CROATICA CHEMICA ACTA CCACAA **57** (6) 1525—1552 (1984)

CCA-1541

YU ISSN 0011-1643
UDC 541
Author's Review

Recent Applications of Group Theoretical Generators to Chemical Physics

*Krishnan Balasubramanian**

Department of Chemistry, Arizona State University, Tempe, Arizona 85287, USA

Received February 8, 1984

The development and the use of generating function methods for several problems in Chemical Physics are reviewed. These applications include applications to NMR, nuclear spin statistics of rovibronic levels, isomerization reactions and NQR spectra of crystals exhibiting phase transitions. The development of symmetry groups of non-rigid molecules as generalized wreath products and the related applications are outlined.

1. INTRODUCTION

One of the most important branches of discrete mathematics is combinatorics or combinatorical mathematics. Unfortunately, as Berge[1] stated, a satisfactory definition of this area does not seem to exist in the literature even though one understands what it means. Berge 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 deals with finding the number of ways of obtaining configurations when they are obtainable. Combinatorics evolved by way of finding methods or algorithms for enumerating configurations (instead of executing the experiment with desired specifications by brute force). One such method, which is the backbone of combinatorics, is the generating-function method discovered by Laplace (though conceived by Euler earlier). For example, 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. For example, chemistry seems to have been a ground for the development of some most important combinatorial theorems. Cayley[2–5] in the year 1857 recognized the correspondence between enumerating the isomers of organic molecules of the formula C_nH_{2n+2} and enumerating trees. Pólya[6] in

---

* Alfred P. Sloan foundation fellow.

1937 published his classical paper on what is now well known as Pólya's theorem which was anticipated by Redfield.[7] This theorem essentially gives generating functions for the enumeration of configurations under group action in terms of what is known as the cycle index of a group. The cycle index of a group defined by Pólya is the same as the group-reduction function of a group defined by Redfield shown below

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

if $x_1^{b_1} x_2^{b_2} \ldots$ is a representation of a typical permutation $g \in G$ having b_1 cycles of length 1, b_2 cycles of length 2 *etc.* Let D and R be two finite sets and G be a group acting on D. Consider all functions from D to R denoted as R^D. Let $f_1, f_2 \in R^D$ be equivalent if there exists a $g \in G$ such that

$$f_1(d) = f_2(gd), \text{ for every } d \in D.$$

Functions that are equivalent belong to the same class. If one associates a weight w(r) with every $r \in R$ then Pólya proved that the generating function for equivalence classes of functions in R^D, is

$$F = P_G(x_k \to \sum_{r \in R} w^k(r)).$$

Redfield obtained the number of equivalence classes in terms of group-reduction functions and in fact the above result of Pólya was implicit in an example given by Redfield for finding the number of ways of coloring the vertices of a cube such that no two colorings are obtainable by any rotation of the cube. However, Redfield did not rigorously prove the above result which was done by Pólya in 1937. A part of the paper of Pólya in fact deals with the enumeration of isomers and it appears that the problem of isomer enumeration was a motivation for this theorem. Subsequently, Harary,[8] Read,[9] Robinson,[10] Sheehan,[11] Williamson[12–14] and several other mathematicians worked on many ramifications of Pólya's theorem.

The other intimately connected field of combinatorics is the theory of finite groups. Finite groups which characterize the algebra of the symmetry of discrete structures are known to be potentially useful in predicting many physical and chemical properties. One of the most important finite groups is the symmetric group whose inherent discrete structure is well known. For example, the conjugacy classes and the number of irreducible representations of the symmetric groups are given by the number of partitions of n if n is the number of objects that are permuted by the symmetric group under consideration. The generating functions for these partitions have to be obtained along purely combinatorial lines. The dimension of each irreducible representation of symmetric groups is obtainable by the well-known Frame-Robinson-Thrall's combinatorial theorem.[15] The characters of symmetric groups can be found through purely combinatorial principles.[16] Difficulties in obtaining the character tables of the symmetry groups of non-rigid molecules have been recognized ever since the work of Longuet-Higgins.[17] The characters of the symmetry groups of non-rigid molecules can be obtained using combinatorial techniques.

Now let us briefly sketch some of the important chemical problems, a few of which were the motivations for new techniques in combinatorics, while the others could be solved using known methods.

A classical example 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 ferro-magnets with nearest neighbor interaction. The problem is soluble for a one-dimensional lattice and Onsager solved the two-dimensional problem. Kasteleyn[18] showed the correspondence between the Ising problem and a graphical problem known as the dimer covering problem on a »bath-room tile lattice.« The dimer covering problem asks for the number of ways of forming disjoint 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 disjoint dimers that can be formed with the molecular graph of the aromatic hydrocarbon. For an elementary review of this topic, see Herndon.[19] Dimers on molecular graphs can be obtained by several combinatorial techniques such as pfaffians,[20] recursive relations *etc.*

The objective of this paper is to review the development and applications of this powerful combinatorial tool, namely, the generating function method. We review several applications of the generating function methods to non-rigid molecules, NMR, nuclear spin statistics, isomerisation reactions and NQR.

In section 2 we review the formulation of symmetry groups of non-rigid molecules as generalized wreath product groups. In section 3 a generating function obtained from generalized character cycle indices is introduced. In section 4 applications of this method to nuclear spin statistics of rovibronic levels are reviewed. In section 5 we outline applications to NMR, section 6 discusses applications to isomerization processes and in the last section applications to NQR spectra are discussed.

2. SYMMETRY GROUPS OF NON-RIGID MOLECULES AS GENERALIZED WREATH PRODUCTS

Formulation

The present author[21-24] showed that the symmetry groups of non-rigid molecules which contain several internal rotors can be expressed as generalized wreath product groups. A summary of the recent developments of generalized wreath product groups and applications appears in the recent paper of Balasubramanian[51] in the book by Serre and Maruani. (Also, see the article by Serre[52] in this book.) We briefly review the theory of generalized wreath product groups here with examples to make this self-contained. We start with an example of the non-rigid hydrazine molecule (N_2H_4). This molecule in its equilibrium conformation contains only a two-fold axis of symmetry. This molecule is non-rigid in that twisting and inversion operations interconvert all the 16 possible conformations into one another. Consider the permutational subgroup of this molecule. All the permutation operations of the non-rigid molecule can be generated by a group product of much simpler groups, known as wreath product. Let us model hydrazine by a particles-in-box model. Consider each nitrogen atom as a box and the protons attached to that atom as

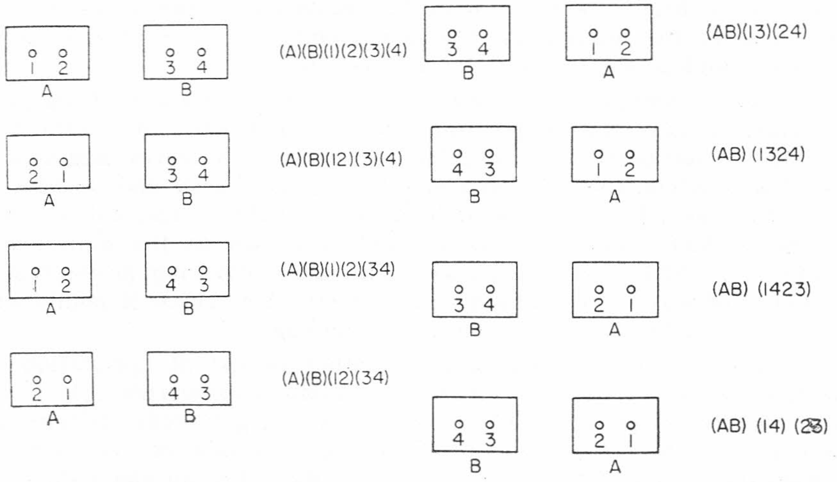

Figure 1. Particle-in-box model for the permutation group of the non-rigid N_2H_4. The permutation group of N_2H_4 is the wreath product of the groups of boxes (S_2) and particles (S_2).

the two particles in the corresponding box (see Figure 1). Then twisting operation permutes the protons or the particles in each box. The two nitrogen atoms (and hence the protons attached to the nitrogen atoms) can be permuted by an operation preserving the rigid symmetry of the molecule. Consequently, we have two permutation groups namely, a permutation group G acting on the boxes themselves and a permutation group H acting on particles in each box. H can be called a torsion group if the particles in each box are permuted by torsion. The symmetry group of the non-rigid molecule consists of permutations of particles in each box (torsional permutations), the permutations of the boxes, which in turn induce permutations of particles in all boxes and inversion operations. All the operations of hydrazine generated by permutations of particles and the permutations of boxes are shown in Figure 1. The resulting operations span a group of order 8. These operations can be generated by knowing the operations in the group G and H. The group of all particles in all the boxes is the wreath product of the group G with the group H, denoted as G [H]. In this example, G and H are both S_2, symmetric group of 2 objects containing 2! elements. Wreath product groups were first formulated by Pólya.[6] The order of G [H], $|G[H]|$, is given by

$$|G[H]| = |G| \cdot |H|^{|B|}$$

where $|B|$ is the number of boxes in the particle-in-box model of a non-rigid molecule. The advantage of this group product is that the symmetry operations, conjugacy class structures, irreducible representations and several chemically interesting generating functions of wreath product G [H] can just be obtained in terms of G and H. A formal definition of the wreath product groups will be given now. Let π be a map from B to H. Let g be an element in G. Then G [H] is the set of possible elements $(g; \pi)$. Products of two elements $(g; \pi)$ and $(g'; \pi')$ is

$$(g;\pi)(g';\pi') = (gg';\pi\pi_g'),\ \pi_g'(i) = \pi'(g^{-1}i),\quad i \in B.$$

Products of two maps π and π' are defined by

$$\pi\pi'(i) = \pi(i)\,\pi'(i),\quad i \in B.$$

This can be illustrated with hydrazine. Let g be the identity (*i. e.*, all the boxes are in their natural positions) and g′ be a permutation of boxes denoted as (AB). Let π and π' be the maps shown below:

$$\pi(1) = (12) \qquad \pi'(1) = (1)(2)$$

$$\pi(2) = (34) \qquad \pi'(2) = (34).$$

Then $(g;\pi) = (12)(34)$ and $(g';\pi') = (AB)(13)(24)(34)$. Note that g′ permutes boxes and, in turn, induces permutation of particles in all boxes. Product of π and π' are shown below:

$$\pi\pi'(1) = \pi(1)\,\pi'(1) = (12)$$

$$\pi\pi'(2) = \pi(2)\,\pi'(2) = (3)(4).$$

Since g is just the identity element π_g' is π' itself. The product $(g;\pi)(g';\pi')$ has the following representation:

$$(g;\pi)(g';\pi') = ((AB);\pi\pi')$$

with $\pi\pi'$ defined by the above definition.

Define a group G′ which is isomorphic to G as

$$G' = \{(g;e') \mid g \in G,\ e'(j) = {}^1H,\ j \in B\},$$

where ^1H is the identity of the group H. The group G [H] is then isomorphic to

$$(H_1 \times H_2 \times \ldots \times H_b) \cdot G',\quad b = |B|$$

where

$$H_i = \{(e;\pi) \mid \pi(j) = {}^1H,\ j \neq i\}$$

with e being the identity of G. Note that $H^* = H_1 \times H_2 \times \ldots \times H_b$ is simply a b-fold direct product of b copies of the grup H. The group H^* is known as the basis group of G [H]. It can be shown that H^* is an invariant subgroup of G [H]. Thus, the permutation representation of G [H] = H^*. G′ is simply a semi-direct product of H^* and G′. Altmann[25] first noted that the symmetry groups of non-rigid molecules can be expressed as semidirect products. Serre[26] used Mackey's theorem for semi-direct products in the chemical contexts. Woodman[27,28] showed the use of semi-direct product groups in representing the NMR groups of non-rigid molecules. However, wreath product representation which is a special case of a semi-direct product representation is superior to semi-direct products in that several properties of G [H] can be simply obtained if the corresponding properties of G and H are known. For example, conjugacy classes of S_n [H] for any H (where S_n is the symmetric group of n objects) can be obtained from the conjugacy classes of S_n and H[29]. The irreducible representations of G [H] can be obtained from the irreducible representations of G and H. The generating functions for several problems concerning spectroscopy of non-rigid molecules can be obtained in terms of G and H. Kerber and co-workers[29-31] have made significant contributions to the representation theory of wreath product groups. We briefly review their methodology here.

