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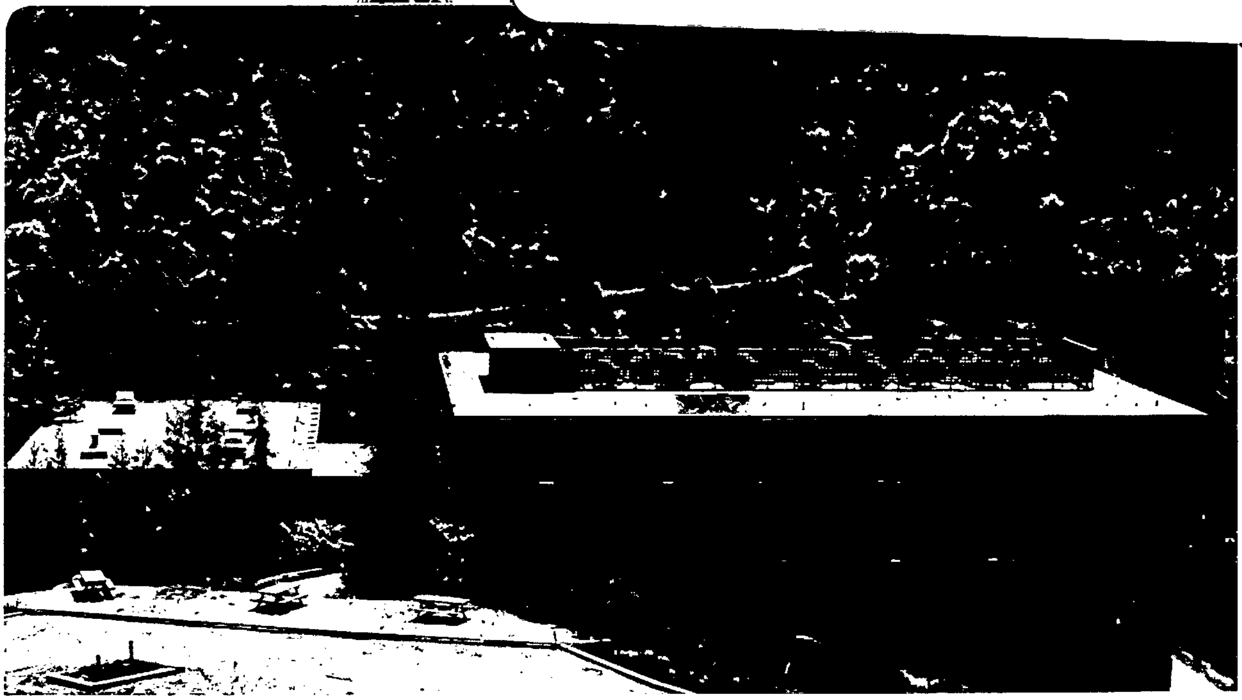

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Operator and Algebraic Methods for NMR Spectroscopy I:

Generation of NMR Spin Species

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Abstract

Algebraic methods are developed for generating NMR spin species and irreducible representations spanned by spin functions. These methods use generalized character cycle indices (S-function when NMR groups are symmetric groups). A correspondence between the unitary group approach and the permutation group method for NMR is established by generating NMR Gel'fand states using Schur functions. The generalized character cycle indices of molecules whose NMR groups are expressible as generalized wreath products are shown to be generalized NMR plethysms of Schur functions. These techniques enable generation of spin species without the knowledge of the character tables of NMR groups. We illustrate the methods developed here with several examples. The use of these techniques in generating symmetry-adapted NMR spin functions can be found in the accompanying paper.

1. Introduction

The first applications of group theory to the simplification of NMR spin interactions are due to McConnell,McLean and Reilly[1] and Wilson.[2] Longuet-Higgins[3] developed the general permutational frame work for the symmetry groups of non-rigid molecules. Woodman[4] showed that the NMR groups of molecules can be expressed as permutation groups and these groups have the structure of semi-direct products. Flurry and Siddall[5] developed the groups for independent particle Hamiltonian operators. Using this, the unitary group structure of NMR groups of several molecules was established by these authors.[6] Further, these authors have considered computational and algebraic techniques for NMR of molecules including the molecules which contain nuclei with spin more than spin ½.[7,8] The present author[9] showed that the NMR group of any molecule can be obtained by collecting the set of permutations that leave the associated spin interaction diagram (known as NMR graph) invariant. Systematic procedures and algorithms were developed for obtaining NMR groups as permutation groups. It was shown in that paper that NMR groups of several non-rigid molecules are generalized wreath product groups. Using the representation theory of generalized wreath products outlined in another paper of the author,[10] we showed that the character tables of NMR groups can be obtained. As pointed out by Woodman[4] and Flurry and co-workers,[5-8] the composite particle method is superior to the complete Hamiltonian methods at every stage of NMR computations. One of the objectives of this paper is to develop algebraic techniques to generate symmetry-adapted composite particle spin functions which in turn factor the composite particle Hamiltonian matrix into matrices of smaller order.

In the present paper we develop techniques to generate irreducible representations contained in the set of spin functions using group generators known as generalized character cycle indices. A correspondence between the unitary group approach and the permutation group method is established by generating NMR

Gel'fand bases using Schur functions. Generalized NMR plethysm techniques are introduced for the generation of NMR spin species of non-rigid molecules. Section 2 outlines preliminary concepts related to NMR groups, cycle indices, NMR spin functions, etc. In Section 3 we demonstrate the use of Imminants and S-functions in NMR and establish a correspondence between the unitary group approach and the permutation group method. Section 4 describes generalized NMR pleythsms and their use in generating NMR spin species. Further formulations of projection operator methods and applications of the methods developed here can be found in the accompanying paper.

2. NMR Groups, Cycle Indices, NMR Spin Functions and NMR Spin Patterns

A. NMR Groups

NMR groups can be defined as the set of permutations of the nuclei that leave the NMR spin Hamiltonian (2.1) invariant.

$$H_{NMR} = \sum_{i} \nu_i I_{zi} + \sum\sum_{i<j} J_{ij} \vec{I}_i \cdot \vec{I}_j \qquad (2.1)$$

where ν_i is the chemical shift of the i^{th} nucleus, J_{ij} is the coupling constant between the nuclei i and j, I_{zi} is the spin component in the z direction (assuming the external magnetic field is in the z direction); $\vec{I}_i \cdot \vec{I}_j$ is the scalar product of the spin operators $\vec{I}_i$ and $\vec{I}_j$. The present author[9] developed a diagrammatic approach for obtaining NMR group as a permutation group. It was shown in that paper that NMR groups are either direct products of symmetric groups (special cases of wreath products) or in the most general cases can be expressed as generalized wreath products of symmetric groups by way of expressing NMR graphs as generalized compositions of smaller graphs. We showed that NMR groups of several molecules are generalized wreath products. The coupling constants among a set of equivalent nuclei which have identical coupling constants among themselves and with the rest of the nuclei do not affect the NMR spectrum. Consequently, one can think of this complete set of magnetically equivalent nuclei as a single composite particle and the NMR Hamiltonian can be expressed in terms of these composite particles as

$$H = \sum_{G} \nu_G I_{z(G)} + \sum\sum_{G<G'} J_{GG'} \cdot \vec{I}_G \cdot \vec{I}_{G'} \qquad (2.2)$$

In 2.2 each "nucleus" G is a composite particle. We also showed in our earlier paper that the NMR group of the composite particle Hamiltonian can also be obtained using diagrammatic techniques.

In this paper we will consider very efficient techniques for generating composite particle spin functions of very complex polyatomic molecules.

