R} \) be the set of substituents which are used to label the vertices of \( \mathbb{D} \). Each map \( f(\mathbb{D} \rightarrow \mathbb{R}) \) 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 \( w_1^{b_1}w_2^{b_2} \). Let this be shortly denoted as \( w_M \). Consider the set \( F \) of all maps from \( \mathbb{D} \) to \( \mathbb{R} \). Let \( F_M \) be a subset of \( F \) consisting of those maps \( \mathbb{D} \rightarrow \mathbb{R} \) with the weight \( w_M \). Now let \( G \) be a group of permutations acting on \( \mathbb{D} \) induced by the rotations in physical space which give the needed isomers of \( M \).

In the above setting two functions \( f_1, f_2 \in F \) are said to be \( G \)-equivalent where \( G \) is the group of 24 rotations of the octahedron acting on the vertices. The \( G \)-equivalence classes of \( F_M \) are said to be the isomers of \( M \). Thus the number of isomers of \( M \) is precisely the number of \( G \)-equivalence classes of \( F_M \).

Pólya’s Theorem gives a formula for the number of various \( G \)-equivalence classes and also a generating polynomial for the number of \( G \)-equivalence classes of \( F_M \) 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 \( G \) be a permutation group. Every permutation of \( G \) has a unique cycle decomposition. Let a typical permutation \( g \in G \) have \( b_1 \) cycles of length 1, \( b_2 \) cycles of length 2, and so on. Then \( x_1^{b_1}x_2^{b_2} \) is said to be the cycle representation of the permutation \( g \). The cycle index of \( G \) is defined as the sum of the cycle representations of various elements in \( G \) divided by \( |G| \), the number of elements in \( G \). It is denoted by \( P_G(x_1, x_2, ...) \). Thus

\[
P_G(x_1, x_2, ...) = \frac{1}{|G|} \sum x_1^{b_1}x_2^{b_2} \ldots
\]

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

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

\[
P_G(x_1, x_2, ...) = \sum_{r \in \mathbb{R}} (w(r))^k
\]

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

\[
P_G(|\mathbb{R}|, |\mathbb{R}|, ...)
\]

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

Let us now apply Pólya’s theorem to enumerate the isomers of certain octahedral molecules. The group \( G \) 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.
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 C₄ 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 x₁x₄. 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

\[ P_{G}(x_1, x_2, ..., x_6) = \frac{1}{24}(x_1^6 + 6x_2x_4 + 3x_1x_2^2 + 8x_3^2 + 6x_3^2) \]  
(6)

The Pattern inventory, which is a generating function for isomers, is obtained by replacing every (w(r))ₖ and is given by

\[ P_{G} = \frac{1}{|G|} \sum_{g \in G} \chi(g) x_1^w x_2^w ... \]  
(12)

where \( x_1^w x_2^w ... \) 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 \( r \in D \). Then a generating function can be obtained for each irreducible representation \( \Gamma \) with character \( \chi \) as

\[ GF^x = P_{G}^x(x_k = \sum_{r \in D} (w(r))^k) \]  
(13)

Finally, the number of isomers of octahedral MABCDEF, where M is the metal atom is the coefficient of \( w_1w_2w_3w_4w_5w_6 \) in (7) and is given by (11).

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

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 \( \Gamma \) in the group \( G \). Then one can define a cycle index for each irreducible representation \( \Gamma \) with character \( \chi \) as

\[ P_{G}^\chi = \frac{1}{|G|} \sum_{g \in G} \chi(g) x_1^w x_2^w ... \]  
(12)

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 \( w_1^iw_2^j ... \) in the generating function for the totally symmetric representation gives the number of totally symmetric representations in the set of functions with the weight \( w_1^iw_2^j ... \) and is given by (11).