The irreducible representations of $H^* = H_1 \times H_2 \times \ldots \times H_b$ are the outer tensor products

$$F^* = F_1 \# F_2 \# \ldots \# F_b$$

where $\#$ denotes outer tensor product. The matrices of outer product are simply the Kronecker products of matrices contained in the outer product. In symbols,

$$F^* (e; \pi) = F_1 [\pi (1)] \times F_2 [\pi (2)] \times \ldots \times F_b [\pi (b)]$$

$$= f_{i_1k_1} [\pi (1)] \cdot f_{i_2k_2} [\pi (2)] \ldots f_{i_bk_b} [\pi (b)].$$

For each representation F^* there is a group known as inertia group of F^* which consists of elements in G [H] that leave F^* invariant. Symbolically, the inertia group $G_{F^*} [H]$ is

$$G_{F^*} [H] = \{ (g;\pi) \mid F^{*(g;\pi)} \sim F^* \}.$$

where

$$F^{*(g;\pi)} (e; \pi') = F^* (g; \pi)^{-1} (e; \pi') (g; \pi).$$

The group G_{F^*} [H], by definition is isomorphic to $H^* \cdot G_F'$. The group G_F' is known as the inertia factor of F^* and it is of the form

$$G'_{F^*} = \{ (g; e') \mid F^{*(g;e')} \sim F^*\}.$$

Two representations F^* and $F^{*\prime}$ are said to be equivalent if

$$g F^* = F^{*\prime},$$

where g acts on F^* as

$$g F^* = g (F_1 \# F_2 \# \ldots \# F_t) = F_{g1^{-1}} \# F_{g2^{-1}} \# \ldots \# F_{gt^{-1}}.$$

To illustrate consider hydrazine for which the representations $A_1 \# A_2$ and $A_2 \# A_1$ are equivalent by the above rule. Let K be the set of inequivalent representations among the possible representations F^* .If one knows the representation matrices of $F^* (e; \pi)$ one can obtain the representation matrices of $F^* (g; \pi)$ by

$$\breve{F}^* (g; \pi) = f_{i_1k_{g1^{-1}}} [\pi (1)] f_{i_2k_{g2^{-1}}} [\pi (2)] \ldots f_{i_bk_{gb^{-1}}} [\pi (b)].$$

$\breve{F}^* (g; \pi)$ is simply a permutation of the columns of the matrix $F^* (e; \pi)$ induced by g^{-1}. Each irreducible representation in the set K of inequivalent representations from the inertia group G_{F^*} [H] induces a representation in G [H], which is irreducible. In symbols, the irreducible representations of G [H] are given by

$$\Gamma = (\breve{F}^* \otimes F') \uparrow G [H]$$

where the arrow stands for an induced representation, F′ is an irreducible representation in the inertia factor group G_{F^*}.

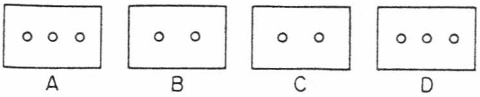

Figure 2. Particle-in-box model for the generalized wreath product $S_2[S_3, S_2]$. This group is the NMR group of butane.

Generalization of the wreath product groups to generalized wreath product groups is possible. The simplest non-trivial example of such a system is shown in Figure 2 in particle-in-box model. In Figure 2, let $G = \{(A)(B)(C)(D), (AD)(BC)\}$ be a permutation group of boxes. Note that G does not permute boxes containing different number of particles. Equivalently, the cycle products of G can be divided into disjoints sets. If the cycle products of a group can be divided into more than one disjoint set it is known as an intransitive group. The cyclic group C_5 of 5 objects is an example of a transitive group and the group G shown above is intransitive. The cycle products of G can be divided into the disjoint sets $Y_1 = \{A, D\}$, $Y_2 = \{B, C\}$. Alternatively G does not permute elements in different Y sets. Let H_i be the group acting on particles in the boxes belonging to the set Y_i (with $1 \leqslant i \leqslant t$). Let G be the group acting on the boxes such that the boxes can be divided into disjoint sets $Y_1, Y_2, \ldots, Y_t$. Then the group of all the particles in all the boxes is the generalized wreath product group $G[H_1, H_2, \ldots, H_t]$ defined as

$$G[H_1, H_2, \ldots, H_t] = \{(g; \pi_1, \pi_2, \ldots, \pi_t)/g \in G, \pi_i : Y_i \to H_i\}.$$

The product of any two elements $(g; \pi_1, \pi_2, \ldots, \pi_t)$ and $(g'; \pi_1', \pi_2', \ldots, \pi_t')$ is

$$(g; \pi_1, \pi_2, \ldots, \pi_t)(g'; \pi_1', \pi_2', \ldots, \pi_t') = (gg'; \pi_1 \pi_{1g}', \pi_2 \pi_{2g}', \ldots, \pi_t \pi_{tg}')$$

with

$$\pi_{ig}(j) = \pi_i(g^{-1} j), j \in Y_i.$$

The order of $G[H_1, H_2, \ldots, H_t]$ is given by

$$|G[H_1, H_2, \ldots, H_t]| = |G| |H_1|^{|Y_1|} |H_2|^{|Y_2|} \ldots |H_t|^{|Y_t|}.$$

The representation theory of wreath product groups can be extended to generalized wreath groups as shown by the present author[24]. We now briefly review this here. Let $|Y_i| = m_i$. Then $G[H_1, H_2, \ldots, H_t]$ has the following permutation representations:

$$G[H_1, H_2, \ldots, H_t] = (H_1^{m_1} \times H_2^{m_2} \times \ldots \times H_t^{m_t}) \cdot G'$$

where

$$G' = \{(g; e_1, e_2, \ldots e_t) \mid e_i(j) = {}^1H_i\},$$

$$H_i^{m_i} = \{(e; e_1, e_2, \ldots, \pi_i, e_{i+1}, \ldots, e_t)\}.$$

The irreducible representations of $H_1^{m_1} \times H_2^{m_2} \times \ldots \times H_t^{m_t}$ are of the form $F^* = F_1^{m_1*} \# F_2^{m_2*} \# \ldots \# F_t^{m_t*}$ with $F_i^{m_i*} = F_{i1} \# F_{i2} \# \ldots \# F_{im_1}$. Let the inertia group of F^* be $G_{F^*}[H_1, H_2, \ldots, H_t]$ and the corresponding inertia factor be G_{F^*}'. Let the inequivalent representations of the form F^* constitute the set K. Then the irreducible representations of $G[H_1, H_2, \ldots, H_t]$ are

$$(\breve{F}^* \otimes F') \uparrow G[H_1, H_2, \ldots, H_t]$$

TABLE I

*The Character Table of the Molecular Group of the Nonrigid Triphenyl. The Asterisk on the Permutations Indicates Permutation Followed by Inversion.**

Conjugacy classes	E	(1,3)(4,5)	(1,3)(4,5) (10,14)(11,13)	(1,11)(2,12)(3,13) (4,14)(5,10)(6,8) (7,9)	(2,12)(1,13,3,11) (6,8)(7,9)(4,10,5,14)	(6,9)(7,8)	(1,3)(4,5)(6,9)(7,8)	(1,3)(4,5)(10,14) (11,13)(6,9)(7,8)	(1,11)(2,12)(5,10) (3,13)(4,14)(6,7)(8,9)	(2,12)(1,13,3,11) (6,7)(8,9)(4,10,5,14)	E*	(1,3)(4,5)*	(1,3)(4,5) (10,14)(11,13)*	(1,11)(2,12)(3,13) (4,14)(5,10)(6,8)(7,9)*	(2,12)(1,13,3,11) (6,8)(7,9)(4,10,5,14)*	(6,9)(7,8)*	(1,3)(4,5)(6,9) (7,8)*	(1,3)(4,5)(10,14) (11,13)(6,9)(7,8)*	(1,11)(2,12)(5,10) (3,13)(4,14)(6,7)(8,9)*	(2,12)(1,13,3,11) (6,7)(8,9)(4,10,5,14)*
Order	1	2	1	2	2	1	2	1	2	2	1	2	1	2	2	1	2	1	2	2
A'_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
B'_{1g}	1	1	1	-1	-1	1	1	1	-1	-1	1	1	1	-1	-1	1	1	1	-1	-1
A'_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	1	-1	1	-1	1	1	-1	1	-1	1
B'_{2g}	1	-1	1	1	-1	1	-1	1	1	-1	1	-1	1	1	-1	1	-1	1	1	-1
A''_{1g}	1	1	1	1	1	-1	-1	-1	-1	-1	1	1	1	1	1	-1	-1	-1	-1	-1
B''_{1g}	1	1	1	-1	-1	-1	-1	-1	1	1	1	1	1	-1	-1	-1	-1	-1	1	1
A''_{2g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
B''_{2g}	1	-1	1	1	-1	-1	1	-1	-1	1	1	-1	1	1	-1	-1	1	-1	-1	1
A'_{1u}	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
B'_{1u}	1	1	1	-1	-1	1	1	1	-1	-1	-1	-1	-1	1	1	-1	-1	-1	1	1
A'_{2u}	1	-1	1	-1	1	1	-1	1	-1	1	-1	1	-1	1	-1	-1	1	-1	1	-1
B'_{2u}	1	-1	1	1	-1	1	-1	1	1	-1	-1	1	-1	-1	1	-1	1	-1	-1	1
A''_{1u}	1	1	1	1	+1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1
B''_{1u}	1	1	1	-1	-1	-1	-1	-1	1	1	-1	-1	-1	1	1	1	1	1	-1	-1
A''_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1	-1	1
B''_{2u}	1	-1	1	1	-1	-1	1	-1	-1	1	-1	1	-1	-1	1	1	-1	1	1	-1
E'_g	2	0	-2	0	0	2	0	-2	0	0	2	0	-2	0	0	2	0	-2	0	0
E''_g	2	0	-2	0	0	-2	0	2	0	0	2	0	-2	0	0	-2	0	2	0	0
E'_u	2	0	-2	0	0	2	0	-2	0	0	-2	0	2	0	0	-2	0	2	0	0
E''_u	2	0	-2	0	0	-2	0	2	0	0	-2	0	2	0	0	2	0	-2	0	0

* From K. Balasubramanian, *J. Chem. Phys.* **72** (1980) 665.

where F′ is a representation of G'_{F^*} The tilde symbol has the same meaning as in the representation theory of wreath product groups. The F*'s are chosen from K. Consider the non-rigid triphenyl as an example. The symmetry group of this molecule is the generalized wreath product $C_{2v}\,[S_2, S_2]$. The character table of this group was obtained in an earlier paper of the present author.[24] It is shown in Table I.

3. GENERATING FUNCTION TECHNIQUES

The method of generating functions is reviewed here with nuclear spin statistics as an example. Thus we first outline the definitions and preliminaries applied to nuclear spin statistics. The importance of nuclear spin statistics in molecular spectroscopy is well known. The nuclear spin statistical weights of the rotational levels provide the intensity patterns of rotational lines.