B. Cycle Indices, NMR Spin Patterns and Functions

Consider a set D of nuclei (whose NMR is under consideration) and let R be the set of possible spin states of the nuclei in D. If M is the molecular symmetry group then M partitions D into equivalence classes. For non-rigid molecules possessing internal rotors M can be expressed as generalized wreath products and methods were formulated[14] for obtaining the number of equivalence classes. Let $Y_1, Y_2, \ldots Y_t$ be the equivalence classes of D under the action of M. Note that t is the number of NMR signals in the low resolution spectrum since this corresponds to the number of the magnetic equivalence classes of the nuclei in D. Let F be a set of maps from D to R (i.e., the set of possible spin functions). It can be seen that $|F| = |R|^{|D|}$, where $|S|$ is the number of elements in a set S. Let G be the NMR group of the molecule under consideration. Any $g \varepsilon G$ acts on an $f \varepsilon F$ (the set of NMR spin functions) by the recipe shown below.

$$gf(i) = f(g^{-1}i) \text{ for every } i \varepsilon D.$$

To illustrate, consider the methane molecule. A map f_1 which generates the spin function (for protons) $\alpha\ \alpha\ \beta\ \beta$ is shown below.

$$\begin{aligned} f_1(1) &= \underset{\sim}{\alpha} \\ f_1(2) &= \underset{\sim}{\alpha} \\ f_1(3) &= \underset{\sim}{\beta} \\ f_1(4) &= \underset{\sim}{\beta}\ . \end{aligned}$$

Then the permutation (1234) acts on f_1 to generate f_2.

$$\begin{aligned} f_2(1) &= (1234)\ f_1(1) = f_1((1432)1) = f_1(4) = \underset{\sim}{\beta} \\ f_2(2) &= f_1(1) = \underset{\sim}{\alpha} \\ f_2(3) &= f_1(2) = \underset{\sim}{\alpha} \\ f_2(4) &= f_1(3) = \underset{\sim}{\beta}\ . \end{aligned}$$

Thus the NMR spin function $\underset{\sim}{\alpha}\ \underset{\sim}{\alpha}\ \underset{\sim}{\beta}\ \underset{\sim}{\beta}$ gets permuted to the NMR spin function $\underset{\sim}{\beta}\ \underset{\sim}{\alpha}\ \underset{\sim}{\alpha}\ \underset{\sim}{\beta}$ by the action of the permutation (1234) in the NMR group of methane. Two maps f_i and f_j $(i \neq j)$ are equivalent if $gf_i = f_j$. Define a generalized character cycle index (GCCI) of G corresponding to the character χ of an irreducible representation Γ in the group G as follows.

$$\mathrm{GCCI}^{\chi} = \frac{1}{|G|} \sum_{g \varepsilon G} \chi(g)\ x_1^{b_1} x_2^{b_2} \ldots . x_n^{b_n} .$$

where $x_1^{b_1} x_2^{b_2} \ldots . x_n^{b_n}$ is a representation of a typical permutation $g \varepsilon G$ which generates b_1 cycles of length 1, b_2 cycles of length 2,....b_n cycles of length n under the action of g on the set D. In order to book-keep the number of various nuclear spin states in a given NMR spin function let us introduce the concept of the weight of a NMR function. With each spin state in R let us associate a formal symbol w(r). Then define the weight of an $f \varepsilon F$ which generates a NMR spin function as

$$W(f) = \prod_{d \varepsilon D} w(f(d))$$

To illustrate the weight of the spin function $\underset{\sim}{\alpha}\ \underset{\sim}{\alpha}\ \underset{\sim}{\beta}\ \underset{\sim}{\beta}$ of methane would be $\alpha^2\ \beta^2$ if α is the weight corresponding to the spin state $\underset{\sim}{\alpha}$ and β is the weight corresponding to $\underset{\sim}{\beta}$. When Γ is the identity representation of the NMR group of the molecule (which we can denote by A_1) the following substitution generates the equivalence classes of NMR spin functions.

$$\text{G.F.}^{A_1} = \text{GCCI}^{A_1}\ (x_k \rightarrow \sum_{r\varepsilon R} w^k(r)).$$

The coefficient of a typical term $w_1^{b_1} w_2^{b_2}$...gives the number of equivalence classes of NMR spin functions containing b_1 spin states of the type 1, b_2 spin states of the type 2, etc. This is because the number of A_1 representations in an equivalence class is the number of equivalence classes both by Pólya's[11] (a more general theorem) theorem and Frobenius theorem. To illustrate if we let G be the NMR group of methane, then the coefficient of $\alpha^2\beta^2$ in the GCCI^{A_1} gives the number of equivalence classes of NMR spin functions which contain 2 α's and 2 β's. Each equivalence class of NMR spin functions can be called a NMR spin pattern. Note that functions in a NMR spin pattern will only mix in any symmetry-adapted NMR spin function used to factor the NMR spin Hamiltonian. Thus obtaining the NMR spin patterns is crucial in the actual construction of symmetry-adapted functions. The meaning and use of GCCI^{χ} for any χ (other than the character of the A_1 representation) will be seen in subsequent sections.

3. Imminants, S-functions and NMR Gel'fand States

Let A be a matrix of order nxn. Let s be a permutation in S_n (the symmetric group of n objects containing n! permutations) of the type $e_1, e_2, \ldots e_n$ (i.e., i goes to e_i) of the numbers 1,2,... ..n. Define P_s as the product

$$P_s = a_{1e_1}\ a_{2e_2} \ldots a_{ne_n}.$$

Any irreducible representation of S_n can be characterized by a partition of the integer n denoted as $(\lambda_1, \lambda_2, \ldots \lambda_p) = (\lambda)$, with $\lambda_i > 1$ and $\lambda_j \leq \lambda_i \ (j \geq i)$. Thus an irreducible representation of S_n can be denoted as $[\lambda]$. Let $\chi^{(\lambda)}$ be its character. Then we can define the imminant of the matrix A as

$$|A|^{(\lambda)} = \sum_s \chi^{(\lambda)}(s) \ P_s$$

where s runs over all the elements of S_n. In particular if $\lambda = (1,1,1,\ldots 1)$ note that $|A|^{(\lambda)}$ is simply the antisymmetriser used in quantum mechanics of fermions. Define a symmetric function s_r of quantities $\alpha_1, \alpha_2, \ldots \alpha_n$ as

$$s_r = \sum_{i=1}^{n} \alpha_i^r .$$

Let Z_n be the matrix shown below.

$$Z_n = \begin{bmatrix} s_1 & 1 & 0 & 0 & . & . & 0 \\ s_2 & s_1 & 2 & 0 & . & . & 0 \\ s_3 & s_2 & s_1 & 3 & 0 & . & . \\ . & & & & & & \\ . & & & & & & \\ . & & & & & & \\ . & & & & & & \\ s_{n-1} & s_{n-2} & . & . & . & s_1 & n-1 \\ s_n & s_{n-1} & . & . & . & s_2 & s_1 \end{bmatrix} .$$

The Schur function also known as S-function corresponding to the irreducible representation $[\lambda]$ of the symmetric group S_n, denoted by $\{\lambda\}$ is defined below.

$$\{\lambda\} = \frac{1}{n!}\,|Z_n|^{(\lambda)}$$

where $|Z_n|^{(\lambda)}$ is the imminant of the matrix Z_n associated with (λ). The above expression can be reduced to a more convenient form. There is a one-to-one correspondence between the conjugacy classes and the corresponding cycle types in the symmetric group S_n. Suppose a representative in a conjugacy class C has b_1 cycles of length 1, b_2 cycles of length 2 etc. and $|C|$ is the number of elements in the conjugacy class C then

$$\{\lambda\} = \frac{1}{n!}\sum_{C} |C|\,\chi_C^{(\lambda)}\,s_C$$

where

$$s_C = s_1^{b_1} s_2^{b_2} s_3^{b_3} \ldots\ldots$$

by Cayley's counting principle $|C|$ can be seen to be

$$|C| = \frac{n!}{1^{b_1} b_1!\; 2^{b_2} b_2! \ldots\ldots}$$

To illustrate consider the S-functions of the symmetric group S_4. The character table is shown in Table I. One can immediately write

$$\{4\} = \frac{1}{24}\,(s_1^4 + 6s_1^2 s_2 + 8s_1 s_3 + 6s_4 + 3s_2^2)$$

$$\{3,1\} = \frac{1}{24}\,(3s_1^4 + 6s_1^2 s_2 - 6s_4 - 3s_2^2)$$

$$\{2,2\} = \frac{1}{24}\,(2s_1^4 - 8s_1 s_3 + 6s_2^2)$$

$$\{2,1,1\} = \frac{1}{24}\,(3s_1^4 - 6s_1^2 s_2 + 6s_4 - 3s_2^2)$$

$$\{1,1,1,1\} = \frac{1}{24}\,(s_1^4 - 6s_1^2 s_2 + 8s_1 s_3 - 6s_4 + 3s_2^2)$$

Generating functions for S functions can also be obtained very easily using the GCCI's which correspond to A_1 representations of the smaller groups as outlined in an earlier paper of the author.[15] Using this we have the result

$$\{p_1, p_2, \ldots p_n\} = \det\left(P_{S_{(p_i - i + j)}}\right)$$

where

$P_{S(p_i-i+j)}$ is the cycle index of the group $S_{(p_i-i+j)}$ corresponding to A_1 representation. To illustrate, consider $\{4,2\}$ in the group S_6.

$$\{4,2\} = \begin{vmatrix} P_{S_4} & P_{S_5} \\ P_{S_1} & P_{S_2} \end{vmatrix} = P_{S_4}P_{S_2} - P_{S_5}P_{S_1}$$

$$P_{S_5} = \frac{1}{120}\left(s_1^5 + 10s_1^3s_2 + 20s_1^2s_3 + 15s_1s_2^2 + 30s_1s_4 + 20\ s_2s_3 + 24s_5\right)$$

$$P_{S_4} = \frac{1}{24}\left(s_1^4 + 6s_1^2s_2 + 8s_1s_3 + 3s_2^2 + 6s_4\right)$$

$$P_{S_2} = \frac{1}{2}\left(s_1^2 + s_2\right)$$

$$P_{S_1} = s_1.$$

Substituting the above expressions for P_{S_1}, P_{S_2} etc. in the expression for $\{4,2\}$ we get

$$\{4,2\} = \frac{1}{720}\left[9s_1^6 + 45s_1^4s_2 - 90s_1^2s_4 + 45s_1^2s_2^2 - 144s_1s_5 + 90s_2s_4 + 45s_2^3\right]$$

Thus S-functions can be generated without knowing the character tables of the symmetric group S_n and thus they are generators of the character table of S_n since the coefficient of the cycle type which corresponds to C gives $|C|\ \chi^{(\lambda)}$.