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

Thus, the number of isomers of PtBr₄Cl₂ is simply the coefficient of \( w_1^2w_2^2 \) in expression 7. Expression 7 is thus a generation function for all possible isomers of octahedral molecules. For example, the number of isomers of RuCl₄(H₂O)(CO) is given by the coefficient of \( w_1w_2w_3w_4 \) in (7) which is

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

The number of isomers of RhClI(CH₂CO(PPh₃)₂ is given by the coefficient of \( w_1w_2w_3w_4w_5 \) shown.
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. 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 \(=\). For example, the first two graphs in Figure 5 are isomorphic 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

\[
A_{ij} = \begin{cases} 
1 & \text{if } i \text{ is connected to } j \\
0 & \text{otherwise} 
\end{cases} \tag{14}
\]

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

\[
\begin{bmatrix}
0 & 1 & 1 & 1 \\
1 & 0 & 1 & 1 \\
1 & 1 & 0 & 1 \\
1 & 1 & 1 & 0
\end{bmatrix}
\]

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.

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

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 Ramaraj and Motoyama and Hosoya.

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. 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 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

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

Two maps \(f\) and \(f'\) \(\in F\) are equivalent if

\[
f_i(d) = f'(gd) \quad \text{for every } d \in D \tag{16}
\]
Maps in $F$ that are equivalent can be grouped into the same equivalence class. Thus the group $G$ partitions $F$ into equivalence classes. Let us restrict ourselves to the maps in $F$ which have the following structure. Let the elements of $R$ be denoted by $\alpha_1$ and $\alpha_2$. Let the elements of $D$ be $d_1, d_2, \ldots, d_n$ with $n = |D|$. Then consider a subset $F_w$ of $F$ with every $f_i \in F_w$ defined as

$$f_i(d_j) = \alpha_i \text{ if } i \neq j, d_j \in D \quad \alpha_i \text{ if } i = j \quad (17)$$

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 $F_w$ are the magnetic equivalence classes of nuclei in the set $D$. Hence the number of equivalence classes gives the number of NMR signals of the molecule.

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

$$GF = P_G(x_1 \rightarrow \alpha_1^6 + \alpha_2^6) \quad (18)$$

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

Consider the molecule CH$_3$CHCICICCH$_3$. 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. The generating function for CH$_3$CHCICICCH$_3$ is shown.

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

The coefficient of $\alpha_1^3 \alpha_2$ in the above expression is the number of proton signals at low resolution and is given by

$$\frac{1}{4}(10) + 2(3) = 4 \quad (20)$$

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 7](image-url) - 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).

The symmetry of such a system can in general be described by generalized wreath product groups. The symmetry group of this nonrigid molecule is $C_4 \times C_3$. 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 the $^{13}C$ NMR is

$$P_G = \frac{1}{24}[2x_1^{16} + 4x_2^{16} + 4x_3^{16} + 8x_4^{16} + 6x_5^{16}] \quad (21)$$

The number of $^{13}C$ signals is the coefficient of $\alpha_1^6 \alpha_2$ 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

$$P_G = \frac{1}{12}[x_1^{24} + 7x_2^{22} + 2x_3^{16} + 2x_4^{16}] \quad (22)$$

The coefficient of $\alpha_1^3 \alpha_2$ 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. 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

$$P_G = \frac{1}{4}[x_1^{16} + 2x_2^{16} + x_3^{16}] \quad (23)$$

From the coefficient of $\alpha_1^3 \alpha_2$ 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 the $^{13}C$ NMR is

$$P_G = \frac{1}{4}[x_1^{16} + 2x_2^{16} + x_3^{16}] \quad (24)$$

where $Z_i = (1/3)(x_i^{10} + 2x_i^{12})$. When the torsional permutations can be differentiated by NMR at feasible experimental conditions, the group becomes $C_4$ and the cycle index is

$$P_G = \frac{1}{4}[x_1^{16} + 2x_2^{16} + 3x_3^{16}] \quad (25)$$

The coefficients of $\alpha_1^3 \alpha_2$ 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 PCI₃ molecule. Our method will explain the classical and well-known result that the NMR spectrum of the molecule PCI₃ contains only one signal. Even though the point group of the rigid PCI₃ molecule is D₃ᵥ, the rotational group of the nonrigid molecule, the nonrigidity introduced through the Berry mechanism, is S₅. (S₅ stands for the symmetric group, containing 5! elements.) The coefficients of α₁α₂ 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.