3.1. *Preliminaries*

Let D be the set of nuclei of the same kind and R be the set of possible spin states of the nuclei in the set D. To illustrate, consider the nonrigid hydrazine molecule. D is the set of four hydrogen nuclei and R is the set of two spin states. The nitrogen nuclei will be treated as a separate D set. We consider each kind of nuclei as a separate D set and obtain the spin species of each kind of nuclei separately. Then the overall nuclear spin species is obtained as a direct product of different kinds of nuclear spin species. The symmetry group of the nonrigid hydrazine molecule is given by the wreath product $C_{2v}\,[C_2]$. In this example, the PI group is a direct product of P and I groups and thus the nuclear spin statistics can be treated either in P or in PI groups. The group $C_{2v}\,[C_2]$ acts on the set D in that it permutes the nuclei in D. Consider the set F of maps from D to R. Image of each such map in F is a spin function. An example of such a map for hydrazine is shown below

$$f_1\,(1) = \underset{\sim}{\beta},\ \ f_1\,(2) = \underset{\sim}{\alpha},$$

$$f_1\,(3) = \underset{\sim}{\alpha},\ \ f_1\,(4) = \underset{\sim}{\beta}.$$

The PI group which acts on D also acts on F by the recipe shown below. $h\,[f\,(i)] = f\,(h^{-1}\,i)$ for every $i \in D$, $h \in G\,[H_1, H_2, \ldots H_t]$. To illustrate, consider h as $(1324) \in C_{2v}\,[C_2]$. Since $h^{-1} = (1423)$, the action of, h on the map f_1 is shown below:

$$hf_1\,(1) = f_1\,(h^{-1}\,1) = f_1\,(4) = \underset{\sim}{\beta},$$

$$hf_1\,(2) = f_1\,(h^{-1}\,2) = f_1\,(3) = \underset{\sim}{\alpha},$$

$$hf_1\,(3) = f_1\,(h^{-1}\,3) = f_1\,(1) = \underset{\sim}{\beta},$$

$$hf_1\,(4) = f_1\,(h^{-1}\,4) = f_1\,(2) = \underset{\sim}{\alpha}.$$

Consequently, (1324) acts on $\underset{\sim}{\beta}\,\underset{\sim}{\alpha}\,\underset{\sim}{\alpha}\,\underset{\sim}{\beta}$ to produce the spin function $\underset{\sim}{\beta}\,\underset{\sim}{\alpha}\,\underset{\sim}{\beta}\,\underset{\sim}{\alpha}$.

In order to account for the number of various possible spin states in a spin function let us introduce the concept of weight of an element r in the set R. To each r ∈ R assign a weight $\omega(r)$, which is just a formal symbol used to differentiate the various spin states in the set R. For example, we may assign a weight α to the spin state $\underset{\sim}{\alpha}$, and a weight β to the spin state $\underset{\sim}{\beta}$ for the spin 1/2 problem. Then define the weigth of any function f ∈ F as the products of the weights of the images of f. In symbols, the weight of f, W (f) is given by

$$W(f) = \underset{d \in D}{\Pi} \omega[f(d)].$$

The weight of the map f_1 defined above is $\alpha^2 \beta^2$ since its image contains 2 $\underset{\sim}{\alpha}$'s and 2 $\underset{\sim}{\beta}$'s and the weight of $\underset{\sim}{\alpha}$ is α and that of $\underset{\sim}{\beta}$ is β.

3.2. *Spin Projection Operators of Groups*

Let us denote the PI group $(G[H_1, H_2, \ldots, H_t])$ of a nonrigid molecule simply by H. Let V be a vector space of dimension $|R|$, the number of elements in the set R. For example, V is a three-dimensional vector space for the spin 1 problem. Let V^d be the d-fold tensor product of d copies of the vector space V. Symbolically,

$$V^d = \otimes_{d \in D} V.$$

Let $e_1, e_2, \ldots e_{|R|}$ be a basis for the vector space V. Then to each f ∈ F, we can assign an e_f defined as follows:

$$e_f = e_{f(1)} \times e_{f(2)} \times \ldots \times e\, f_{f(d)}.$$

e_f is a tensor in the space V^d. The set of tensors $S = \{e_f : f \in F\}$ forms a basis for V^d. For any h ∈ H, define an operator P (h) by its action on e shown below:

$$P(h)\, e_f = e_{hf} = e_{f(h^{-1} 1)} \times e_{f(h^{-1} 2)} \times \ldots \times e_{f(h^{-1} d)}.$$

Thus P (h) is a permutation operator relative to the basis S, since it permutes the tensors in S by way of the action of h on f. Let $h \rightarrow \chi(h)$ be the character of an irreducible representation Γ in H. Williamson,[12] in his general theorem for any group considered χ to be the character of one dimensional representations. However, Merris[32] generalized this result to irreducible representations of any dimension. Define an operator T_H^χ as follows:

$$T_H^\chi = \frac{1}{|H|} \sum_{h \in H} \chi(h) P(h).$$

T_H^χ is easily shown to be an idempotent operator, *i. e.*, $(T_H^\chi)^2 = T_H^\chi$. Equivalently, T_H^χ is a projection operator in the space V^d.

The projection operator T_H^χ projects all spin functions from D to R which transform according to the irreducible representation whose character is χ. However, if one wishes to project spin functions according to their total spin quantum number then one needs to consider a subspace of V^d in which only functions having the same total m_z spin quantum number are projected. For this purpose consider the subspace V_x^d of V^d spanned by all the tensors that have the same weight x. That is, V_x^d is spanned by the set $S_x = \{e_f : W(f) = x\}$. All the spin functions in the space S_x will have the same total m_z spin quantum number. Let the restrictions of the operators T_H^χ and P (h) to the subspace V_x^d of V^d spanned by all the tensors that have the same weight x. This is, V_x^d is spanned by the set $S_x = \{e_f : W(f) = x\}$. All the spin functions in the space S_x will have the same total m_z spin quantum number. Let the restrictions of the operator T_H^{χ} and $P(h)$ to the subspace V_x^d be $T_H^{\chi, x}$ and $P_x(h)$, respectively. The operator $T_H^{\chi, x}$ is a spin projector of spin functions with the same weight x. For example, if we consider all spin functions of the type $\alpha\beta\beta\beta$, $\beta\alpha\beta\beta$ *etc.*, which have the same weight $\alpha\beta^3 = x$, then $T_H^{\chi, x}$ projects only those spin functions that have 3β's and 1α. Define a weighted permutation operators $P_w(h)$ and a weighted projector $T_H^{\chi, W}$ as follows:

$$P_W(h) = \bigoplus_x x\, P_x(h),$$

$$T_H^{\chi, W} = \bigoplus_x x\, T_H^{\chi, x},$$

where ⊕ denotes a finite direct sum; x's vary over all the functions. In a matrix representation of $P_W(h)$, trace of $P_W(h)$, $\mathrm{tr}\, P_W(h)$ is

$$\mathrm{tr}\, P_W(h) = \sum_f{}^{(h)} W(f),$$

where the sum is taken over all $f \in F$ such that $hf = f$. To illustrate, if we consider the protons of hydrazine molecule with $R = \{\alpha, \beta\}$ and $h = (12)$ then

$$\mathrm{tr}\, P_W(h) = \alpha^4 + 2\alpha^3\beta + 2\alpha^2\beta^2 + 2\alpha\beta^3 + \beta^4.$$

(This is because by the action of h = (12), αααα, ααβα, αααβ, ααββ, ββαα, ββαβ, βββα, and ββββ are left invariant. Hence $\mathrm{tr}\, P_W(h)$ is the sum of the weights of the functions that are invariant under the action of h.) In this formulation Williamson and later Merris proved the following theorem:

Theorem 1:

$$T_H^{\chi, W} = \frac{1}{|H|} \sum_{h \in H} \chi(h) P_W(h).$$

Thus,

$$\mathrm{tr}\, T_H^{\chi, W} = \frac{1}{|H|} \sum_{h \in H} \chi(h)\, \mathrm{tr}\, P_W(h) = \frac{1}{|H|} \sum_{h \in H} \chi(h) \sum_f{}^{(h)} W(f).$$

The implication of this theorem is that the weighted spin projection operator is the same as the projection operator with permutation operator replaced by the corresponding weighted permutation operator. Trace of the weighted spin projector is the generator of the irreducible representations contained in the set of spin functions and the nuclear spin species.

3.3. *Generalized Character Cycle Indices (GCCI)*

In this section we introduce group structures called generalized character cycle indices, hereafter abbreviated as GCCI, which are potentially useful in expressing Williamson's theorem in a form suitable for applications. We also obtain the GCCI's of generalized wreath products $G[H_1, H_2, \ldots, H_t]$, which are generators of nuclear spin species and nuclear spin statistical weights in terms of GCCI's of $G, H_1, H_2, \ldots,$ and H_t. Consequently, it is not necessary to know the character table of the PI groups of nonrigid molecules in order to obtain the nuclear spin species.

Define the generalized character cycle index (GCCI) of a group H, corresponding to the character χ of an irreducible representation Γ of H as

$$P_H{}^{\chi} = \frac{1}{|H|} \sum_{h \in H} \chi(h)\, x_1^{b_1} \quad x_2^{b_2} \ldots x_n^{b_n},$$

where $x_1{}^{b_1} x_2{}^{b_2} \ldots x_n{}^{b_n}$ is a representation of a typical permutation $h \in H$, which has b_1 cycles of length 1, b_2 cycles of length 2, *etc.* Equivalently, the cycle type of $h \in H$ is $(b_1, b_2, \ldots, b_n)$. For example, the permutation (12) (34) of the PI group of hydrazine has the cycle representation $x_2{}^2$ since it has two cycles of length 2. Similarly the permutation (1324) of the same group has the cycle representation $x_4{}^1$ (1 cycle of length 4), *etc.* The GCCI which corresponds to character χ is just the sum of the product of cycle representations of elements in H and the corresponding character. For example, the character of the A_2 representation of the P group of hydrazine and the corresponding GCCI are shown below:

	e	(12)	(12) (34)	(14) (23)	(1324)
	1	2	1	2	2
A_2	1	—1	1	—1	1

$$P^{A_2}_{C_2\,[C_2]} = \frac{1}{8} (x_1{}^4 - 2x_1{}^2\, x_2 - x_2{}^2 + 2x_4).$$

We proceed to obtain the GCCi's of generalized wreath product G $[H_1, H_2, \ldots, H_t]$ in terms of GCCI's of G, H_1 $H_2, \ldots,$ and H_t. We need the concept of inertia group and inertia factor that we introduced in an earlier section for obtaining the GCCI's of G $[H_1, H_2, \ldots, H_t]$ in terms of the GCCI's of G, $H_1, H_2, \ldots, H_t$. Let the inertia group of a representation $F^* = F_1{}^{m_1} \# F_2{}^{m_2} \# \ldots \# \# F_t{}^{m_t*}$ be G_{F*} $[H_1, H_2, \ldots, H_t]$ and let G_F' be the corresponding inertia factor. By definition, GCCi of G'_{F*} corresponding to the character χ, is

$$P^{\chi}_{G'_{F*}} = \frac{1}{|G'_{F*}|} \sum_{g \in G'_{F*}} \prod_i \prod_j \chi(g) : x_{ij}^{c_{ij}(g)},$$

where $C_{ij}(g)$ is the number of j cycles of $g \in G_{F*}$ in the set Y_i. The GCCI of G'_{F*} takes the above form because g permutes elements only within a set Y_i. Hence $x_1{}^{b_1} x_2{}^{b_2} \ldots x_t{}^{b_t}$ can be written in the above form. Recall that $F_i{}^{m_i*}$ is the m_i-fold outer product of the same irreducible representation F_i. Let λ_k be the character of F_i. Define the GCCI, $Z_i{}^{\lambda_k}$ as

$$Z_i^{\lambda_k} = \frac{1}{|H_i|} \sum_{h \in H_i} \lambda_k(h)\, x_1^{b_1} \quad x_2^{b_2} \ldots .$$

Define $Z_{ij}{}^{\lambda_k}$ by the following substitution:

$$Z_{ij}^{\lambda_k} = Z_i^{\lambda_k} (x_l \to x_{lj}),$$

where the subscripts of the x variables are the products. If we denote an irreducible representation of $G[H_1, H, \ldots, H_t]$ by $\Gamma = (\#_i F_i^{m_i *} \otimes F') \uparrow G[H_1, H_2, \ldots, H_t]$ then a GCCI of $G[H_1, H_2, \ldots, H_t]$ which corresponds to the character of Γ, denoted by $P^{\Gamma}(G[H_1, H_2, \ldots H_t])$ is given by

$$P^{\Gamma}(G[H_1, H_2, \ldots, H_t]) = P^{\chi}_{G'_{F*}}(x_{ij} \rightarrow Z^{\lambda_k}_{ij}),$$

If this j cycle in Y_i is constituted by j copies of the representation whose character is λ_k. For all the irreducible representations, this result can be proved by a method similar to the one used by Williamson for wreath products. In particular, when Γ is an induced representation this result follows from a lemma of Foulkes[33] which relates the GCCI of an induced representation to the GCCI of the inducing representation. The substitution outlined above is reminiscent of plethysms of S-functions (see, Read's paper[34]). The above result is illustrated with hydrazine in Ref. 39. See also Ref. 40 for the use of GCCI.