S-functions with $s_r = \sum_i \alpha_i^r$, where α_i's are the weights of the nuclear spin states have special significance in NMR spectroscopy. They generate the number of times an irreducible representation occurs in the set of NMR spin functions of a chosen weight if the NMR group of the molecule is isomorphic to S_n. Equivalently the coefficient of a typical term $\alpha_1^{b_1}\alpha_2^{b_2}\ldots$ in $\{\lambda\}$ generates the number of times the irreducible representation $[\lambda]$ occurs in the set of NMR spin functions containing b_1 spin states with the weight α_1, b_2 spin states with the weight α_2, etc. Let us now illustrate this with an example. The NMR group of CH_4 is S_4. Let us associate a weight α to the $\underset{\sim}{\alpha}$

spin state of the proton and a weight β to the $\underset{\sim}{\beta}$ spin of the proton. Then with $s_r = \alpha^r + \beta^r$, S-functions of S_4 generate the frequency of occurrence of the corresponding irreducible representation in the set of NMR spin functions of methane. To illustrate, consider the S-function $\{3,1\}$ of S_4 for CH_4, with $s_r = \alpha^r + \beta^r$.

$$\begin{aligned}\{3,1;\alpha,\beta\} &= \frac{1}{24}\,[3(\alpha+\beta)^4 + 6(\alpha+\beta)^2(\alpha^2+\beta^2) - 6(\alpha^4+\beta^4) - 3(\alpha^2+\beta^2)^2] \\ &= \alpha^3\beta + \alpha^2\beta^2 + \alpha\beta^3.\end{aligned}$$

Thus there is one [3,1] or F_1 representation in the set of spin functions which have 3$\underset{\sim}{\alpha}$ spin states and 1$\underset{\sim}{\beta}$ spin state, one F_1 in spin functions that have 2$\underset{\sim}{\alpha}$ spin states and 2$\underset{\sim}{\beta}$ spin states and one F_1 representation in the set of spin functions that have 1$\underset{\sim}{\alpha}$ and 3$\underset{\sim}{\beta}$'s. Note that we obtained this information without having to explicitly obtain the character of the representation spanned by all the NMR spin functions. This is quite advantageous for polyatomics in that the number of spin functions for a molecule containing b_1 nuclei with a_1 spin states, b_2 nuclei with a_2 spin states etc. the number of NMR spin functions is $a_1^{b_1} a_2^{b_2}$.... . Consequently to find the character of the representation spanned by these spin functions is, in general, quite difficult. Further, the same S-function generates the frequency of occurrence of NMR spin functions for nuclei with spin more than spin 1/2. To illustrate, consider the CD_4 molecule. Let us denote the 3 spin states of the D nuclei by $\underset{\sim}{\lambda}$, $\underset{\sim}{\mu}$ and $\underset{\sim}{\nu}$ and let the corresponding weights be λ, μ and ν, respectively. Then, for example, the S-function $\{3,1\}$ with $s_r = \lambda^r + \mu^r + \nu^r$ generates the frequency of occurrence of F_1 in D spin functions. To illustrate,

$$\begin{aligned}\{3,1;\lambda\mu\nu\} &= \frac{1}{24}\,[3(\lambda+\mu+\nu)^4 + 6(\lambda+\mu+\nu)^2(\lambda^2+\mu^2+\nu^2) - 6(\lambda^4+\mu^4+\nu^4) - 3(\lambda^2+\mu^2+\nu^2)^2] \\ &= \lambda^3\mu + \lambda^2\mu^2 + \lambda\mu^3 + \lambda^3\nu + 2\lambda^2\mu\nu + 2\lambda\mu^2\nu + \mu^3\nu + \lambda^2\nu^2 + 2\lambda\mu\nu^2 \\ &\quad + \mu^2\nu^2 + \lambda\nu^3 + \mu\nu^3.\end{aligned}$$

Thus, for example there are $2F_1$ representations in the set of functions which have 2λ's, 1 μ and 1 ν, since the coefficient of $\lambda^2\mu\nu$ in $\{3,1;\lambda\mu\nu\}$ is 2. The complete set of generating functions for CD_4 molecule is shown in Table 2.

When the NMR group of a molecule is isomorphic to a symmetric group S_n, the NMR states can be characterized by the associated Gel'fand spin states which we will now define. As we pointed out earlier every irreducible representation of S_n can be characterized by a partition of the integer n. Consider the weights of the spin states of the nuclei in a lexical order (for example, we can assume for the spin 1/2 problem the lexical order $\beta>\alpha$ and for spin 1 problem the lexical order $\nu > \mu > \lambda$). Then a NMR Gel'fand state can be defined as a generalized Young tableau that can be obtained by filling the weights of spin states in the squares of the Young diagram associated with the partition of n such that in any row weights are in non-decreasing order and in any column the weights are in strictly increasing order. All deuterium NMR Gel'fand states of CD_4 are shown in Figure 1. The S-functions of the NMR group of CD_4 (S_4) with s_r replaced by $\lambda^r + \mu^r + \nu^r$ are indeed the generators of the D NMR Gel'fand states enumerated in Figure 1. Gel'fand states are precisely the bases for the unitary group U(n). Thus we have established the correspondence between the permutational symmetry and the unitary group treatment of Flurry and Siddall.[6] The basis vectors for these Gel'fand states can be uniquely labeled by a triangular pattern known as Gel'fand-Tsetlin tableau. A typical Gel'fand-Tsetlin tableau is of the form

$$[m] = \begin{bmatrix} m_n \\ m_{n-1} \\ \vdots \\ m_2 \\ m_1 \end{bmatrix} = \begin{bmatrix} m_{1n} & m_{2n} & & & m_{n-1,n} & m_{nn} \\ & m_{1,n-1} & \cdots & \cdots & m_{n-1,n-1} & \\ & & & & & \\ & & m_{12} & & m_{22} & \\ & & & m_{11} & & \end{bmatrix}$$

Paldus[16] developed this unitary group treatment for electron correlation and the corresponding electronic ABC tableaus are now known as Paldus tableaus.

The integers in the above array satisfy the following conditions:

$$m_{ij} \geq m_{i,j-1} \geq m_{i+1,j}$$

for all i = j, ...n-1, j = 2,3,....n. From a Gel'fand-Tsetlin tableau one can immediately obtain a NMR Gel'fand state. The first row of a Gel'fand-Tsetlin tableau determines the Young diagram. Then one fills integers from the set {1,2,...m} such that in the i^{th} row of the diagram the integer i is filled in the first m_{ii} boxes, i + 1 in the next $m_{i,i+1} - m_{ii}$ boxes etc. Then one can identify the integers 1,2,...m by the various weights of the spin states of the nuclei. For example, the integers {1,2,3} can be identified as λ, μ and ν state for D nuclei.

Before concluding this section we consider NMR groups which are direct products of symmetric groups and the corresponding generating functions. Such NMR symmetries are quite common especially within the spirit of effective NMR spin Hamiltonian approximation which sets coupling constants among a set of completely magnetically equivalent nuclei to zero. The effective NMR group of butane within equal coupling interaction approximation is the direct product $S_6 \times S_4$. Thus this is an example of the above case. When the NMR group is a direct product of two symmetric groups viz., $S_n \times S_m$ then the generators of spin species are the products of the corresponding Schur functions. For example, a generator of the NMR species for $S_6 \times S_4$ will be of the form {4,2}{3,1}. The product of two S-functions can be obtained with the recipe given in Littlewood[12] which we will briefly consider to complete this discussion. The S-functions appearing in the product $\{\lambda_1,\lambda_2...\lambda_p\}$ $\{\mu_1,\mu_2,...\mu_q\}$ can be obtained by adding to the Young tableau $(\lambda_1,\lambda_2,...\lambda_p)$ μ_1 identical symbols α_1, μ_2 identical symbols α_2 etc. such that the resulting tableau will also be a Young tableau. Further, when the symbols α_1, α_2 etc. are read from right to left we should obtain a lattice permutation of $\alpha_1^{\mu_1}\alpha_2^{\mu_2}...$.