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

\[
\frac{1}{120}[(\alpha_1 + \alpha_2)^5 + 10(\alpha_1 + \alpha_2)^3(\alpha_1^2 + \alpha_2^2) + 20(\alpha_1 + \\
\alpha_2)^2(\alpha_1^3 + \alpha_2^3) + 30(\alpha_1 + \alpha_2)(\alpha_1^4 + \alpha_2^4) + 15(\alpha_1 + \\
\alpha_2)(\alpha_1^5 + \alpha_2^5) + 20(\alpha_1^2 + \alpha_2^2)(\alpha_1^3 + \alpha_2^3) + 24(\alpha_1^3 + \alpha_2^3)]
\] (26)

\[
\frac{1}{4}[(\alpha_1 + \alpha_2)^6 + 2(\alpha_1 + \alpha_2)^2(\alpha_1^2 + \alpha_2^2)^3 + (\alpha_1^3 + \alpha_2^3)^4]
\] (28)

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

The coefficients of α₁α₂ in (28) and (29) are given by (30) and (31), respectively.

\[
\frac{1}{4}[(\Omega_i^2) + 2(\Omega_j^2)] = 3
\] (30)

\[
\frac{1}{36}[(\Omega_i^2) + 4(\Omega_j^2) + 6(\Omega_k^2) + 12(\Omega_l^2) + 6(\Omega_m^2)] = 2
\] (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 σᵥ plane of the C₂ᵥ 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. The symmetry group of the nonrigid molecule restricted to tert-butyl group at high temperature is C₃[C₃]. 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[C₃]. If one considers the nine protons of tertiary group alone, the coefficient of α₁α₂ in the generating functions for C₃[C₃] and E[C₃] groups can be seen to be 1 and 3. This is in agreement with the experimentally observed spectrum 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 author 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. 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 Reilly and Wilson. Soon after the development of symmetry groups of nonrigid molecules by Longuet-Higgins, Woodman developed the unitary group treatment for the NMR problem.

The NMR spin Hamiltonian can be defined as

\[H_{\text{NMR}} = \sum_i I_i^2 + \sum_{i<j} J_{ij} I_i I_j\] (32)

where \(v_i\) is the chemical shift of the ith 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 \(P\) satisfies

\[PH_{\text{NMR}}P^{-1} = H_{\text{NMR}}\] (33)

The present author showed that a diagrammatic representation of \(H_{\text{NMR}}\) 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 \(Q\) and \(T_1\) and \(T_2\) shown in Figure 10. The graph in Figure 9 can be obtained by replacing vertices 1 and 3 of \(Q\) in Figure 10 by a copy of \(T_1\), and the vertex 2 by a copy of \(T_2\). Consequently, the NMR group of propane is expressible as a generalized wreath product. This group is \(S_2[S_5S_3]\). For details see ref 195.

One can use GCCI's for classifying NMR spin species. We review this here. Table I shows all the
functions containing $n_1\alpha$'s and $n_2\beta$'s. Note that the term $a^{\alpha}\beta^{\alpha}$ corresponds to the total two-component spin quantum number $M_F = (n_1 - n_2)/2$ so that if the coefficients in $GF_1$'s are sorted in accordance to their $M_F$ values, one obtains the proton NMR $G_1$ species as $G_1(2), G_1(5), G_1(9), G_1(3), G_1(1)$.
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 GCCI’s. 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 $x_i$ in the GCCI’s in Table I by $\lambda^k + \mu^k + \nu^k$, where $\lambda$, $\mu$, and $\nu$ are the weights corresponding to $m_f = -1$, 0, and 1, respectively, of the 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.\(^{195,196,197}\) The readers are referred to these references for further details.