3.4. *Generators of Nuclear Spin Species*

We now show one of the uses of GCCI's. The GCCI's defined in Sec. 3.3 are generators of nuclear spin species. Theorem 1 in Sec. 3.2 can be expressed in a convenient form in terms of the GCCI's. With a little algebraic manipulation it can be shown that Theorem 1 takes the following form:

$$\mathrm{tr}\, T_H^{\chi, W} = P_H^{\chi}\{x_k \rightarrow \sum_{r \varepsilon R} [w(r)]^k\}.$$

The coefficient of a typical term $w_1^{b_1} w_2^{b_2} \ldots$ in $\mathrm{tr}\, T_H^{\chi, W}$ gives the frequency of the irreducible representation Γ whose character is χ in the set of spin functions with the same weight $w_1^{b_1} w_2^{b_2} \ldots$. For example, if we set χ to be the character of A_2 representation of the PI group of hydrazine, then the coefficient of $\alpha^2 \beta^2$ in the polynomial obtained by replacing every x_k by $\alpha^k + \beta^k$ in the corresponding GCCI gives the number of A_2 representations in the set of spin functions that have 2α's and 2β's.

We now illustrate the above procedure with hydrazine. All the GCCI's of the PI group of hydrazine were obtained in Ref. 39. The generating function (GF), for the A_1 representation is given below.

$$\begin{aligned} GF^{A_1} &= P^{\Gamma_1}_{S_2[S_2]}(x_k \rightarrow \alpha^k + \beta^k) \\ &= \frac{1}{8}[(\alpha + \beta)^4 + 2(\alpha + \beta)^2(\alpha^2 + \beta^2) + 3(\alpha^2 + \beta^2)^2 + \\ &+ 2(\alpha^4 + \beta^4)] = \alpha^4 + \alpha^3\beta + 2\alpha^2\beta^2 + \alpha\beta^3 + \beta^4. \end{aligned}$$

Thus, spin function containing all α's has one A_1 representation, spin functions containing 3α's and 1β have one A_1 representation, spin functions containing 2α's and 2β's contain $2A_1$ representations, and so on. The coefficient of a typical term $\alpha^{a_1}\beta^{b_1}$ in this generating function corresponds to the spin quantum number $m_z = (a_1 - b_1)/2$ since α represents $m_z = \frac{1}{2}$ and β represents $m_z = -\frac{1}{2}$. Consequently, if one arragnes the spin species according to their m_z values as given by the above generating function, they separate into spin multiplets with m_z varying from —S to S. For example, from GF^{A_1} one obtains $^5A_1$ and $^1A_1$.

Consider borontrimethyl [$B(CH_3)_3$] as another example. This was considered by the present author[39] in an earlier paper. The PI group of this molecule is the wreath product $D_{3h}[C_3]$ or $D_3[C_3] \Lambda I$, where the symbol Λ denotes a semi-direct product. This is an example of a molecule whose PI group is not a direct product of P and I groups. We first obtain the GCCI's of the P group ($D_3[C_3]$) and then add the additional terms arising from the I group. The GCCI's of the group D_3 and C_3 are shown in Tables II and III, respectively.

TABLE II

The GCCI's of the Group D_3

Irreducible representation	$6 \cdot P_G^{\chi}$
$A_1 = [3]$	$x_1^3 + 2x_3 + 3x_1x_2$
$A_2 = [1^3]$	$x_1^3 + 2x_3 — 3x_1x_2$
$E = [2, 1]$	$2x_1^3 — 2x_3$

TABLE III

The GCCI's of the Cyclic Group C_3

Irreducible representation		$3 \cdot P_G^{\chi}$	
A_1		$x_1^3 + 2x_3$	
E	γ_1	$x_1^3 — x_3$	or $2x_1^3 — 2x_3$
	γ_2	$x_1^3 — x_3$	

The irreducible representation of $D_3[C_3]$, their GCCI's obtained using the GCCI's of D_3 and C_3 are shown in Table IV. When the inversion operations are included, the irreducible representations A_1, A_2, E_1, and I_7 double; the other GCCI's remain the same. The GCCI's of the PI group of $B(CH_3)_3$ are shown in Table V.

We now obtain the nuclear spin species of $^{11}B(^{12}CD_3)_3$ using these GCCI's, where D denotes the deuterium isotope of hydrogen. The total number of nuclear spin functions in this molecule is $4.3^9 = 78\,732$. One first finds the deuterium spin species and then multiplies the Boron spin species by a Clebsch--Gordan series. Denote the three nuclear spin states of D by λ, μ, and ν, which stand for spin states with nuclear spin = —1, 0, and 1, respectively. Then replace every x_k in the GCCI which corresponds to the irreducible representation Γ by $\lambda^k + \mu^k + \nu^k$. Then one obtains the generating function for nuclear spin species, corresponding to Γ. To illustrate, given below is the expression obtained by replacing every x_k in the GCCI of the irreducible representation I_3 of the PI group of $B(CD_3)_3$ by $\lambda^k + \mu^k + \nu^k$

$$GF^{I_3} = GCCI^{I_3}(x_k \rightarrow \lambda^k + \mu^k + \nu^k) = (1/324)\,[6(\lambda + \mu + \nu)^9 —$$

$$— 24(\lambda^3 + \mu^3 + \nu^3)^3 + 18(\lambda + \mu + \nu)^6(\lambda^3 + \mu^3 + \nu^3) + 18(\lambda + \mu + \nu)^3 \, x \, (\lambda^2 + \mu^2 + \nu^2)^3 +$$

$$+ 36(\lambda + \mu + \nu)^3(\lambda^6 + \mu^6 + \nu^6) — 18(\lambda^2 + \mu^2 + \nu^2)^3(\lambda^3 + \mu^3 + \nu^3) —$$

$$— 36(\lambda^3 + \mu^3 + \nu^3)(\lambda^6 + \mu^6 + \nu^6)] = \lambda^8\mu + 2\lambda^7\mu^2 + 3\lambda^6\mu^3 + 4\lambda^5\mu^4 + 4\lambda^4\mu^5 + 3\lambda^3\mu^6 +$$

$$+ 2\lambda^2\mu^7 + \lambda\mu^8 + \lambda^8\nu + 4\lambda^7\mu\nu + 9\lambda^6\mu^2\nu + 14\lambda^5\mu^3\nu + 16\lambda^4\mu^4\nu + 14\lambda^3\mu^5\nu +$$

$$\begin{gathered}
+ 9\lambda^2\mu^6\nu + 4\lambda\mu^7\nu + \mu^8\nu + 2\lambda^7\nu^2 + 9\lambda^6\mu\nu^2 + 20\lambda^5\mu^2\nu^2 + 29\lambda^4\mu^3\nu^2 + 29\lambda^3\mu^4\nu^2 + \\
+ 20\lambda^2\mu^5\nu^2 + 9\lambda\mu^6\nu^2 + 2\mu^7\nu^2 + 3\lambda^6\nu^3 + 14\lambda^5\mu\nu^3 + 29\lambda^4\mu^2\nu^3 + 36\lambda^3\mu^3\nu^3 + 29\lambda^2\mu^4\nu^3 + 14\lambda\mu^5\nu^3 + \\
+ 3\mu^6\nu^3 + 4\lambda^5\nu^4 + 16\lambda^4\mu\nu^4 + 29\lambda^3\mu^2\nu^4 + 29\lambda^2\mu^3\nu^4 + 16\lambda\mu^4\nu^4 + 4\mu^5\nu^4 + 4\lambda^4\nu^5 + \\
+ 14\lambda^3\mu\nu^5 + 20\lambda^2\mu^2\nu^5 + 14\lambda\mu^3\nu^5 + 4\mu^4\nu^5 + 3\lambda^3\nu^6 + 9\lambda^2\mu\nu^6 + 9\lambda\mu^2\nu^6 + \\
+ 3\mu^3\nu^6 + 2\lambda^2\nu^7 + 4\lambda\mu\nu^7 + 2\mu^2\nu^7 + \lambda\nu^8 + \mu\nu^8.
\end{gathered}$$