A lattice permutation of $\alpha_1^{\mu_1}\alpha_2^{\mu_2}\ldots$ is a permutation of the factors in the product such that in any permutation among the first r terms (for any r) the number of times α_1 occurs $\geq$ the number of times α_2 occurs etc. To illustrate $\alpha_1\alpha_1\alpha_2\alpha_2\alpha_3$ is a lattice permutation of $\alpha_1^2\alpha_2^2\alpha_3$ but $\alpha_1\alpha_2\alpha_2\alpha_1\alpha_3$ is not a lattice permutation of $\alpha_1^2\alpha_2^2\alpha_3$. Using this recipe one can easily construct the product of the Schur functions {4,3}{3,1}. As per Littlewood's Convention we will simply replace the symbols in the Young tableau corresponding to (4,2) by 0's to which we will add 3 α's and 1 β. The resulting such tableaux which satisfy the stipulated conditions are shown in Figure 2.

4. Generalized NMR Plethysms and Induced Spin Species Generators

As shown in an earlier paper of the present author[9] the NMR groups of many non-rigid molecules can be expressed as generalized wreath product groups. In fact, even the other NMR groups, such as S_n, direct products of symmetric groups are indeed special cases of generalized wreath products so that a treatment of generalized wreath products would specialize to these cases. Even in the composite particle representation (which we will discuss in a later section), the composite particle NMR groups are generalized wreath products or special cases of generalized wreath products. In this section we will therefore consider powerful projection operator methods which generate NMR spin species of both rigid and non-rigid nuclear structures.

A. Definitions and Preliminaries

Any NMR spin Hamiltonian can be represented by an interaction diagram known as NMR graph with vertices representing nuclei and edges representing nuclear-nuclear spin coupling constants. To illustrate let us consider the non-rigid Boron trimethyl. The NMR graph of this non-rigid molecule is shown in Figure 3. (● is the Boron nucleus). We have assumed the carbon nuclei to be ^{12}C and thus they do not appear in the NMR graph. Let the methyl protons of the first methyl group be labelled 1, 2 and 3, and the second group 4, 5, and 6 etc. Then the proton nuclei can be partitioned into a completely magnetically equivalent sets $t_1 = \{1,2,3\}$, $t_2 = \{4,5,6\}$ and $t_3 = \{7,8,9\}$. Two nuclei are said to be completely magnetically equivalent if they are magnetically equivalent and have identical coupling constants with the rest of the system. The NMR graph in Figure 3 can be expressed as a generalized composition of a quotient graph which is obtained by condensing the set of complete magnetically equivalent nuclei into a single vertex and creating "types" which give interactions among the nuclei in the sets t_1, t_2 etc. The original NMR graph is obtained by replacing a vertex of Q (the quotient graph) by a copy of the corresponding type T_i. To illustrate, the NMR graph in Figure 3 is a composition of Q and the type T in Figure 4. Each vertex (except B nucleus) in Q is replaced by a copy of T to obtain the NMR graph in Figure 3. The quotient graph in Figure 4 is indeed the diagramatic representation of the interaction of composite particles as shown in an earlier paper of the author[9] where one can find several illustrative examples of NMR graphs also. Let Y_i be the set of vertices in Q that are replaced by the same copy T_i to obtain the original NMR graph. Let H_i be the group acting on T_i which permutes the nuclei in T_i such that the coupling constants in T_i are preserved. Since the nuclei in T_i are completely equivalent if T_i contains ℓ vertices, $H_i = S_\ell$ where S_ℓ is the symmetric group containing $\ell!$ elements. In this set up the present author showed that the NMR group of any NMR graph is the generalized wreath product $G[H_1,H_2,\ldots,H_t]$ where G is the NMR group of the quotient graph Q. To illustrate, thus the NMR group of the non-rigid $B(CH_3)_3$ molecule is simply the wreath product $S_3[S_3]$. The order of $G[H_1,H_2,\ldots,H_t]$ is $|G|\ |H_1|^{|Y_1|}\,|H_2|^{|Y_2|}\ \ldots\ldots|H_t|^{|Y_t|}$. The character tables of generalized wreath products and their representation matrices can be constructed using the methods described elsewhere.[10] In this paper we will consider operator methods which generate NMR spin species and spin functions both in total and composite particle representations. In this paper we will briefly review the important concepts in the representation theory of generated wreath products since this is needed in constructing their projectors and generators of spin species.

Let π_i be a map from Y_i to H_i. Then the generalized wreath product $G[H_1,H_2,\ldots,H_t]$ can be defined in formal terms as the set

$$\{(g;\pi_1,\pi_2,\ldots,\pi_t)/g\varepsilon G,\ \pi_i:Y_i\to H_i\}$$

with

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

where

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

Let $m_i = |Y_i|$ and $H_i^{m_i}$ denote m_i-fold direct product of m_i copies of the same group H_i. Then $G[H_1,H_2,\ldots,H_t]$ is isomorphic to $(H_1^{m_1} \times H_2^{m_2} \times\ldots\times H_t^{m_t})\cdot G'$

where

$$G' = \{(g;e_1e_2,\ldots.,e_t)/g\varepsilon G,\ e_i(j) = {}^1H_i\}\ .$$

where ${}^1H_i$ is the identity of the group H_i. Since $H_1^{m_1} \times H_2^{m_2} \times\ldots\times H_t^{m_t}$ is a direct product, the irreducible representations of this group are given by $F^* = F_1^{m_1*} \# F_2^{m_2*} \#\ldots.\# F_t^{m_t*}$, where $F_i^{m_i*}$ is the outer product $F_{i1} \# F_{i2} \# \ldots \# F_{im_i}$ with F_{ij} being an irreducible representation of the group H_i. The symbol # is used for outer products. The definition of outer tensor products can be found in several books like Messiah.[17] The representation matrices of outer tensor products are simply the Kronecker products of the matrices of the constituting representations. For every representation Γ shown above an important key group known as the inertia group which corresponds to F* can be defined as the set of elements in the generalized wreath product $G[H_1,H_2,\dots,H_t]$ that leave F* invariant. In symbols the inertia group of F* is defined as

$$G_{F*}[H_1,H_2,\dots,H_t] = \{(g;\pi_1,\pi_2,\dots\pi_t)/F^{*(g;\pi_1,\pi_2,\dots\pi_t)} \sim F^*\}$$

with

$$F^{*(g;\pi_1,\pi_2,\dots\pi_t)}(e;\pi_1',\pi_2',\dots\pi_t') = F^*(g;\pi_1,\pi_2,\dots\pi_t)^{-1}\,(e;\pi_1',\pi_2',\dots\pi_t')(g;\pi_1,\pi_2,\dots\pi_t).$$

The group $G_{F*}[H_1,H_2,\dots,H_t]$ has the permutation representation $(H_1^{m_1} \times H_2^{m_2} \times\dots\times H_t^{m_t})\cdot G'_{F*}$ (by definition). G'_{F*} is known as the inertia factor corresponding to F^*. Let $\{F_1^{m_1*} \# F_2^{m_2*} \#\dots\# F_t^{m_t*}\}$ be the set of inequivalent representations. From the representation matrices of $F_1^{m_1*} \# F_2^{m_2*} \#\dots\# F_t^{m_t*}$ $(e;\pi_1,\pi_2,\dots\pi_t)$ (which can be trivially found by obtaining the Kronecker products of the matrices of the constituting representations), the representation matrices of $\underline{F_1^{m_1*} \# F_2^{m_2*} \#\dots\# F_t^{m_t*}}$ $(g;\pi_1,\pi_2,\dots,\pi_t)$ can be obtained easily by a suitable permutation of the columns of the former determined by g by the recipe given in an earlier paper of the present author.[10] The underline symbol is used to denote a suitable permutation of the columns of the Kronecker product of the matrices of $F_1^{m_1*}$, $F_2^{m_2*}$ etc. If F' is an irreducible representation of G'_Γ then the irreducible representations of $G[H_1,H_2,\dots,H_t]$ are given by $(\underline{\#_i} F_i^{m_i*} \otimes F') \uparrow G[H_1,H_2,\dots,H_t]$, where the arrow stands for an induced representation. The concept of induced representation has been reviewed by Coleman.[18]