The use of GCCI’s 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 GCCI’s 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 GCCI’s 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 molecules 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 $a_1^b a_2^b \ldots$ 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, GCCI’s are useful in generating the irreducible representations in a straightforward manner. For the problem of nuclear spin statistics, D is the set of nuclei and R is the set of possible spin states of the nuclei in D. For a set of spin $1/2$ nuclei, R would be a set consisting of two elements which can be denoted by $\alpha$ (spin up) and $\beta$ (spin down). The image of F is the set of spin functions. For example, the map $f_1$ from a set D, consisting of four nuclei, labeled 1, 2, 3, and 4, to R, which consists of the spin states $\alpha$ and $\beta$, is shown.

\[ f_1(1) = \alpha \quad f_1(2) = \beta \quad f_1(3) = \beta \quad f_1(4) = \alpha \]  

(36)

Then the spin function generated by $f_1$ is $a_1 a_2 a_3$. G acts on the elements of F by the procedure shown.

\[ g(f(i)) = g(f^{-1}i) \]  

for every $i \in D$

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

\[ g(f_1(1)) = f_1(g^{-1}1) = f_1(4) = \alpha \]

\[ g(f_1(2)) = f_1(g12) = f_1(1) = \alpha \]

\[ g(f_1(3)) = f_1(g^{-3}13) = f_1(2) = \beta \]

\[ g(f_1(4)) = f_1(g^{-4}14) = f_1(3) = \beta \]  

(37)

Thus by the action of the permutation (1234) on $f_1$, the spin function $a_1 a_2 a_3$ gets permuted to $a_3 a_1 a_2$. Two functions $f_1$ and $f_2$ in F are equivalent if there is a g in G such that

\[ f_1(d) = f_2(gd) \]  

for every $d \in D$  

(38)

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

If one associates a weight $\alpha$ to the spin state $\alpha$ and a weight $\beta$ to the spin state $\beta$, then the generating function corresponding to the irreducible representation $\Gamma$ with character $\chi$ is given by

\[ GF = P_{G_1}(x_i = \alpha^k + \beta^k) \]  

(39)
TABLE IV. Generating Functions of Fluorine Species of $SF_6$

<table>
<thead>
<tr>
<th>Irreducible representation</th>
<th>GF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>$\alpha^8 + \alpha^6 \beta + 2 \alpha^4 \beta^2 + 2 \alpha^2 \beta^3 + \alpha \beta^4 + \beta^6$</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>$\alpha^8 \beta + 2 \alpha^6 \beta^2 + 2 \alpha^4 \beta^3 + \alpha \beta^4 + \beta^6$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>$0$</td>
</tr>
<tr>
<td>$T_{1u}$</td>
<td>$\alpha^8 \beta^3 + \alpha^6 \beta^4$</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>$0$</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>$0$</td>
</tr>
<tr>
<td>$E_u$</td>
<td>$0$</td>
</tr>
<tr>
<td>$T_{2g}$</td>
<td>$\alpha^8 \beta^3 + \alpha^6 \beta^4$</td>
</tr>
</tbody>
</table>

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

$$n_{\Gamma} = P_{\Gamma}(x_k \to |R|)$$

(40)

where $|R|$ is the number of elements in one set $R$.