TABLE IV

The GCCI's of $D_3\,[C_3]$, the P Group of $B(CH_3)_3$

Irreducible Representation	$162\ P^{X}_{D_3[C_3]}$
$(A_1\#A_1\#A_1)\otimes[3]'$ $= A_1$	$x_1^9 + 6x_1^6x_3 + 12x_1^3x_3^2 + 26x_3^3 + 36x_9 + 9x_1^3x_2^3$ $+ 18x_1^3x_6 + 18x_2^3x_3 + 36x_3x_6$
$(A_1\#A_1\#A_1)\otimes[1^3]'$ $= A_2$	$x_1^9 + 6x_1^6x_3 + 12x_1^3x_3^2 + 26x_3^3 + 36x_9$ $- 9x_1^3x_2^3 - 18x_1^3x_6 - 18x_2^3x_3 - 36x_3x_6$
$(A_1\#A_1\#A_1)\otimes[2,1]'$ $= E_1$	$2x_1^9 + 12x_1^6x_3 + 24x_1^3x_3^2 - 2x_3^3 - 36x_9$
$\left\{\begin{matrix}(\gamma_1\#\gamma_1\#\gamma_1)\\(\gamma_2\#\gamma_2\#\gamma_2)\end{matrix}\right\}\otimes[3]'$ $= E_3$	$2x_1^9 - 6x_1^6x_3 + 6x_1^3x_3^2 + 34x_3^3 + 18x_1^3x_2^3$ $- 18x_1^3x_6 - 18x_3x_2^3 + 18x_3x_6 - 36x_9$
$\left\{\begin{matrix}(\gamma_1\#\gamma_1\#\gamma_1)\\(\gamma_2\#\gamma_2\#\gamma_2)\end{matrix}\right\}\otimes[1^3]'$ $= E_4$	$2x_1^9 - 6x_1^6x_3 + 6x_1^3x_3^2 + 34x_3^3 - 18x_1^3x_2^3$ $+ 18x_1^3x_6 + 18x_3x_2^3 - 18x_3x_6 - 36x_9$
$\left\{\begin{matrix}(\gamma_1\#\gamma_1\#\gamma_1)\\(\gamma_2\#\gamma_2\#\gamma_2)\end{matrix}\right\}\otimes[2,1]'$ $= G$	$4x_1^9 - 12x_2^6x_3 + 12x_1^3x_3^2 - 40x_3^3 + 36x_9$
$\left\{\begin{matrix}A_1\#\gamma_1\#\gamma_1\\A_1\#\gamma_2\#\gamma_2\end{matrix}\right\}\otimes[2]'$ $\uparrow D_3[C_3] = I_1$	$6x_1^9 - 18x_1^3x_3^2 + 18x_1^3x_2^3 - 18x_1^3x_6 + 12x_3^3$ $+ 36x_2^3x_3 - 36x_3x_6$
$\left\{\begin{matrix}A_1\#\gamma_1\#\gamma_1\\A_1\#\gamma_2\#\gamma_2\end{matrix}\right\}\otimes[1^2]'$ $\uparrow D_3[C_3] = I_2$	$6x_1^9 - 18x_1^3x_3^2 - 18x_1^3x_2^3 + 18x_1^3x_6 + 12x_3^3$ $- 36x_2^3x_3 + 36x_3x_6$
$\left\{\begin{matrix}A_1\#A_1\#\gamma_1\\A_1\#A_1\#\gamma_2\end{matrix}\right\}\otimes[2]'$ $\uparrow D_3[C_3] = I_3$	$6x_1^9 + 18x_1^6x_3 + 18x_1^3x_2^3 + 36x_1^3x_6 - 24x_3^3$ $- 18x_2^3x_3 - 36x_3x_6$
$\left\{\begin{matrix}A_1\#A_1\#\gamma_1\\A_1\#A_1\#\gamma_2\end{matrix}\right\}\otimes[1^2]'$ $\uparrow D_3[C_3] = I_4$	$6x_1^9 + 18x_1^6x_3 - 18x_1^3x_3^2 - 36x_1^3x_6 - 24x_3^3$ $+ 18x_2^3x_3 + 36x_3x_6$
$\left\{\begin{matrix}\gamma_1\#\gamma_1\#\gamma_2\\\gamma_2\#\gamma_2\#\gamma_1\end{matrix}\right\}\otimes[2]'$ $\uparrow D_3[C_3] = I_5$	$6x_1^9 - 18x_1^6x_3 + 18x_1^3x_3^2 + 18x_1^3x_2^3 - 18x_1^3x_6$ $- 6x_3^3 - 18x_2^3x_3 + 18x_3x_6$
$\left\{\begin{matrix}\gamma_1\#\gamma_1\#\gamma_2\\\gamma_2\#\gamma_2\#\gamma_1\end{matrix}\right\}\otimes[1^2]'$ $\uparrow D_3[C_3] = I_6$	$6x_1^9 - 18x_1^6x_3 + 18x_1^3x_3^2 - 18x_1^3x_2^3 + 18x_1^3x_6$ $- 6x_3^3 + 18x_2^3x_3 - 18x_3x_6$
$(A_1\#\gamma_1\#\gamma_2)$ $\uparrow D_3[C_3] = I_7$	$6x_1^9 - 18x_1^3x_3^2 + 12x_3^3$

TABLE V

The GCCI's of the PI Group of $B(CH_3)_3$

Irreducible Representation	$324\ P_G^X$
A_1	$x_1^9 + 26x_3^3 + 6x_1^6x_3 + 12x_1^3x_3^2 + 36x_9 + 36x_1^3x_2^3 + 18x_1^3x_6 + 18x_2^3x_3 + 90x_3x_6 + 27x_1x_2^4 + 54x_1x_2x_6$
A_2	$x_1^9 + 26x_3^3 + 6x_1^6x_3 + 12x_1^3x_3^2 + 36x_9 - 36x_1^3x_2^3 - 18x_1^3x_6 - 18x_2^3x_3 - 90x_3x_6 + 27x_1x_2^4 + 54x_1x_2x_6$
A_3	$x_1^9 + 26x_3^3 + 6x_1^6x_3 + 12x_1^3x_3^2 + 36x_9 - 18x_1^3x_2^3 + 18x_1^3x_6 + 18x_2^3x_3 - 18x_3x_6 - 27x_1x_2^4 - 54x_1x_2x_6$
A_4	$x_1^9 + 26x_3^3 + 6x_1^6x_3 + 12x_1^3x_3^2 + 36x_9 + 18x_1^3x_2^3 - 18x_1^3x_6 -18x_2^3x_3 + 18x_3x_6 - 27x_1x_2^4 - 54x_1x_2x_6$
E_1	$2x_1^9 - 2x_3^3 + 12x_1^6x_3 + 24x_1^3x_3^2 - 36x_9 + 54x_1^3x_2^3 - 54x_3x_6$
E_2	$2x_1^9 - 2x_3^3 + 12x_1^6x_3 + 24x_1^3x_3^2 - 36x_9 - 54x_1^3x_2^3 + 54x_3x_6$
E_3	$2x_1^9 + 34x_3^3 - 6x_1^6x_3 + 6x_1^3x_3^2 - 36x_9 + 18x_1^3x_2^3 - 18x_1^3x_6 - 18x_2^3x_3 + 18x_3x_6$
E_4	$2x_1^9 + 34x_3^3 - 6x_1^6x_3 + 6x_1^3x_3^2 - 36x_9 - 18x_1^3x_2^3 + 18x_1^3x_6 + 18x_2^3x_3 - 18x_3x_6$
G	$4x_1^9 - 40x_3^3 - 12x_1^6x_3 + 12x_1^3x_3^2 + 36x_9$
I_1	$6x_1^9 + 12x_3^3 - 18x_1^3x_3^2 + 18x_1^3x_2^3 - 18x_1^3x_6 + 36x_2^3x_3 - 36x_3x_6$
I_2	$6x_1^9 + 12x_3^3 - 18x_1^3x_3^2 - 18x_1^3x_2^3 + 18x_1^3x_6 - 36x_2^3x_3 + 36x_3x_6$
I_3	$6x_1^9 - 24x_3^3 + 18x_1^6x_3 + 18x_1^3x_2^3 + 36x_1^3x_6 - 18x_2^3x_3 - 36x_3x_6$
I_4	$6x_1^9 - 24x_3^3 + 18x_1^6x_3 - 18x_1^3x_2^3 - 36x_1^3x_6 + 18x_2^3x_3 + 3x_3x_6$
I_5	$6x_1^9 - 6x_3^3 - 18x_1^6x_3 + 18x_1^3x_3^2 + 18x_1^3x_2^3 - 18x_1^3x_6 - 18x_2^3x_6 + 18x_3x_6$
I_6	$6x_1^9 - 6x_3^3 - 18x_1^6x_3 + 18x_1^3x_3^2 - 18x_1^3x_2^3 + 18x_1^3x_6 + 18x_2^3x_3 - 18x_3x_6$
I_7	$6x_1^9 + 12x_3^3 - 18x_1^3x_3^2 + 54x_1x_2^4 - 54x_1x_2x_6$
I_8	$6x_1^9 + 12x_3^3 - 18x_1^3x_3^2 - 54x_1x_2^4 + 54x_1x_2x_6$

The coefficient of a typical term $\lambda^{a_1}\mu^{a_2}\nu^{a_3}$ in the GF^Γ gives the number of irreducible representations Γ in the set of nuclear spin functions containing $a_1\lambda$ states, $a_2\mu$ states, and $a_3\nu$ states. Thus, this coefficient corresponds to the number of spin functions transforming as Γ with the spin quantum number m_z equal to $a_3 — a_1$. If one groups the symmetry species as generated by GF^Γ, they separate into multiplets with their m_z varying from —S to S. For example,

TABLE VI

Generating Functions for Deuterium Species of $B(CH_3)_3$*

Γ	λ^9	$\lambda^8\mu$	$\lambda^7\mu^2$	$\lambda^6\mu^3$	$\lambda^5\mu^4$	$\lambda^4\mu^5$	$\lambda^3\mu^6$	$\lambda^2\mu^7$	$\lambda\mu^8$	μ^9	$\lambda^8\nu$	$\lambda^7\mu\nu$	$\lambda^6\mu^2\nu$	$\lambda^5\mu^3\nu$	$\lambda^4\mu^4\nu$	$\lambda^3\mu^5\nu$	$\lambda^2\mu^6\nu$	$\lambda\mu^7\nu$	$\mu^8\nu$	$\lambda^7\nu^2$	$\lambda^6\mu\nu^2$	$\lambda^5\mu^2\nu^2$	$\lambda^4\mu^3\nu^2$	$\lambda^3\mu^4\nu^2$	$\lambda^2\mu^5\nu^2$	$\lambda\mu^6\nu^2$	$\mu^7\nu^2$	$\lambda^6\nu^3$
A_1	1	1	2	3	3	3	3	2	1	1	1	2	4	5	6	5	4	2	1	2	4	8	10	10	8	4	2	3
A_2	0	0	0	0	0	0	0	0	0	0	0	0	1	1	2	1	1	0	0	0	1	2	3	3	2	1	0	0
A_3	0	0	0	0	0	0	0	0	0	0	0	1	1	2	2	2	1	1	0	0	1	2	3	3	2	1	0	0
A_4	0	0	0	1	1	1	1	0	0	0	0	1	2	4	4	4	2	1	0	0	2	4	6	6	4	2	0	1
E_1	0	1	2	3	4	4	3	2	1	0	1	3	6	9	10	9	6	3	1	2	6	12	16	16	12	6	2	3
E_2	0	0	0	0	0	0	0	0	0	0	0	1	2	3	4	3	2	1	0	0	2	4	6	6	4	2	0	0
E_3	0	0	0	1	1	1	1	0	0	0	0	0	1	3	4	3	1	0	0	0	1	4	8	8	4	1	0	1
E_4	0	0	0	0	0	0	0	0	0	0	0	0	0	1	2	1	0	0	0	0	0	2	5	5	2	0	0	0
G	0	0	0	0	1	1	0	0	0	0	0	0	1	4	6	4	1	0	0	0	1	6	13	13	6	1	0	0
I_1	0	0	1	2	3	3	2	1	0	0	0	1	5	10	12	10	5	1	0	1	5	16	25	25	16	5	1	2
I_2	0	0	0	1	1	1	1	0	0	0	0	1	4	8	10	8	4	1	0	0	4	12	21	21	12	4	0	1
I_3	0	1	2	3	4	4	3	2	1	0	1	4	9	14	16	14	9	4	1	2	9	20	29	29	20	9	2	3
I_4	0	0	1	2	3	3	2	1	0	0	0	2	7	12	14	12	7	2	0	1	7	18	26	26	18	7	1	2
I_5	0	0	0	1	2	2	1	0	0	0	0	0	2	7	10	7	2	0	0	0	2	10	21	21	10	2	0	1
I_6	0	0	0	0	1	1	0	0	0	0	0	0	1	5	8	5	1	0	0	0	1	8	18	18	8	1	0	0
I_7	0	0	1	2	3	3	2	1	0	0	0	1	5	9	12	9	5	1	0	1	5	16	25	25	16	5	1	2
I_8	0	0	0	1	1	1	1	0	0	0	0	1	4	9	10	9	4	1	0	0	4	12	21	21	12	4	0	1