B. NMR Plethysms

Recall that F^* denotes $F_1^{m_1*} \# F_2^{m_2*} \#\dots\# F_t^{m_t*}$ and the inertia group corresponding to the representation F* is $G_{F^*}[H_1,H_2,\dots,H_t]$. The corresponding inertia factor is G'_{F^*}. Note that G'_{F^*} is isomorphic to a symmetric group if G is a symmetric group. G'_{F^*} is, of course, a subgroup of G. G'_{F^*} is isomorphic to G when the inertia group for F* is $G[H_1,H_2,\ldots,H_t]$. The GCCI of G'_{F^*} corresponding to the character χ can be cast into the form

$$\mathrm{GCCI}^{\chi}_{G'_{F^*}} = \{\chi\} = \frac{1}{|G'_{F^*}|}\sum_{g\in G'_{F^*}} \prod_i \prod_j \chi(g)\, x_{ij}^{C_{ij}(g)} \tag{4.1}$$

where $C_{ij}(g)$ is the number of j cycles of g in the set Y_i. (Note that Y_i is the set of vertices in Q that are replaced by the same copy T_i to obtain the NMR graph). It is possible to express a GCCI of G'_{F^*} in the above form since the elements of G (and therefore those of G'_{F^*}) permute the vertices in Q such that they are permuted only within the Y-sets. Equivalently, G is intransitive i.e., a vertex in Y_i does not get permuted to a vertex in Y_j by any g∈G (j ≠ i). Consequently, $x_1^{b_1}x_2^{b_2}\ldots x_n^{b_n}$ can be recast in a convenient form viz. $\prod_i \prod_j x_{ij}^{C_{ij}(g)}$. Let λ_k be the character of the representation F_i which constitutes the m_i-fold outer product $F_i^{m_i*}$. Since F_i is a representation of the group H_i which is a symmetric group, the GCCI's of H_i's are S-functions. In particular, the S-function corresponding to λ_k is shown below.

$$Z_i^{\lambda_k} = \{\lambda_k\}_i = \frac{1}{|H_i|}\sum_{h\in H_i} \lambda_k(h)\, x_1^{b_1}x_2^{b_2}\ldots \tag{4.2}$$

Define $Z_{ij}^{\lambda_k}$ or $\{\lambda_k\}_{ij}$ as shown below.

$$Z_{ij}^{\lambda_k} = \{\lambda_k\}_{ij} = Z_i^{\lambda_k}(x_\ell \to x_{\ell j}) \tag{4.3}$$

where the ℓj subscripts on the x variables are products. If we denote an irreducible representation $\#_i F_i^{m_i*} \otimes F' \uparrow G[H_1,H_2,\ldots,H_t]$ by Γ then the GCCI of $G[H_1,H_2,\ldots H_t]$ corresponding to Γ can be obtained by the following substitution which we call generalized plethysm.

$$\mathrm{GCCI}^{\Gamma}(G[H_1,H_2,\ldots.,H_t]) = \{\chi\}\ (x_{ij} \rightarrow \{\lambda_k\}_{ij}) \qquad (4.4)$$

It is obtained by replacing a x_{ij} in $\{\chi\}$ defined in (4.1) by $\{\lambda_k\}_{ij}$ if this j cycle in Y_i is constituted by j copies of the representation whose character is λ_k. A special case of this substitution for wreath product group $S_k[S_\ell]$ when the inertia factor is isomorphic to S_k itself is the well-known plethysms of S-functions found in Read's paper.[13] A further specialization to identify representation was used and illustrated by the author in isomer enumeration and enumeration of NMR signals.[14]

Let us now illustrate generalized NMR plethysms with an example and demonstrate their significance in NMR spectroscopy. We consider here the NMR group of the non-rigid butane molecule. The NMR group of this molecule is the generalized wreath product $S_2[S_3,S_2]$ and its order is 288. As far as the author is aware the character table or the set of irreducible representations of this group was not obtained in the literature. Even Littlewood's book does not have its character table. The two Y-sets are $Y_1 = \{1,4\}$ and $Y_2 = \{2,3\}$ where we can take 1 and 4 as methyl carbon and 2 and 3 as methylene carbon. The irreducible representations of the NMR group of non-rigid butane are shown in Table 3. In that table one can also find the dimension of each representation and a designation A_1, A_2, E_1 etc. We denote all one dimensional representations as A's, all 2 dimensional representations as E's, three as F's etc. The representations of S_3 and S_2 in that table are designated by the appropriate partitions of integers. Let us now illustrate plethysms by two examples. Consider $\Gamma_{24} = A_6$ which is $\underline{[1^3]\ \#\ [1^3]\ \#\ [2]\ \#\ [2]}\ \otimes\ ]1^2]'$ in Table 3. The inertia factor corresponding to $[1^3]\ \#\ [1^3]\ \#\ [2]\ \#\ [2]$ is S_2' and the S-function of S_2' corresponding to $[1^2]'$ cast in the form of (4.1) is shown below.

$$\mathrm{GCCI}^{[1^2]'}_{S_2'} = \frac{1}{2}\,(x_{11}^2\, x_{21}^2 - x_{12}\, x_{22}) \qquad (4.5)$$

The various $\{\lambda_k\}_i$'s and $\{\lambda_k\}_{ij}$'s are shown below

$$\{[1^3]\}_1 = \frac{1}{6}(x_1^3 + 2x_3 - 3x_1x_2)$$

$$\{[2]\}_2 = \frac{1}{2}(x_1^2 + x_2)$$

$$\{[1^3]\}_{11} = \{[1]^3\}_1$$

$$\{[1^3]\}_{12} = \{[1^3]\}_1(x_k \rightarrow x_{2k}) = \frac{1}{6}(x_2^3 + 2x_6 - 3x_2x_4)$$

$$\{[2]\}_{21} = \{[2]\}_1$$

$$\{[2]\}_{22} = \frac{1}{2}(x_2^2 + x_4)$$

Replacing every x_{ij} in (4.5) by the appropriate $\{\lambda_k\}_{ij}$ we get (4.6)

$$\begin{aligned} \mathrm{GCCI}^{A_6} &= \frac{1}{2}\,[(\tfrac{1}{6}(x_1^3 + 2x_3 - 3x_1x_2))^2 \cdot (\tfrac{1}{2}(x_1^2 + x_2))^2 \\ &- \frac{1}{6}(x_2^3 + 2x_6 - 3x_2x_4) \cdot \frac{1}{2}(x_2^2 + x_4)] \\ &= \frac{1}{288}\,[x_1^{10} - 4x_1^8x_2 - 2x_1^6x_2^2 + 12x_1^4x_2^3 + 4x_1^7x_3 \\ &- 4x_1^5x_2x_3 - 20x_1^3x_2^2x_3 + 9x_1^2x_2^4 - 12x_1x_2^3x_3 \\ &+ 4x_1^4x_3^2 + 8x_1^2x_2x_3^2 + 4x_2^2x_3^2 + 12x_2^5 - 24x_2^3x_4 \\ &+ 24x_2^2x_6 - 36x_2x_4^2 + 24x_4x_6] \end{aligned} \tag{4.6}$$

Let us give another example of an induced representation namely the representation $\Gamma_6 = G_1 = [3] \# [2,1] \# [2] \# [2] \uparrow S_2[S_3,S_2]$ in Table 3. The inertia factor for $[3] \# [2,1] \# [2] \# [2]$ is just S_1', the group containing the identity and thus it is an induced representation. (This is because inertia factor is not isomorphic to G). The various S-functions are shown below.

$$\mathrm{GCCI}_{S_1'} = x_{11}^2\, x_{12}^2$$

$$\{[3]\}_{11} = \frac{1}{6}\,(x_1^3 + 3x_1x_2 + 2x_3)$$

$$\{[2,1]\}_{11} = \frac{1}{6}\,(2x_1^3 - 2x_3)$$

$$\{[2]\}_{12} = \frac{1}{2}\,(x_1^2 + x_2).$$

Thus the GCCI of G_1 using the plethysm substitution is

$$\begin{aligned}\mathrm{GCCI}^{G_1} &= \frac{1}{6}\,(x_1^3 + 3x_1x_2 + 2x_3) \cdot \frac{1}{6}\,(2x_1^3 - 2x_3) \cdot [\tfrac{1}{2}\,(x_1^2 + x_2)]^2 \\ &= \frac{1}{288}\,[4x_1^{10} + 20x_1^8x_2 + 28x_1^6x_2^2 + 12x_1^4x_2^3 \\ &+ 4x^7x_3 - 4x_1^5x_2x_3 - 20x_1^3x_2^2x_3 - 12x_1x_2^3x_3 - 8x_1^4x_3^2 \\ &- 16x_1^2x_2x_3^2 - 8x_2^2x_3^2]. \end{aligned} \qquad (4.7)$$

Note that the resulting GCCI's that we obtain for the various irreducible representations of the NMR group of butane can be directly obtained if one had the character table of this group. Then all that one needs to do is to obtain the cycle representation of each conjugacy class and the corresponding character and summing over all the conjugacy classes. Nevertheless, the above techniques of generalized plethysms did not require the character table of the NMR group of butane of order 288. We generated the GCCI's of this group as either pleythysm or product of S-functions of much smaller groups (namely, groups S_3 and S_2). It is this aspect of this technique that makes it very useful for generating NMR spin species of non-rigid molecules. For non-rigid molecules the NMR groups increase in an exponential order that it is not feasible to obtain their character tables even in the composite particle treatment. The NMR group of butane is also the NMR group of the molecule 2,2,3,3,4,4,5.5 octamethyl hexane in the composite particle representation.