Consider the $^{35}$SF$_6$ molecule as an example. The set $D$ is the set of $^{19}$F nuclei. The set $R$ for F nuclei contains two elements since $^{19}$F is a spin $\frac{1}{2}$ nucleus and hence can take two possible spin states. We may associate the weights $\alpha$ and $\beta$ to these states. To illustrate, consider the species $E_u$ of the $O_h$ group. The nuclear species which belong to this species can be obtained by replacing every $x_k$ by $(\alpha^2 + \beta^2)$ in the corresponding $P_{E_u}$. The result of this substitution is shown.

$$P_{E_u} = \frac{1}{48} [2x_1^4 - 8x_1^2 + 6x_1^2x_2 + 2x_2^4 - 8x_6 + 6x_4x_2]$$

(41)

Thus

$$GF_{E_u} = \frac{1}{48}[(2(\alpha + \beta)^6 - 8(\alpha^3 + \beta^3)^2 + 6(\alpha^2 + \beta^2)^3 + 2(\alpha^2 + \beta^2)^3 - 8(\alpha^3 + \beta^3)^2 + 6(\alpha^2 + \beta^2)^3]$$

(42)

The above expression on simplification yields

$$\alpha^3 \beta + 2 \alpha^2 \beta^2 + 2 \alpha \beta^3 + 2 \alpha^2 \beta^3 + \alpha \beta^4 + \beta^6$$

(43)

Thus there is one $E_u$ in the reducible representation spanned by spin functions containing $5\alpha$'s and $1\beta$, $2E_u$ in the reducible representation spanned by spin functions containing $4\alpha$'s and $2\beta$'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 $\alpha^p \beta^q$ in a generating function corresponding to the species $\Gamma$ gives the number of functions belonging to the species $\Gamma$ with the spin quantum number $m_z = (a_1 - b_1)/2$. When these species are arranged according to their multiplicities times the frequency of the same species, the number of elements of each species is given by

$$N(E') = \frac{1}{6}(x_1^3 + 2x_1^2 + 3x_2)$$

(44)
recently, applications of GCCI's and other group theoretical techniques to nonrigid molecules. A1'(178940928), A1(178973696), E'(3579136001, -1 with respect to permutations for fermions. For bosons it must be +1. Since 18 13C nuclei of [13C]triphenylene transform as x^2 under the operation c2 and since they are fermions, Πr is A2′ or A1′. Thus the statistical weights are as follows:

\[
N(A_1') = \frac{1}{6}(2^{18} + 2^{26} + 3^{2}) = 43968 \\
N(A_2') = \frac{1}{6}(2^{18} + 2^{26} - 3^{2}) = 43456 \\
N(E') = \frac{1}{6}(2^{18} - 2^{26}) = 87360
\]

Hence

\[
\Gamma_c^{\text{spin}} = 43968 A_1' + 43456 A_2' + 87360 E'
\]

The overall species, \( \Gamma_c^{\text{spin}} = \Gamma_c^{\text{spin}} \times \Gamma_h^{\text{spin}} \), is given by (61).

\[\Gamma_c^{\text{spin}} = \frac{178973696 A_1' + 178940928 A_2' + 357913600 E'}{178940928 A_1' + 178973696 A_2' + 357913600 E'}\]

One can obtain the statistical weights from \( r_{\text{spin}} \) easily. This is done by stipulating that \( P_{\text{in}} \) should contain \( r_{\text{in}} \), where

\[P_{\text{in}} = 610 \text{ Chemical Reviews, 1985, Vol. 85, No. 6}

Balasubramanian and Dyke\(^{216}\) 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

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 Armstrong\(^{226}\) have recently studied the NQR spectra of antifluorite 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 G be the point group corresponding to the space group of the crystal. Let D be the set of nuclei. Then each operation g ∈ G can be considered as a permutation or permutation-inversion operation on D. Let R be a set containing just two elements denoted by \( \alpha_1 \) and \( \alpha_2 \). Let \( f_i \) be a map from D to R defined as follows

\[f_i(d_j) = \begin{cases} \alpha_1, & i \neq j, d_j \in D \\ \alpha_2, & i = j \end{cases} \]

(62)
Two maps \( f_i \) and \( f_j \) \((i \neq j)\) are equivalent if there is a \( g \in G \) such that
\[
f_i(gd) = f_j(d) \quad \text{for every } d \in D
\] (63)