Γ	$\lambda^5\mu\nu^3$	$\lambda^4\mu^2\nu^3$	$\lambda^3\mu^3\nu^3$	$\lambda^2\mu^4\nu^3$	$\lambda\mu^5\nu^3$	$\mu^6\nu^3$	$\lambda^5\nu^4$	$\lambda^4\mu\nu^4$	$\lambda^3\mu^2\nu^4$	$\lambda^2\mu^3\nu^4$	$\lambda\mu^4\nu^4$	$\mu^5\nu^4$	$\lambda^4\nu^5$	$\lambda^3\mu\nu^5$	$\lambda^2\mu^2\nu^5$	$\lambda\mu^3\nu^5$	$\mu^4\nu^5$	$\lambda^3\nu^6$	$\lambda^2\mu\nu^6$	$\lambda\mu^2\nu^6$	$\mu^3\nu^6$	$\lambda^2\nu^7$	$\lambda\mu\nu^7$	$\mu^2\nu^7$	$\lambda\nu^8$	$\mu\nu^8$	ν^9
A_1	5	10	11	10	5	3	3	6	10	10	6	3	3	5	8	5	3	3	4	4	3	2	2	2	1	1	1
A_2	1	3	3	3	1	0	0	2	3	3	2	0	0	1	2	1	0	0	1	1	0	0	0	0	0	0	0
A_3	2	3	5	3	2	0	0	2	3	3	2	0	0	2	2	2	0	0	1	1	0	0	1	0	0	0	0
A_4	4	6	9	6	4	1	1	4	6	6	4	1	1	4	4	4	1	1	2	2	1	0	1	0	0	0	0
E_1	9	16	19	16	9	3	4	10	16	16	10	4	4	9	12	9	4	3	6	6	3	2	3	2	1	1	0
E_2	3	6	7	6	3	0	0	4	6	6	4	0	0	3	4	3	0	0	2	2	0	0	1	0	0	0	0
E_3	3	8	12	8	3	1	1	4	8	8	4	1	1	3	4	3	1	1	1	1	1	0	0	0	0	0	0
E_4	1	5	8	5	1	0	0	2	5	5	2	0	0	1	2	1	0	0	0	0	0	0	0	0	0	0	0
G	4	13	18	13	4	0	1	6	13	13	6	1	1	4	6	4	1	0	1	1	0	0	0	0	0	0	0
I_1	10	25	33	25	10	2	3	12	25	25	12	3	3	10	16	10	3	2	5	5	2	1	1	1	0	0	0
I_2	8	21	29	21	8	1	1	10	21	21	10	1	1	8	12	8	1	1	4	4	1	0	1	0	0	0	0
I_3	14	29	36	29	14	3	4	16	29	29	16	4	4	14	20	14	4	3	9	9	3	2	4	2	1	1	0
I_4	12	26	32	26	12	2	3	14	26	26	14	3	3	12	18	12	3	2	7	7	2	1	2	1	0	0	0
I_5	7	21	30	21	7	1	2	10	21	21	10	2	2	7	10	7	2	1	2	2	1	0	0	0	0	0	0
I_6	5	18	26	18	5	0	1	8	18	18	8	1	1	5	8	5	1	0	1	1	0	0	0	0	0	0	0
I_7	9	25	31	25	9	2	3	12	25	25	12	3	3	9	16	9	3	2	5	5	2	1	1	1	0	0	0
I_8	9	21	31	21	9	1	1	10	21	21	10	1	1	9	12	9	1	1	4	4	1	0	1	0	0	0	0

* From K. Balasubramanian, *J. Chem. Phys.* **75** (1981) 4572.

TABLE VII

Nonrigid Deuterium Spin Species of $B(CD_3)_3$

Γ'	Spin species
A_1	${}^3A_1(6)$, ${}^5A_1(2)$, ${}^7A_1(8)$, ${}^9A_1(3)$, ${}^{11}A_1(4)$, ${}^{13}A_1(2)$, ${}^{15}A_1(2)$, ${}^{19}A_1(1)$
A_2	${}^3A_1(2)$, ${}^5A_2(1)$, ${}^7A_2(2)$, ${}^9A_2(1)$, ${}^{11}A_2(1)$
A_3	${}^1A_3(3)$, ${}^5A_3(3)$, ${}^7A_3(1)$, ${}^9A_3(2)$, ${}^{13}A_3(1)$
A_4	${}^1A_4(3)$, ${}^3A_4(1)$, ${}^5A_4(4)$, ${}^7A_4(3)$, ${}^9A_4(4)$, ${}^{11}A_4(1)$, ${}^{13}A_4(2)$
E_1	${}^1E_1(1)$, ${}^3E_1(7)$, ${}^5E_1(8)$, ${}^7E_1(9)$, ${}^9E_1(7)$, ${}^{11}E_1(6)$, ${}^{13}E_1(3)$, ${}^{15}E_1(2)$, ${}^{17}E_1(1)$
E_2	${}^1E_2(2)$, ${}^3E_2(2)$, ${}^5E_2(4)$, ${}^7E_2(3)$, ${}^9E_2(3)$, ${}^{11}E_2(1)$, ${}^{13}E_2(1)$
E_3	${}^1E_3(2)$, ${}^3E_3(4)$, ${}^5E_3(4)$, ${}^7E_3(5)$, ${}^9E_3(3)$, ${}^{11}E_3(1)$, ${}^{13}E_3(1)$
E_4	${}^1E_4(2)$, ${}^3E_4(3)$, ${}^5E_4(3)$, ${}^7E_4(3)$, ${}^9E_4(1)$
G	${}^1G(2)$, ${}^3G(7)$, ${}^5G(9)$, ${}^7G(6)$, ${}^9G(4)$, ${}^{11}G(2)$
I_1	${}^1I_1(4)$, ${}^3I_1(12)$, ${}^5I_1(14)$, ${}^7I_1(14)$, ${}^9I_1(9)$, ${}^{11}I_1(6)$, ${}^{13}I_1(2)$, ${}^{15}I_1(1)$
I_2	${}^1I_2(5)$, ${}^3I_2(10)$, ${}^5I_2(13)$, ${}^7I_2(11)$, ${}^9I_2(8)$, ${}^{11}I_2(3)$, ${}^{13}I_2(2)$
I_3	${}^1I_3(4)$, ${}^3I_3(13)$, ${}^5I_3(17)$, ${}^7I_3(15)$, ${}^9I_3(12)$, ${}^{11}I_3(8)$, ${}^{13}I_3(4)$, ${}^{15}I_3(2)$, ${}^{17}I_3(1)$
I_4	${}^1I_4(4)$, ${}^3I_4(11)$, ${}^5I_4(15)$, ${}^7I_4(14)$, ${}^9I_4(11)$, ${}^{11}I_4(7)$, ${}^{13}I_4(3)$, ${}^{15}I_4(1)$
I_5	${}^1I_5(4)$, ${}^3I_4(11)$, ${}^5I_5(13)$, ${}^7I_5(11)$, ${}^9I_5(7)$, ${}^{11}I_5(3)$, ${}^{13}I_5(1)$
I_6	${}^1I_6(4)$, ${}^3I_6(10)$, ${}^5I_6(12)$, ${}^7I_6(9)$, ${}^9I_6(5)$, ${}^{11}I_6(2)$
I_7	${}^1I_7(2)$, ${}^3I_7(14)$, ${}^5I_7(12)$, ${}^7I_7(15)$, ${}^9I_7(8)$, ${}^{11}I_7(6)$, ${}^{13}I_7(2)$, ${}^{15}I_7(1)$
I_8	${}^1I_8(7)$, ${}^3I_8(8)$, ${}^5I_8(15)$, ${}^7I_8(10)$, ${}^9I_8(9)$, ${}^{11}I_8(3)$, ${}^{13}I_8(2)$

when we group the coefficients in the generating function corresponding I_3 in accordance to their m_z values, we obtain ${}^{17}I_3$ (1), ${}^{15}I_3$ (2), ${}^{13}I_3$ (4), ${}^{11}I_3$ (8), ${}^9I_3$ (12), ${}^7I_3$ (15), ${}^5I_3$ (17), ${}^3I_3$ (13), and ${}^1I_3$ (4) as the nuclear spin species. The numbers in the parentheses indicate the frequency of the corresponding spin species. In this manner all the nuclear spin species can be found from the generating functions. Generating functions thus obtained for the D species of $B(CD_3)_3$ are shown in Table VI. In that table the various terms appearing in the generating functions are shown in the first row. The coefficients in the generating functions for all the irreducible representations are shown in the subsequent rows. The nuclear spin species thus obtained from these generating functions are shown in Table VII. Since the nuclear spin of ${}^{11}B$ is $\frac{3}{2}$ and this nucleus is the center of the molecule, the nuclear spin species of ${}^{11}B$ is ${}^4A_1$. The overall nuclear spin species of this molecule is the direct product of the boron and the deuterium spin species.

4. THE STATISTICAL WEIGHTS OF ROVIBRONIC LEVELS FROM GENERATING FUNCTIONS

The nuclear spin statistical weights of the rovibronic levels of nonrigid molecules can also be obtained from the GCCI's. If one is interested in the statistical weights of rovibronic levels instead of the possible nuclear spin species, it is possible to obtain them directly from GCCI's. Evidently, the number of times an irreducible representation Γ occurs in Γ^{spin}, the reducible representation of all nuclear spin functions, is given by the sum of the coefficients of all the terms in the corresponding nuclear spin generating function. For example, the number of A_1 representations in the set of deuterium spin functions of $B(CD_3)_3$ is the sum of the coefficients in the row corresponding to A_1 in Table VI which is 230. The sum of the coefficients in any generating function is obtained by setting all the weights to unity in the generating function. This amounts to replacing every x_k in P_H^{χ} by $\Sigma_{r \in R} [w(r)]^k = |R|$, since $w(r) = 1$ for all $r \in R$. Thus the number of times the irreducible representation Γ whose character is χ appears in Γ^{spin} is given by

$$N(\Gamma) = P_H^{\chi}(x_k \rightarrow |R|).$$

We now illustrate this with $B(CD_3)_3$. The GCCI's of this molecule are in Table V. The number of I_1 representations in Γ_D^{spin} is obtained by replacing every x_k in $P_G^{I_1}$ by 3 since the number of possible nuclear spin states of D is 3. Consequently,

$$N(I_1) = \frac{1}{324}(6.3^9 + 12.3^3 - 18.3^3.3^2 + 18.3^3.3^3 - 18.3^3.3 + 36.3^3.3 - 36.3.3) = 396.$$

In this manner one obtains

$$\Gamma_D^{spin} = 230A_1 + 45A_2 + 56A_3 + 120A_4 + 340E_1 + 100E_2 + 120E_3 + 56E_4 + 168G + \\ + 396I_1 + 308I_2 + 528I_3 + 440I_4 + 288I_5 + 224I_6 + 388I_7 + 316I_8.$$

We arrive at the same result by adding the multiplicity times the frequency of deuterium spin species in Table VII. Since ^{11}B nuclear spin functions span the representation $4A_1$, the overall spin species Γ^{spin}, is given by

$$\Gamma^{spin} = \Gamma_D^{spin} \otimes \Gamma_B^{spin} = 920A_1 + 180A_2 + 224A_3 + 480A_4 + 1360E_1 + 400E_2 + 480E_3 + \\ + 224E_4 + 672G + 1584I_1 + 1232I_2 + 2112I_3 + 1760I_4 + 1152I_5 + 896I_6 + 1552I_7 + 1264I_8.$$

The nuclear spin statistical weight of a rovibronic level transforming as Γ^{rve} representation is obtained by stipulating that $\Gamma^{rve} \otimes \Gamma^{spin}$ should contain Γ^{int}, where Γ^{int} is the symmetry species of the total internal wave function. By Pauli exclusion principle Γ^{int} must be antisymmetric with respect to permutations alone for Fermions. For Bosons Γ^{int} must be symmetric with respect to permutations alone. There is no restriction placed on inversion operations. Since deuterium nuclei are Bosons Γ^{int} can be A_1 or A_3. This way one obtains the nuclear spin statistical weights of all the rovibronic levels and they are shown below in parenthesis:

$$A_1(1144),\ A_2(660),\ A_3(1144),\ A_4(660),\ E_1(1760),\ E_2(1760),\ E_3(960),\ E_4(448), \\ G(1344),\ I_1(3168),\ I_2(2464),\ I_3(4224),\ I_4(3520),\ I_5(2304),\ I_6(1792),\ I_7(2816),\ I_8(2816).$$

5. APPLICATIONS TO NMR SPECTROSCOPY

The applications of group theory to simplifying NMR spin Hamiltonian go back to McConnell, McLean, and Reilly[36] and Wilson[37]. Soon after the development of symmetry groups of non-rigid molecules by Longuet-Higgins, Woodman[72,28] showed that NMR groups of these molecules can be expressed as semi-direct product groups. Flurry and co-workers[38] developed the unitary group treatment for the NMR problem. The present author[35] showed that the NMR group of any molecule can be obtained by a diagrammatic technique in which the NMR spin Hamiltonian is represented by an interaction diagram known as NMR graph.