In Table 4 we give all the GCCI's of the butane molecule obtained with this technique. Note that GCCI's of the representation pairs (E_3,E_4), (G_2,G_3), (G_{10},G_{11}) are the same. Consequently, Table 4 lists only the unique GCCI's. When one replaces the appropriate nuclear spin weights in the NMR plethysms 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 $\alpha^k+\beta^k$. Let us further exemplify this point with the GCCI of G_1. To obtain the proton spin multiplets of non-rigid butane corresponding to G_1 we replace every x_k by $\alpha^k+\beta^k$ in (4.7). Expression (4.8) is the result of such a replacement.

$$\begin{aligned}\text{G.F.}^{G_1} = \frac{1}{288}\,[&4(\alpha+\beta)^{10} + 20(\alpha+\beta)^8(\alpha^2+\beta^2) + 28(\alpha+\beta)^6\\ &\cdot(\alpha^2+\beta^2)^2 + 12(\alpha+\beta)^4(\alpha^2+\beta^2)^3 + 4(\alpha+\beta)^7(\alpha^3+\beta^3)\\ &- 4(\alpha+\beta)^5(\alpha^2+\beta^2)(\alpha^3+\beta^3) - 20(\alpha+\beta)^3(\alpha^2+\beta^2)^2(\alpha^3+\beta^3)\\ &- 12(\alpha+\beta)(\alpha^2+\beta^2)^3(\alpha^3+\beta^3) - 8(\alpha+\beta)^4(\alpha^3+\beta^3)^2\\ &- 16(\alpha+\beta)^2(\alpha^2+\beta^2)(\alpha^3+\beta^3)^2 - 8(\alpha^2+\beta^2)^2(\alpha^3+\beta^3)^2] \end{aligned} \tag{4.8}$$

Expression (4.8) up on simplification yields (4.9)

$$\begin{aligned}\text{G.F.}^{G_1} &= \alpha^9\beta + 4\alpha^8\beta^2 + 9\alpha^7\beta^3 + 14\alpha^6\beta^4 + 16\alpha^5\beta^5\\ &+ 14\alpha^4\beta^6 + 9\alpha^3\beta^7 + 4\alpha^2\beta^8 + \alpha\beta^9\end{aligned} \tag{4.9}$$

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 $n_1\underset{\sim}{\alpha}$'s and $n_2\underset{\sim}{\beta}$'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 when the coefficients in G.F.'s are sorted in accordance to their M_F values one immediately infers that the proton NMR G_1 species are

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

The numbers in parenthesis give the number of G_1 multiplets of the appropriate multiplicity. This can be briefly summarized in Table 6 where we give all the proton NMR multiplets of non-rigid butane obtained using the NMR plethysm 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[9] where we 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 plethysms in Table 4 by $\lambda^k + \mu^k + \nu^k$, where λ, μ and ν are the weights corresponding to $m_f = -1, 0, 1$, respectively of 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. The deuterium NMR spin multiplets thus obtained for butane (D) are shown in Table 7.

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Table 1. The Character Table of S_4, the NMR Group of Methane

Γ Orders	(1)(2)(3)(4) 1	(1)(2)(34) 6	(1)(234) 8	(1234) 6	(12)(34) 3
$A_1 = [4]$	1	1	1	1	1
$F_1 = [3,1]$	3	1	0	-1	-1
$E_1 = [2^2]$	2	0	-1	0	2
$F_2 = [21^2]$	3	-1	0	1	-1
$A_2 = [1^4]$	1	-1	1	-1	1

Table 2. Generators of the NMR D Species of CD_4

Γ	λ^4	$\lambda^3\mu$	$\lambda^2\mu^2$	$\lambda\mu^3$	μ^4	$\lambda^3\nu$	$\lambda^2\mu\nu$	$\lambda\mu^2\nu$	$\mu^3\nu$	$\lambda^2\nu^2$	$\lambda\mu\nu^2$	$\mu^2\nu^2$	$\lambda\nu^3$	$\mu\nu^3$	ν^4
A_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
E_1	0	0	1	0	0	0	1	1	0	1	1	1	0	0	0
F_1	0	1	1	1	0	1	2	2	1	1	2	1	1	1	0
F_2	0	0	0	0	0	0	1	1	0	0	1	0	0	0	0

Table 3. Irreducible Representations of the NMR Group of Non-rigid Butane. This Group is also Isomorphic to the NMR Group of 2,2,3,3,4,4,5,5 Octamethyl Hexane in the Composite Particle Representation. Note that there are 8 A representations, 6 E representations, 12 G representations and 1 K representation satisfying $8\cdot 1^2+6\cdot 2^2+{}^{1}2+1\cdot 8^2 = 288$.

Γ	Dimension
$\Gamma_1 = A_1 = \underline{[3] \# [3] \# [2] \# [2]} \otimes [2]'$	1
$\Gamma_2 = A_2 = \underline{[3] \# [3] \# [2] \# [2]} \otimes [1^2]'$	1
$\Gamma_3 = E_1 = [3] \# [3] \# [2] \# [1^2] \uparrow S_2[S_3,S_2]$	2
$\Gamma_4 = A_3 = \underline{[3] \# [3] \# [1^2] \# [1^2]} \otimes [2]'$	1
$\Gamma_5 = A_4 = \underline{[3] \# [3] \# [1^2] \# [1^2]} \otimes [1^2]'$	1
$\Gamma_6 = G_1 = [3] \# [2,1] \# [2] \# [2] \uparrow S_2[S_3,S_2]$	4
$\Gamma_7 = G_2 = [3] \# [2,1] \# [2] \# [1^2] \uparrow S_2[S_3,S_2]$	4
$\Gamma_8 = G_3 = [3] \# [2,1] \# [1^2] \# [2] \uparrow S_2[S_3,S_2]$	4
$\Gamma_9 = G_4 = [3] \# [2,1] \# [1^2] \# [1^2] \uparrow S_2[S_3,S_2]$	4
$\Gamma_{10} = E_2 = [3] \# [1^3] \# [2] \# [2] \uparrow S_2[S_3,S_2]$	2
$\Gamma_{11} = E_3 = [3] \# [1^3] \# [2] \# [1^2] \uparrow S_2[S_3,S_2]$	2
$\Gamma_{12} = E_4 = [3] \# [1^3] \# [1^2] \# [2] \uparrow S_2[S_3,S_2]$	2
$\Gamma_{13} = E_5 = [3] \# [1^3] \# [1^2] \# [1^2] \uparrow S_2[S_3,S_2]$	2
$\Gamma_{14} = G_5 = \underline{[2,1] \# [2,1] \# [2] \# [2]} \otimes [2]'$	4
$\Gamma_{15} = G_6 = \underline{[2,1] \# [2,1] \# [2] \# [2]} \otimes [1^2]'$	4
$\Gamma_{16} = K_1 = [2,1] \# [2,1] \# [2] \# [1^2] \uparrow S_2[S_3,S_2]$	8
$\Gamma_{17} = G_7 = \underline{[2,1] \# [2,1] \# [1^2] \# [1^2]} \otimes [2]'$	4
$\Gamma_{18} = G_8 = \underline{[2,1] \# [2,1] \# [1^2] \# [1^2]} \otimes [1^2]'$	4
$\Gamma_{19} = G_9 = [2,1] \# [1^3] \# [2] \# [2] \uparrow S_2[S_3,S_2]$	4
$\Gamma_{20} = G_{10} = [2,1] \# [1^3] \# [2] \# [1^2] \uparrow S_2[S_3,S_2]$	4
$\Gamma_{21} = G_{11} = [2,1] \# [1^3] \# [1^2] \# [2] \uparrow S_2[S_3,S_2]$	4

Table 3 (continued)