The above relation divides the set \( F \) of all maps from \( D \) to \( R \) into equivalence classes. It can be easily seen that the equivalence classes of \( F \) 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 \( r \in R \) let us associate a weight \( w(r) \). For example, with \( \alpha_1 \) associate a weight \( c_1 \) and with \( \alpha_2 \) associate a weight \( c_2 \). Define the weight of any \( f \in F \) as in section II of this review. The weight of any map \( f_i \) is \( \alpha_i^{-1}c_0 \) if \( N \) is the number of nuclei in \( D \). Pólya's theorem gives a generating function for the equivalence classes of maps by the following substitution in the cycle index.

\[
GF = P_G[x_k \to \sum_{r \in R} w(r)^k] \tag{64}
\]

The coefficient of \( \alpha_i^{-1}c_0 \) \((N \text{ being the total number of nuclei})\) gives the number of equivalence classes of nuclei under the action of \( G \).

This can be illustrated with the example of fluorine NQR spectrum of antifluorite 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

\[
GF_{O_h} = \frac{1}{48}[(\alpha_1 + \alpha_2)^6 + 8(\alpha_1^2 + \alpha_2^2)^2 + 9(\alpha_1 + \alpha_2)^2(\alpha_1^2 + \alpha_2^2) + (\alpha_1^3 + \alpha_2^3)^2 + 2(\alpha_1^4 + \alpha_2^4)]
\]

(65)

The coefficient of \( \alpha_1^N\alpha_2 \) 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 \( C_{4v} \) and \( C_1 \) subgroups of the \( O_h \) group. The cycle indices for \( C_{4v} \) and \( C_1 \) are

\[
P_{C_{4v}} = \frac{1}{2}[x_1^4 + 2x_1^2x_2 + x_2^2] \tag{66}
\]

\[
P_{C_1} = \frac{1}{2}[x_1^4 + x_2^2] \tag{67}
\]

The corresponding generating functions are

\[
GF_{C_{4v}} = \frac{1}{48}[(\alpha_1 + \alpha_2)^6 + 2(\alpha_1 + \alpha_2)^2(\alpha_1^2 + \alpha_2^2) + \alpha_1(\alpha_1^2 + \alpha_2^2)^2 + \alpha_2(\alpha_1^2 + \alpha_2^2)^2 + 2(\alpha_1^4 + \alpha_2^4)]
\]

(68)

\[
GF_{C_1} = \frac{1}{2}[(\alpha_1 + \alpha_2)^6 + (\alpha_1^2 + \alpha_2^2)^3] \tag{69}
\]

The coefficient of \( \alpha_1^2\alpha_2 \) in these generating functions are 2 and 3, indicating 2 and 3 equivalence classes under the action of \( C_{4v} \) and \( C_1 \) symmetries. Thus a single fluorine NQR line of an antifluorite crystal splits into two lines for a distorted crystal with \( C_{4v} \) symmetry and three lines for a crystal with \( C_1 \) symmetry. This is consistent with the observation of Sutton and Armstrong.226

\section{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.

Sinan6glu229-231 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. Sinan6glu 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.

Mezey242-246 has formulated a new framework called "reaction topology". This enables description of molecular structure, conformational changes, and reaction mechanisms. 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. Bader248 has shown, for example, the formation and destruction of a cage structure in the molecule \( C_9 H_4 \) ([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.