The NMR spin Hamiltonian can be defined as

$$H_{NMR} = \sum_{i} \nu_i I_{Zi} + \sum_{i<j}\sum J_{ij} I_i \cdot I_j.$$

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 P satisfies

$$PH_{NMR} P^{-1} = H_{NMR}.$$

The present author[35] showed that a diagrammatic representation of H_{NMR} can be obtained by representing nuclei as vertices and edges by the coupling constants. Such a diagram is shown in Figure 3 for $B(CH_3)_3$ where the center is the ^{11}B nucleus. The NMR graph in Figure 3 can be expressed as a composition of the graphs Q and T shown in Figure 4. The graph in Figure 3 can be obtained by replacing every vertex of Q in Figure 4 by a copy of T. In particle-in-box analogy vertices in Q are the boxes and the vertices in T are the particles in boxes. The group S_3 preserves the couplings restricted to Q and T. Consequently,

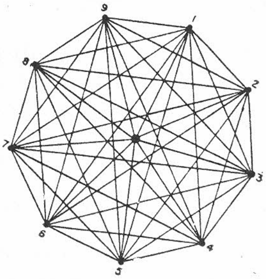

Figure 3. NMR graph of $B(CH_3)_3$. The B and C nuclei are assumed to be ^{11}B and ^{12}C.

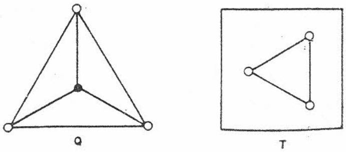

Figure 4. The NMR graph in Figure 3 expressed as a composition of Q and T in this figure. The graph in Figure 3 is obtainable by replacing every open vertex of Q by a copy of T.

the NMR group of $B(CH_3)_3$ is the wreath product $S_3[S_3]$. Figure 2 shows the particle-in-box picture for the NMR group of butane which is the generalized wreath product $S_2[S_3, S_2]$.

The use of GCCI's for the NMR problem was recently demonstrated by the author[41,42]. We review this here. In Table VIII we give all the GCCI's of the NMR group of the butane molecule. Note that GCCI's of the representation pairs (E_3, E_4), (G_2, G_3), (G_{10}, G_1) are the same. Hence, Table VIII lists only the unique GCCI's. When one replaces the appropriate nuclear spin weights in the NMR GCCI's one obtains the generators of nuclear spin species. To illustrate, if one needs to obtain the proton NMR species of the non-rigid butane molecule then one replaces every x_k in the GCCI's by $\alpha^k + \beta^k$. Consider the GCCI of G_1 representation in Table VIII. To obtain the proton spin multiplets of the non-rigid butane corresponding to G_1 we replace every x_k by $\alpha^k + \beta^k$ in the GCCI of G_1. This results in

$$\begin{aligned}\mathrm{G.F.}^{G_1} = \frac{1}{288} [&4(\alpha+\beta)^{10} + 20(\alpha+\beta)^8(\alpha^2+\beta^2) + 28(\alpha+\beta)^6 \cdot \\ &\cdot (\alpha^2+\beta^2)^2 + 12(\alpha+\beta)^4(\alpha^2+\beta^2)^3 + 4(\alpha+\beta)^7(\alpha^3+\beta^3) - \\ &- 4(\alpha+\beta)^5(\alpha^2+\beta^2)(\alpha^3+\beta^3) - 20(\alpha+\beta)^3(\alpha^2+\beta^2)^2(\alpha^3+\beta^3) - \\ &- 12(\alpha+\beta)(\alpha^2+\beta^2)^3(\sigma^3+\beta^3) - 8(\alpha+\beta)^4(\alpha^3+\beta^3)^2 - \\ &- 16(\alpha+\beta)^2(\alpha^2+\beta^2)(\alpha^3+\beta^3)^2 - 8(\alpha^2+\beta^2)^2(\alpha^3+\beta^3)^2].\end{aligned}$$

The above expression upon simplification yields

$$\mathrm{G.F.}^{G_1} = \alpha^9\beta + 4\alpha^8\beta^2 + 9\alpha^7\beta^3 + 14\alpha^6\beta^4 + 16\alpha^5\beta^5 + 14\alpha^4\beta^6 + 9\alpha^3\beta^7 + 4\alpha^2\beta^8 + \alpha\beta^9$$

Thus there is $1G_1$ representation in the set of spin functions that have 9 α's and 1β, $4G_1$'s in the set of spin functions containing 8α's and 2β's, $9G_1$'s in 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 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 2 component spin quantum number $M_F = (n_1 - n_2)/2$ so that if the coefficients in G. F.'s are sorted in accordance to their M_F values one obtains the proton NMR G_1 species as

$$^1G_1\,(2),\ ^3G_1\,(5),\ ^5G_1\,(5),\ ^7G_1\,(3),\ ^9G_1\,(1).$$

The numbers in parentheses give the number of G_1 multiplets of the appropriate multiplicity. This can be briefly summarized in Table IX where we give all the proton NMR multiplets of non-rigid butane obtained using the NMR generators described in this section. Note that one needs to construct the spin species and spin functions in this representation for butane if one is interested in a dynamic high resolution NMR spectrum as a function of temperature. This is because the composite particle representation breaks down at lower temperatures since methyl protons become inequivalent, and thus appropriate correlation of spin species is not possible. Such a correlation can be easily obtained in the total representation as shown by the author in an earlier paper[35] where he called the resulting diagram a coalescence diagram.

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 NMR generators in Table VIII

TABLE VIII

GCCI's of $S_2[S_3, S_2]$, NMR Group of Butane

	x_1^{10}	$x_1^8x_2$	$x_1^6x_2^2$	$x_1^4x_2^3$	$x_1^7x_3$	$x_1^5x_2x_3$	$x_1^3x_2^2x_3$	$x_1^2x_2^4$	$x_1x_2^3x_3$	$x_1^4x_3^2$	$x_1^2x_2x_3^2$	$x_2^2x_3^2$	x_2^5	$x_2^3x_4$	$x_2^2x_6$	$x_2x_4^2$	x_4x_6
A1	1	8	22	24	4	20	28	9	12	4	8	4	12	48	24	36	24
A2	1	8	22	24	4	20	28	9	12	4	8	4	-12	-48	-24	-36	-24
A3	1	4	-2	-12	4	4	-20	9	12	4	-8	4	12	24	24	-36	-24
A4	1	4	-2	-12	4	4	-20	9	12	4	-8	4	-12	-24	-24	36	24
A5	1	-4	-2	12	4	-4	-20	9	-12	4	8	4	12	-24	24	-36	24
A6	1	-4	-2	12	4	-4	-20	9	-12	4	8	4	-12	24	-24	36	-24
A7	1	-8	22	-24	4	-20	28	9	-12	4	-8	4	12	-48	24	36	-24
A8	1	-8	22	-24	4	-20	28	9	-12	4	-8	4	-12	48	-24	-36	24
E1	2	12	16	-12	8	24	-8	-18	-24	8	0	-8	0	0	0	0	0
E2	2	4	-16	-36	8	16	8	-18	0	8	16	8	0	0	0	0	0
E3	2	0	-20	0	8	0	-8	18	0	8	0	-8	0	0	0	0	0
E5	2	-4	-16	36	8	-16	8	-18	0	8	-16	8	0	0	0	0	0
E6	2	-12	16	12	8	-24	-8	-18	24	8	0	-8	0	0	0	0	0
G1	4	20	28	12	4	-4	-20	0	-12	-8	-16	-8	0	0	0	0	0
G2	4	12	-4	-12	4	-12	-4	0	12	-8	0	8	0	0	0	0	0
G4	4	4	-20	12	4	-20	28	0	-12	-8	16	-8	0	0	0	0	0
G5	4	8	4	0	-8	-16	-8	0	0	4	8	4	24	24	-24	0	-24
G6	4	8	4	0	-8	-16	-8	0	0	4	8	4	-24	-24	24	0	24
G7	4	-8	4	0	-8	16	-8	0	0	4	-8	4	24	-24	-24	0	24
G8	4	-8	4	0	-8	16	-8	0	0	4	-8	4	-24	24	24	0	-24
G9	4	-4	-20	-12	4	20	28	0	12	-8	-16	-8	0	0	0	0	0
G10	4	-12	-4	12	4	12	-4	0	-12	-8	0	8	0	0	0	0	0
G12	4	-20	28	-12	4	4	-20	0	12	-8	16	-8	0	0	0	0	0
K1	8	0	-8	0	-16	0	16	0	0	8	0	-8	0	0	0	0	0

by $\lambda^k + \mu^k + \nu^k$, where λ, μ and ν are the weights corresponding to $m_f = -1, 0, 1$, 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 the spin multiplets can be generated. Powerful operator methods and related generating function methods have been developed for the NMR problem. The readers are referred to the present author's recent papers.[41,42] The method of generating functions using GCCI's has also been computerized.[43,44]

TABLE IX

Proton NMR Species of Butane. Numbers are the Frequencies of that Spin Species

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

6. APPLICATIONS TO THE ENUMERATION OF ISOMERIZATION REACTIONS

In this section we review the use of GCCI's for enumerating isomerization reactions, a problem of current interest in dynamic stereochemistry. This is essentially a review of the results contained in Ref. 45. The readers are also referred to references 46 and 47 in this connection. The GCCI's are used here to construct the isomerization graphs.

We start with the trigonal bipyramidal compounds which exhibit large amplitude nonrigid motions by way of the pseudorotation proposed by Berry. The rotational subgroup of this nonrigid molecule is the group S_5. The character table of the rotational subgroup of the nonrigid trigonal bipyramid molecule is shown in Table X. Table XI contains all the GCCI's of this molecule. Consider the H_1 representation of this molecule. We consider the case of

TABLE X

Character Table of S_5, the Rotational Subgroup of the Nonrigid Trigonal Bipyramidal Phosphorous Compounds

Γ	E	(12)	(123)	(1234)	(12)(34)	(12)(345)	(12345)
Order	1	10	20	30	15	20	24
A_1	1	1	1	1	1	1	1
A_2	1	—1	1	—1	1	—1	1
G_1	4	2	1	0	0	—1	—1
G_2	4	—2	1	0	0	1	—1
H_1	5	1	—1	—1	1	1	0
H_2	5	—1	—1	1	1	—1	0
I	6	0	0	0	—2	0	1

TABLE XI

GCCI's of the Group in Table X. 120 P_G^χ are Shown

Γ	x_1^5	$x_1^3x_2$	$x_1^2x_3$	x_1x_4	$x_1x_2^2$	x_2x_3	x_5
A_1	1	10	20	30	15	20	24
A_2	1	—10	20	—30	15	—20	24
G_1	4	20	20	0	0	—20	—24
G_2	4	—20	20	0	0	20	—24
H_1	5	10	—20	—30	15	20	0
H_2	5	—10	—20	30	15	—20	0
I	6	0	0	0	—30	0	24

three different substituents with the weights a, b, and c. The GCCI and the GF^{H_1} are shown below:

$$GCCI^{H_1} = \frac{1}{120}(5x_1^5 + 10x_1^3x_2 - 20x_1^2x_3 - 30x_1x_4 + 15x_1x_2^2 + 20x_2x_3),$$

$$GF^{H_1} = GCCI^{H_1}(x_k \to a^k + b^k + c^k)$$

$$= \frac{1}{120}[5(a+b+c)^5 + 10(a+b+c)^3(a^2+b^2+c^2) -$$

$$- 20(a+b+c)^2(a^3+b^3+c^3) - 30(a+b+c)(a^4+b^4+c^4) +$$

$$+ 15(a+b+c)(a^2+b^2+c^2)^2 + 20(a^2+b^2+c^2)(a^3+b^3+c^3)] =$$

$$= a^3b^2 + a^2b^3 + a^3bc + 2a^2b^2c + ab^3c + a^3c^2 + 2a^2bc^2 +$$

$$+ 2ab^2c^2 + b^3c^2 + a^2c^3 + abc^3 + b^2c^3.$$

Thus there is one H_1 representation in the set of structures with the formula PCl_3Br_2, $2H_1$ representations in the set of structures with the formula PCl_2Br_2I, *etc.* The GCCI corresponding to the totally symmetric representation enumerates the isomers since this GCCI is just the ordinary cycle index used by several authors for enumerating isomers. Table XII shows the generating functions for three substituents with the weights a, b, and c. The first row in Table XII shows the various terms appearing in the generating function. All the subsequent rows give the coefficients of the corresponding terms in the generating