Γ	Dimension
$\Gamma_{22} = G_{12} = [2,1] \# [1^3] \# [1^2] \# [1^2] \uparrow S_2[S_3,S_2]$	4
$\Gamma_{23} = A_5 = \underline{[1^3] \# [1^3] \# [2] \# [2]} \otimes [2]'$	1
$\Gamma_{24} = A_6 = \underline{[1^3] \# [1^3] \# [2] \# [2]} \otimes [1^2]'$	1
$\Gamma_{25} = E_6 = [1^3] \#]1^3] \# [2] \# [1^2] \uparrow S_2[S_3,S_2]$	2
$\Gamma_{26} = A_7 = \underline{[1^3] \# [1^3] \# [1^2] \# [1^2]} \otimes [2]'$	1
$\Gamma_{27} = A_8 = \underline{[1^3] \# [1^3] \# [1^2] \# [1^2]} \otimes [1^2]'$	1

Table 4. 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

Table 5. Generating Functions for the Proton NMR Spin Species Butane. GF's for E_3 and E_4, G_2 and G_3, and G_{10} and G_{11} are the same

Γ	α^{10}	$\alpha^9\beta$	$\alpha^8\beta^2$	$\alpha^7\beta^3$	$\alpha^6\beta^4$	$\alpha^5\beta^5$	$\alpha^4\beta^6$	$\alpha^3\beta^7$	$\alpha^2\beta^8$	$\alpha\beta^9$	β^{10}
A_1	1	2	6	9	14	14	14	9	6	2	1
A_2	0	2	4	9	11	14	11	9	4	2	0
A_3	0	0	1	1	2	2	2	1	1	0	0
A_4	0	0	0	1	1	2	1	1	0	0	0
A_5	0	0	0	0	0	0	0	0	0	0	0
A_6	0	0	0	0	0	0	0	0	0	0	0
A_7	0	0	0	0	0	0	0	0	0	0	0
A_8	0	0	0	0	0	0	0	0	0	0	0
E_1	0	1	3	6	9	10	9	6	3	1	0
E_2	0	0	0	0	0	0	0	0	0	0	0
E_3	0	0	0	0	0	0	0	0	0	0	0
E_5	0	0	0	0	0	0	0	0	0	0	0
E_6	0	0	0	0	0	0	0	0	0	0	0
G_1	0	1	4	9	14	16	14	9	4	1	0
G_2	0	0	1	3	5	6	5	3	1	0	0
G_4	0	0	0	1	2	2	2	1	0	0	0
G_5	0	0	1	2	5	5	5	2	1	0	0
G_6	0	0	0	2	3	5	3	2	0	0	0
G_7	0	0	0	0	1	1	1	0	0	0	0
G_8	0	0	0	0	0	1	0	0	0	0	0
G_9	0	0	0	0	0	0	0	0	0	0	0
G_{10}	0	0	0	0	0	0	0	0	0	0	0
G_{12}	0	0	0	0	0	0	0	0	0	0	0
K_1	0	0	0	1	3	4	3	1	0	0	0

Table 6. Proton NMR Species of Butane. Numbers are the Frequencies of Occurrence of that Spin Species

$2S+1$ Γ	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

Table 7. Deuterium NMR Spin Species of Butane. Numbers under each Symmetry Species and Multiplicity give the Frequency of Occurrence of that Spin Multiplet

2S+1 Γ	1	3	5	7	9	11	13	15	17	19	21
A_1	17	23	47	39	43	26	22	9	6	1	1
A_2	7	33	37	46	36	31	17	11	4	2	0
A_3	7	7	16	11	13	6	5	1	1	0	0
A_4	1	12	11	15	9	8	3	2	0	0	0
A_5	2	0	2	0	1	0	0	0	0	0	0
A_6	0	1	1	1	0	0	0	0	0	0	0
A_7	1	0	1	0	0	0	0	0	0	0	0
A_8	0	1	0	0	0	0	0	0	0	0	0
E_1	11	35	45	49	40	30	17	9	3	1	0
E_2	2	11	11	13	8	6	2	1	0	0	0
E_3	3	5	8	6	5	2	1	0	0	0	0
E_4	3	5	8	6	5	2	1	0	0	0	0
E_5	1	4	4	4	2	1	0	0	0	0	0
E_6	0	2	1	1	0	0	0	0	0	0	0
G_1	22	59	80	81	67	46	26	12	4	1	0
G_2	13	35	46	45	35	22	11	4	1	0	0
G_3	13	35	46	45	35	22	11	4	1	0	0
G_4	8	21	27	25	18	10	4	1	0	0	0
G_5	17	27	45	35	31	15	9	2	1	0	0
G_6	7	36	36	41	25	18	6	3	0	0	0
G_7	8	10	17	10	8	2	1	0	0	0	0
G_8	2	15	12	13	5	3	0	0	0	0	0
G_9	4	11	13	11	7	3	1	0	0	0	0
G_{10}	3	7	8	6	3	1	0	0	0	0	0
G_{11}	3	7	8	6	3	1	0	0	0	0	0
G_{12}	2	5	5	3	1	0	0	0	0	0	0
K_1	15	39	48	42	28	14	5	1	0	0	0

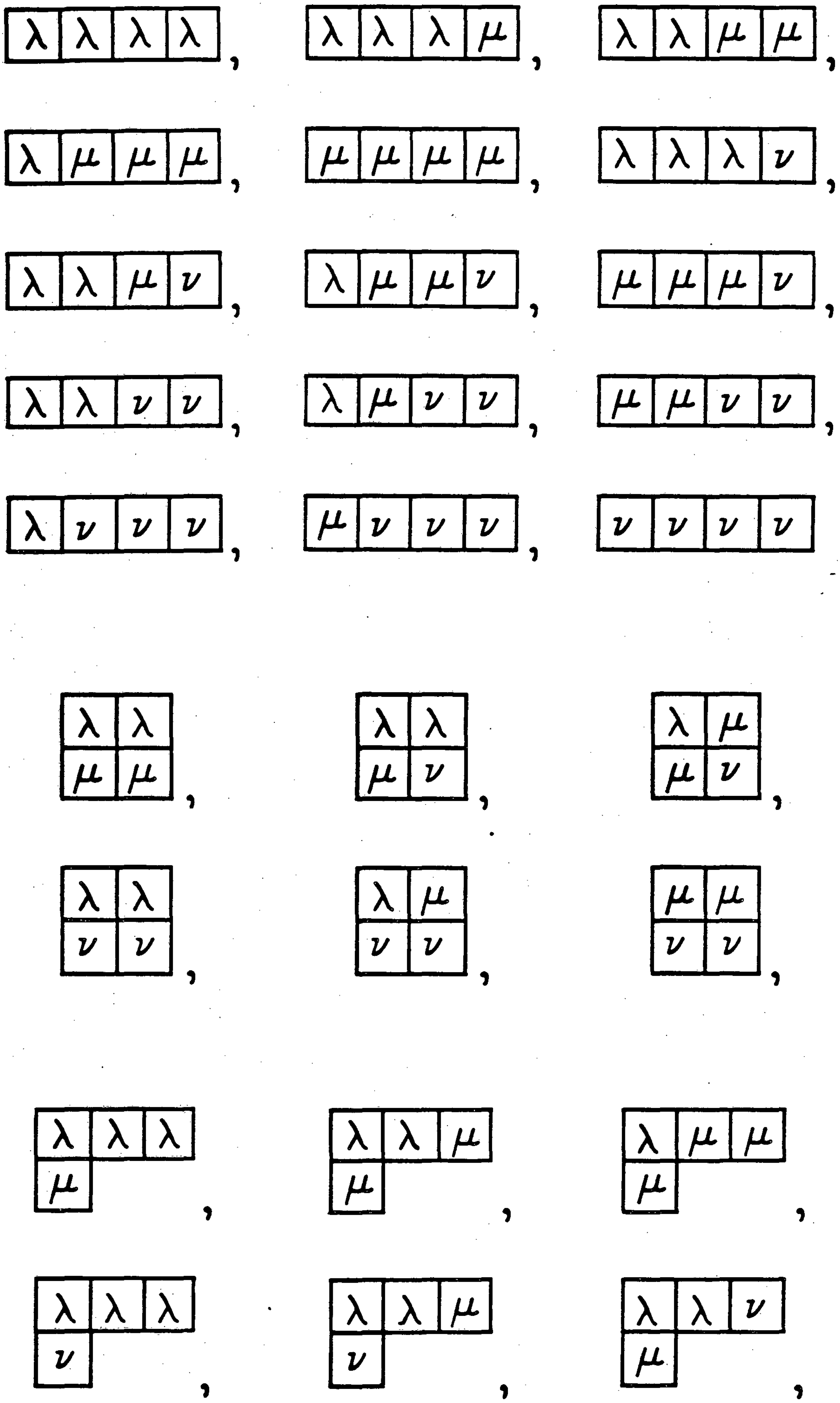
Figure Captions

Figure 1. NMR Gel'fand states of CD_4. λ, μ, and ν are the weights corresponding to the 3 spin states of D nuclei with $m_F = -1$, 0 and 1. The lexical ordering of the weight is $\nu > \mu > \lambda$.