\subsection{Characteristic Polynomials of Graphs}

Characteristic polynomials of graphs are structural invariants and have several important applications to
chemical problems.282-287 (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 $\pi$ 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 $\pi$-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.281,296 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 Bonchev288 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

$$P_G(\lambda) = |A - \lambda I|$$

where I is the identity matrix of the same order as 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 author288 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 IV-A.](image1)

![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.](image2)

![Figure 13. $Q_3$ is the tree obtained by pruning the tree $Q_1$ in Figure 12. $T_{12}$ is a typical fragment.](image3)

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 $\Gamma$ 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 Balasubramanian284 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 \( Y_1, Y_2, \ldots \) 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

\[
A_{ij} = \begin{cases} 
H_{h_{ij}} & \text{if } i = j \text{ and } i \in Y_h \\
-H_{h_{ij}} q_{ij} & \text{if } i \neq j \text{ and } i \in Y_h
\end{cases}
\]  

(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 \( Q_i \) 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 \( Q_i \) 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 \( t^{(ij)}_{m,l} \). Then define a matrix \( D^{(ij)} \) as follows

\[
D^{(ij)} = \begin{cases} 
H_{h_{ij}} & \text{if } l = m \text{ and } l \in Y_{h_{ij}} \\
-H_{h_{ij}} t^{(ij)}_{m,l} & \text{if } l = m \text{ and } l \in Y_{h_{ij}}
\end{cases}
\]  

(71)

where \( H_{h_{ij}} \) is the secular determinant of the matrix \( D^{(k,j-1)} \) and \( H_{h_{ij}}^{(j)} \) 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 \( T_{h_{ij}} \). \( H_i \) is simply the characteristic polynomial of the type \( T_{h_i} \). If the type \( T_{h_i} \) contains \( i \) vertices, this characteristic polynomial will be denoted as \( h_i \) and the polynomial obtained by deleting the root of \( T_{h_i} \) 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

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

(72)

where \( q^{(n)}_{lm} \) 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.
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 \( \chi \) to be the character of the identity representation in the GCCI's. Let \( D \) be the set of 20 carbon nuclei. Let \( R \) be a set containing two elements. Let \( \alpha_1 \) and \( \alpha_2 \) be the weights of elements in \( R \). Then for this case

\[
GF = \frac{1}{16} [2(\alpha_1 + \alpha_2)^{20} + 4(\alpha_1^5 + \alpha_2^5) + 6(\alpha_1^2 + \alpha_2^2)]^{10} + 
\]

\[
4(\alpha_1 + \alpha_2)^2(\alpha_1^2 + \alpha_2^2)^9 \] (90)

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

\[
\frac{2}{16} \{ (\chi^0) + 2\{f\} \} = 3 \] (91)

The classes of nuclei are

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

\[
C_2 = \{ 3, 5, 8, 10, 13, 15, 18, 20 \} \] (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 \( C_1 \) can be obtained by finding the generating function restricted to \( C_1 \), with the following definition of \( P_G^{\chi} \). Let \( d_i \) denote a vector centered on the atom \( d_i \) perpendicular to the plane of the paper. Then define

\[
P_G^{\chi}(g) = \frac{1}{|G|} \sum_{g \in G} \chi^{\chi}(g) x_i^{d_i} x_i^{\chi} \ldots 
\]

where

\[
\chi = \{ \begin{array}{ll} -1 & \text{if } d_i = d_k \text{ for some } k \\ 1 & \text{otherwise} \end{array} \] (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

\[
GFC_j(C_j) = P_G^{\chi}(C_j) \chi h_k \Rightarrow \sum_{i} \alpha_i \] (95)

where \( \chi \) is the character of the irreducible representation \( \Gamma_i \). Expressions thus obtained for all irreducible representations of \( D_{2h} \) and for each equivalence class are shown in Table VII. The coefficient of \( \alpha_1^{m} \alpha_2 \) in each expression, where \( m = |C_j| \) gives the number of times the irreducible representation \( \Gamma_i \) 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 \( F \) is shown in Table VII, even though for the present problem only the coefficient of \( \alpha_1^{m} \alpha_2 \) is significant. However, the other coefficients do have combinatorial significance, viz., a typical coefficient \( \alpha_1^{m} \alpha_2 \) in the generating function which corresponds to the irreducible representation \( \Gamma \) 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 \( \Gamma \) and the class \( C_j \). The projection operator which corresponds to each irredu-