TABLE XII

Generating Functions for Nonrigid Phosphorous Compounds with at most Three Substituents

	a^5	a^4b	a^3b^2	a^2b^3	ab^4	b^5	a^4c	a^3bc	a^2b^2c	ab^3c	b^4c	a^3c^2	a^2bc^2	ab^2c^2	b^3c^2	a^2c^3	abc^3	b^2c^3	ac^4	bc^4	c^5
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
G_1	0	1	1	1	1	0	1	2	2	2	1	1	2	2	1	1	2	1	1	1	0
G_2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H_1	0	0	1	1	0	0	0	1	2	1	0	1	2	2	1	1	1	1	0	0	0
H_2	0	0	0	0	0	0	0	0	1	0	0	0	1	1	0	0	0	0	0	0	0
I	0	0	0	0	0	0	0	1	1	1	0	0	1	1	0	0	1	0	0	0	0

functions corresponding to the irreducible representations for which they stand. Consider a particular molecule with the formula Px_2y_2z. The enumerators corresponding to this formula are the coefficients of a^2b^2c in the various generating functions. The coefficient of a^2b^2c in the totally symmetric representation A_1 gives the number of isomers which is just 1 in this case. Thirty equivalent functions representing this isomer span the representation $A_1 + 2G_1 + 2H_1 + + H_2 + I$. This is obtained by collecting the coefficient of a^2b^2c in the generating function of each irreducible representation. For example, the coefficient of a^2b^2c in G_1 is 2; in H_1 it is 2, in H_2 it is 1 and in I it is 1. Thus we arrive at the above result. Isomerization reactions are obtained when one finds the set of representations spanned by the same 30 structures in the rotational subgroup of the rigid molecule (D_3). This is easily done by correlating the species A_1, G_1, H_1, H_2 and I to the species of the group D_3. These 30 maps span the representation $6A_1 + 4A_2 + 10E$ in D_3. Note that these sets of maps contain $6A_1$ representations in D_3 when they contained only one A_1 in S_5. Since the number of A_1 representations gives the number of isomers we arrive at the conclusion that the single isomer of the nonrigid molecule Px_2y_2z splits into six isomers when the molecule becomes rigid. Conversely, the six isomers of the rigid molecule are transformed into one another by pseudorotation. This is represented by the reaction graph in Figure 5. A reaction graph has an edge between two vertices i and j if the rigid isomers i and j are transformable by a rotation in the nonrigid molecular group. Consequently, the reaction graph contains components that are always complete. Hence once we know the number of vertices in the reaction graph, the number of components and the number of vertices in each component, the reaction graph is immediately constructed.

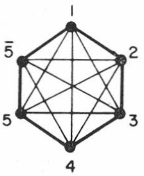

Figure 5. Isomerization reaction graph of the non-rigid molecule $Px_2y_2z_2$.

7. APPLICATIONS TO NQR SPECTRA OF CRYSTALS

NQR spectroscopy of crystals employs a quadrupolar nucleus as a probe to detect and estimate electric field gradients in crystals.[48–49] The electric field gradient is very sensitive to the environment. 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. 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.[50]

In this section we review the use of GCCI for NQR. Let G be the point group corresponding to the space group of the crystal. Let D be the set of nuclei. Then each operation $g \in G$ can be considered as a permutation or permutation-inversion operation on D. Let R be a set containing just 2 elements denoted by α_1 and α_2. Let f_i be a map from D to R defined as follows

$$\begin{aligned} f_i(d_j) &= \alpha_1 \text{ if } i \neq j,\ d_j \in D \\ &= \alpha_2 \text{ if } i = j. \end{aligned}$$

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

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

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 α_1 associate a weight α_1 and with α_2 associate a weight α_2. Define the weight of any $f \in F$ as in the introduction 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 D. Pólya's theorem gives a generating function for the equivalence classes of maps by the following substitution in the cycle index.

$$\text{G. F.} = P_G[x_k \to \sum_{r \in R} w(r))^k].$$

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 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

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

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. Consider the same 6 nuclei in C_{4h} and C_i subgroups of the O_h group. The cycle indices for C_{4h} and C_i are

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

$$P_{C_i} = \frac{1}{2} [x_1^6 + x_2^3].$$

The corresponding generating functions are

$$\text{G.F.}_{C_{4h}} = \frac{1}{8} [(\alpha_1 + \alpha_2)^6 + 2 (\alpha_1 + \alpha_2)^2 (\alpha_1^4 + \alpha_2^4) +$$

$$+ (\alpha_1 + \alpha_2)^2 (\alpha_1^2 + \alpha_2)^2 + (\alpha_1 + \alpha_2)^4 (\alpha_1^2 + \alpha_2^2) + (\alpha_1^2 + \alpha_2^2)^3]$$

$$\text{G.F.}_{C_i} = \frac{1}{2} [(\alpha_1 + \alpha_2)^2 + (\alpha_1^2 + \alpha_2^2)^3].$$

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

Acknowledgement. — The author thanks the Research Corporation and the Arizona State University faculty grant-in-aid program for a partial support of this research. Many of the results reviewed here were obtained during the author's stay at the Lawrence Berkeley Laboratory, University of California, Berkeley. The author thanks Professor Kenneth S. Pitzer for his encouragements and the director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy, under contract number DE-AC03-76SF00098 for the support of a part of this research carried out during the author's stay at Berkeley.

REFERENCES

1. *Principles of Combinatorics,* C. Berge, New York and London, Academic Press, 1971.
2. A. Cayley, *Philos. Mag.* **13** (1857) 19.
3. A. Cayley, *ibid* **67** (1874) 444.
4. A. Cayley, *Ber. Dtsch. Chem. Ges.* **8** (1875) 1056.
5. A. Cayley, *Am. J. Math.* **4** (1881) 266.
6. G. Pólya, *Acta Math.* **68** (1937) 145.
7. J. H. Redfield, *Am. J. Math.* **49** (1927) 433.
8. See, for example, *Graphical Enumeration,* F. Harary and E. M. Plamer, New York and London, Academic Press, 1975.
9. R. C. Read, in: A. T. Balaban (Ed.), *Chemical Applications of Graph Theory,* Academic Press, New York and London 1976.
10. R. W. Robinson, *J. Combinatorial Theory,* **9** (1970) 327.
11. J. Sheehan, *Can. J. Math.* **19** (1967) 792.
12. S. G. Williamson, *J. Combinatorial Theory* **8** (1970) 163.
13. S. G. Williamson, *ibid* **11** (1971) 122.
14. S. G. Williamson, *J. London Math. Soc.* **3** (1971) 411.
15. J. S. Frame, G. De. B. Robinson, and R. M. Thrall, *Can. J. Math.* **6** (1954) 316.
16. *Group-theory and its Application to Physical Problems,* M. Hammermesh, Addison Wesley Reading, Mass., 1962.
17. H. C. Longuet-Higgins, *Mol. Phys.* **6** (1963) 445.

18. P. W. Kasteleyn, in: F. Harary (Ed.), *Graph Theory and Theoretical Physics*, Academic, London and New York 1967, pp. 43—110.
19. W. C. Herndon, *J. Chem. Educ.* **51** (1974) 10.
20. E. W. Montroll, in: E. F. Beckenbach (Ed.), *Applied Combinatorial Mathematics*, John Wiley Inc., 1964, pp. 96.
21. K. Balasubramanian, *Theor. Chim. Acta* **51** (1979) 37.
22. K. Balasubramanian, *Theor. Chim. Acta* **53** (1979) 129.
23. K. Balasubramanian, *Ann. N. Y. Acad. Sci.* **319** (1979) 33.
24. K. Balasubramanian, *J. Chem. Phys.* **72** (1980) 665.
25. S. L. Altmann, *Proc. Roy. Soc. London Ser. A* **298** (1967) 184.
26. J. Serre, *Int. J. Quantum. Chem. Symp.* **1** (1967) 713; J. Serre, *Int. J. Quantum Chem. Symp.* **2** (1968) 107.
27. C. M. Woodman, *Mol. Phys.* **11** (1966) 109.
28. C. M. Woodman, *Mol. Phys.* **19** (1970) 753.
29. A. Kerber, *Lecture Notes in Mathematics Vol.* **240** (1971) pp. 192, Vol. **495** (1975) pp. 175.
30. P. Hoffman, *Discrete Math.* **23** (1978) 37.
31. A. Kerber, *Discrete Math.* **13** (1975) 13.
32. R. Merris, *Linear Algebra and Appl.* **29** (1980) 225.
33. H. O. Foulkes, *Can. J. Math.* **15** (1963) 272,
34. R. C. Read, *Can. J. Math.* **20** (1968) 808.
35. K. Balasubramanian, *J. Chem. Phys.* **73** (1980) 3321.
36. H. M. McConnell, A. D. McLean, and C. A. Reilly, *J. Chem. Phys.* **23** (1955) 1152.
37. E. B. Wilson, Jr., *J. Chem. Phys.* **27** (1957) 60.
38. R. L. Flurry and T. H. Siddall, in: J. C. Donini (Ed.), *Recent Advances in Group Theory and Their Applications*, Plenum, N. Y., 1979, pp. 249.
39. K. Balasubramanian, *J. Chem. Phys.* **75** (1981) 4572.
40. K. Balasubramanian, *J. Chem. Phys.* **74** (1981) 6824.
41. K. Balasubramanian, *J. Chem. Phys.* **78** (1983) 6358.
42. K. Balasubramanian, *J. Chem. Phys.* **78** (1983) 6369.
43. K. Balasubramanian, *J. Comput. Chem.* **3** (1982) 69.
44. K. Balasubramanian, *J. Comput. Chem.* **3** (1982) 75.
45. K. Balasubramanian, *Int. J. Quantum Chem.* **22** (1982) 385.
46. K. Balasubramanian, *Int. J. Quantum Chem.* **21** (1982) 411.
47. K. Balasubramanian, *ibid* **22** (1982) 1013.
48. *Magnetism in Crystalline Materials,* A. F. Cracknell, New York, Pergamor, 1975.
49. *Fundamentals of Molecular Spectroscopy* C. N. Banwell, New York, McGraw Hill, 1975.
50. K. Balasubramanian, *Theor. Chim. Acta* **64** (1984) 415.
51. K. Balasubramanian, in: J. Maruani and J. Serre (Eds.), *Symmetries and Properties of Non-Rigid Molecules. Studies in Physical and Theoretical Chemistry* **28** Elsevier, 1983, pp. 243—51.
52. J. Serre, *Studies in Physical and Theoretical Chemistry* **28** Elsevier, 1983, pp. 1—12.

SAŽETAK

Neke primjene teorije grupa u kemijskoj fizici

Krishnan Balasubramanian

Dan je revijski prikaz razvoja i primjene metode generirajućih funkcija na neke probleme kemijske fizike. Razmatrana je primjena u NMR, na NQR-spektrima kristala s faznim pretvorbama, kao i na problemima rovibronskih razina te izomerizacijskih reakcija. Posebna pažnja posvećena je simetriji molekula koje nisu krute.