**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 Cotton\(^{303}\)) used in quantum calculations of symmetric molecules. The present author\(^{304}\) 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 porphine 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 \( \chi \) to be the character of the identity representation in the GCCI's. Let \( D \) be the set of 20 carbon nuclei. Let \( R \) be a set containing two elements. Let \( \alpha_1 \) and \( \alpha_2 \) be the weights of elements in \( R \). Then for this case

\[
GF = \frac{1}{16} [2(\alpha_1 + \alpha_2)^{20} + 4(\alpha_1^5 + \alpha_2^5) + 6(\alpha_1^2 + \alpha_2^2)]^{10} + 
\]

\[
4(\alpha_1 + \alpha_2)^2(\alpha_1^2 + \alpha_2^2)^9 \] (90)

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

\[
\frac{2}{16} \{ (\chi^0) + 2\{f\} \} = 3 \] (91)

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 combintorial methods (see Section IVB).
TABLE VII. The Combinatorics of Symmetry Adaptation

<table>
<thead>
<tr>
<th>irreducible representation</th>
<th>class</th>
<th>GF</th>
<th>freq of occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 A_R</td>
<td>C_R, C_S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2 A_R</td>
<td>C_R, C_S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3 B_R</td>
<td>C_R, C_S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4 B_R</td>
<td>C_R, C_S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5 E_g</td>
<td>C_R, C_S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6 A_u</td>
<td>C_R, C_S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7 A_u</td>
<td>C_R, C_S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8 B_u</td>
<td>C_R, C_S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9 B_u</td>
<td>C_R, C_S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10 E_u</td>
<td>C_R, C_S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11 A_R</td>
<td>C_R, C_S</td>
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<td>12 A_R</td>
<td>C_R, C_S</td>
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<td>0</td>
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<tr>
<td>13 B_R</td>
<td>C_R, C_S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>14 B_R</td>
<td>C_R, C_S</td>
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</tr>
<tr>
<td>20 E_u</td>
<td>C_R, C_S</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The combinatorics of p orbitals are 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 Pauli305-310 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. Shavitt311,312,317 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-workers318,319 have developed computer programs based on GUGA which enable CI calculations involving a very large number of configurations. Schaefer's318,319 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^r with the character x generates the Gel'fand states formed by the spin states with the Young diagram associated with the irreducible representation whose character is x.

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

\[
P_G^{(3,1)} = \frac{1}{24} \left[ 3x_1 + 6x_1^2 x_2 - 6x_4 - 3x_2^3 \right]
\]

If x_1, x_2, and x_3 are the weights of three spin states, then GF is given by

\[
GF^{(3,1)} = \frac{1}{24} \left[ 3(x_1^4 + x_2 + x_3)^4 + 6(x_1 + x_2 + x_3)^2(x_1^2 + x_2^2) + x_2^3 + 3x_1x_2 - 6(x_1^4 + x_2^4 + x_3^4) - 3(x_1^2 + x_2^2 + x_3^2)^2 \right]
\]

This on simplification yields

\[
x_1^3 + x_2^3 + x_3^3 + x_4 + x_2x_3 + x_1x_2 + x_1x_3 + x_1x_2^2 + x_1x_3^2 + x_2x_3^2 + 2x_2x_3 + x_1x_2^2 + 2x_1x_3^2 + 2x_1x_2x_3 + 2x_2x_3^2 + 2x_1x_2 + 2x_1x_3 + 2x_2x_3 + x_1 + x_2 + x_3 + x_4
\]

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

\[
\frac{1}{24} \left[ 3 - 3^2 - 6 - 3^2 \right] = 15
\]

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-workers showed that a combinatorial problem known as the cell-growth problem has potential applications in the enumeration of carboxenic benzenoid hydrocarbons and in the construction of potentially carboxenic 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-workers have recently reviewed the use of group theory and related topics in stereochemistry. Bader has recently provided a concise review of applications of topology to molecular structure. Kerber and James 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. 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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