Figure 2. Possible tableaus that can be obtained by adding 3 α's and 1 β to the Young graph of (4,2). When the symbols α's and β's are read from right to left one obtains a lattice permutation of $\alpha^3\beta$. These tableaus determine the s-functions contained in the product $\{4,2\}\{3,1\}$.

Figure 3. NMR graph of $B(CH_3)_3$. The center circle is the boron nucleus.

Figure 4. The NMR graph in Figure 3 as a composition of the graphs Q and T.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λ ν ν ν, μ ν ν ν, ν ν ν ν
λ λ / μ μ, λ λ / μ ν, λ μ / μ ν,
λ λ / ν ν, λ μ / ν ν, μ μ / ν ν,
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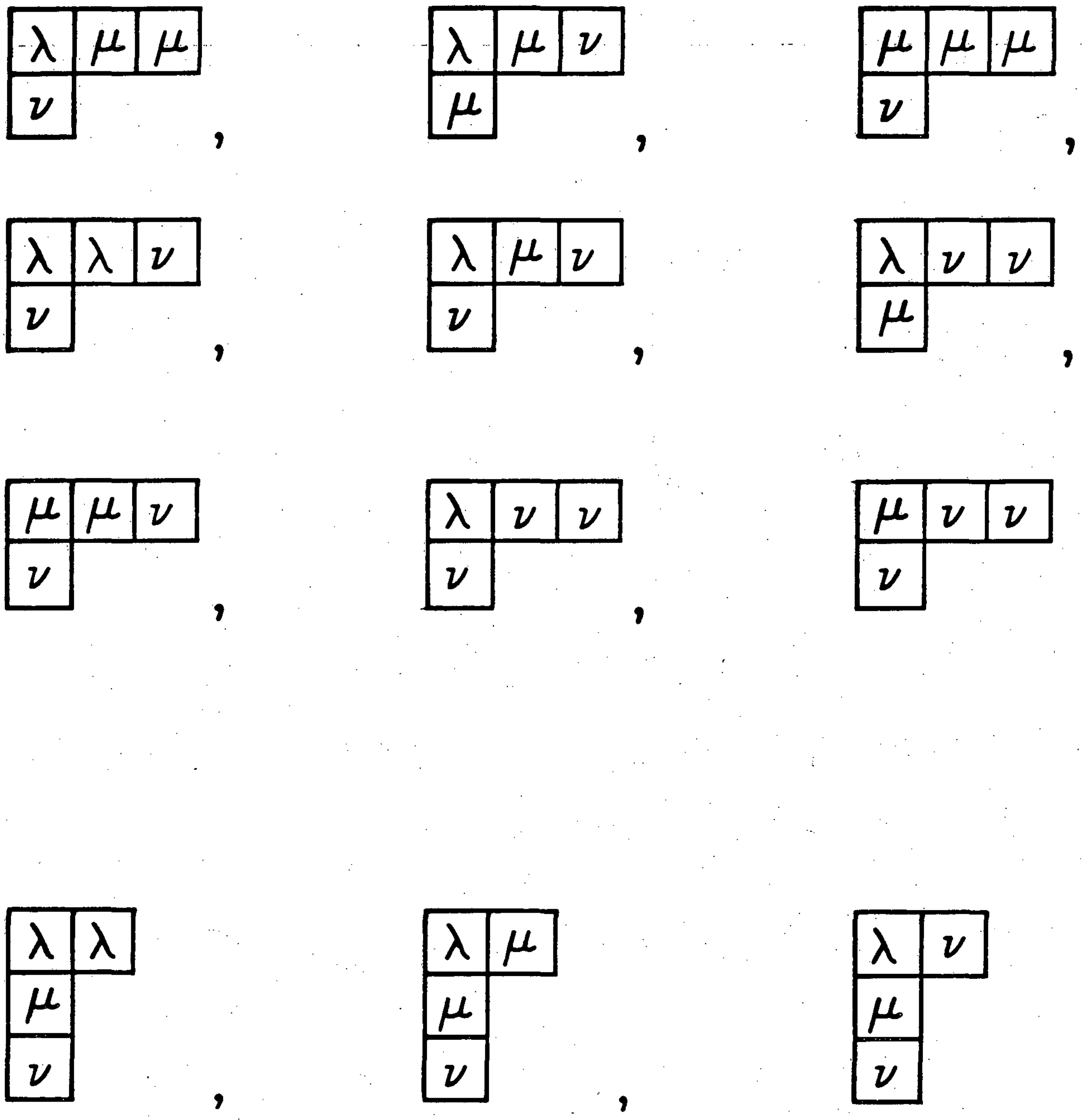

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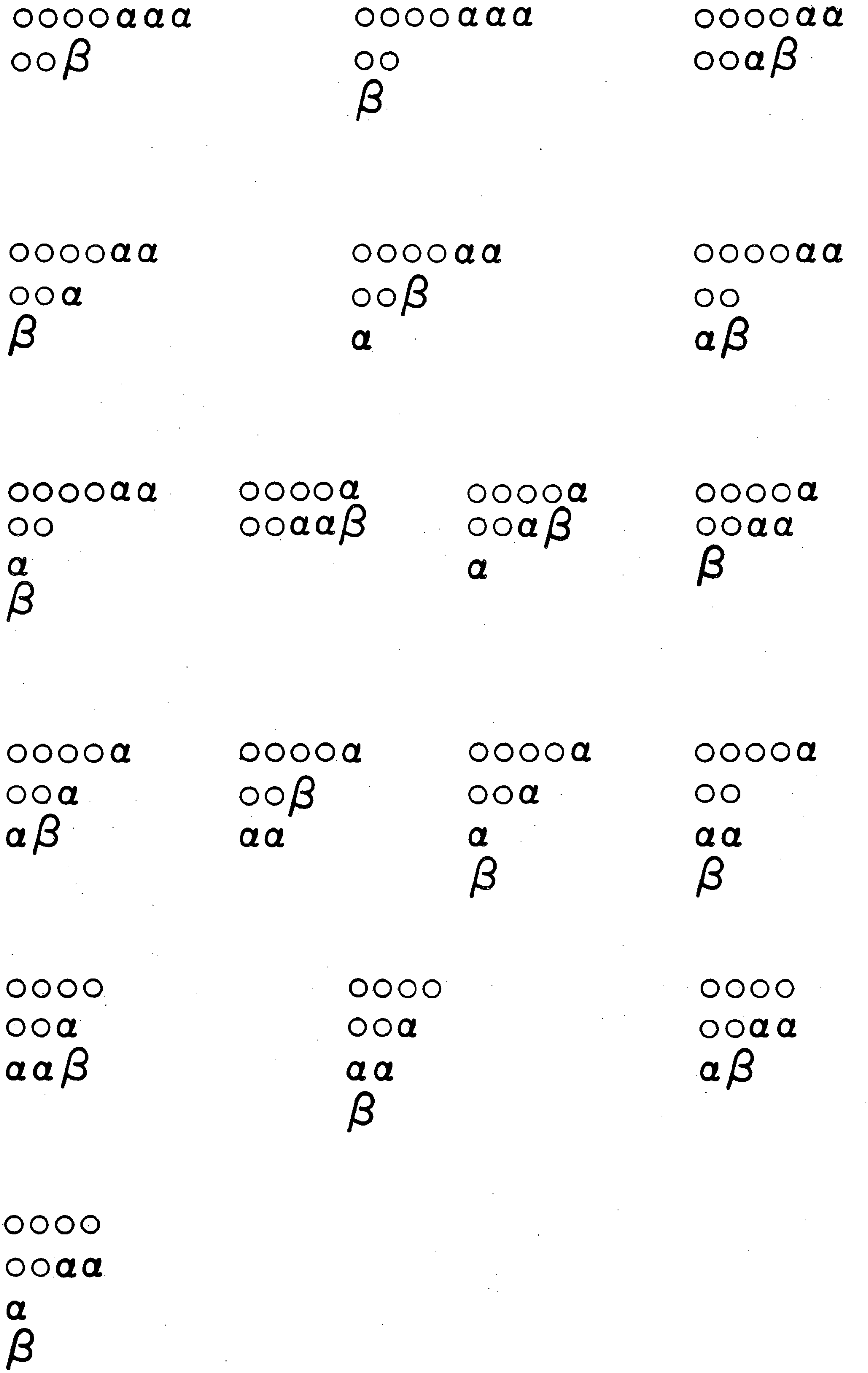

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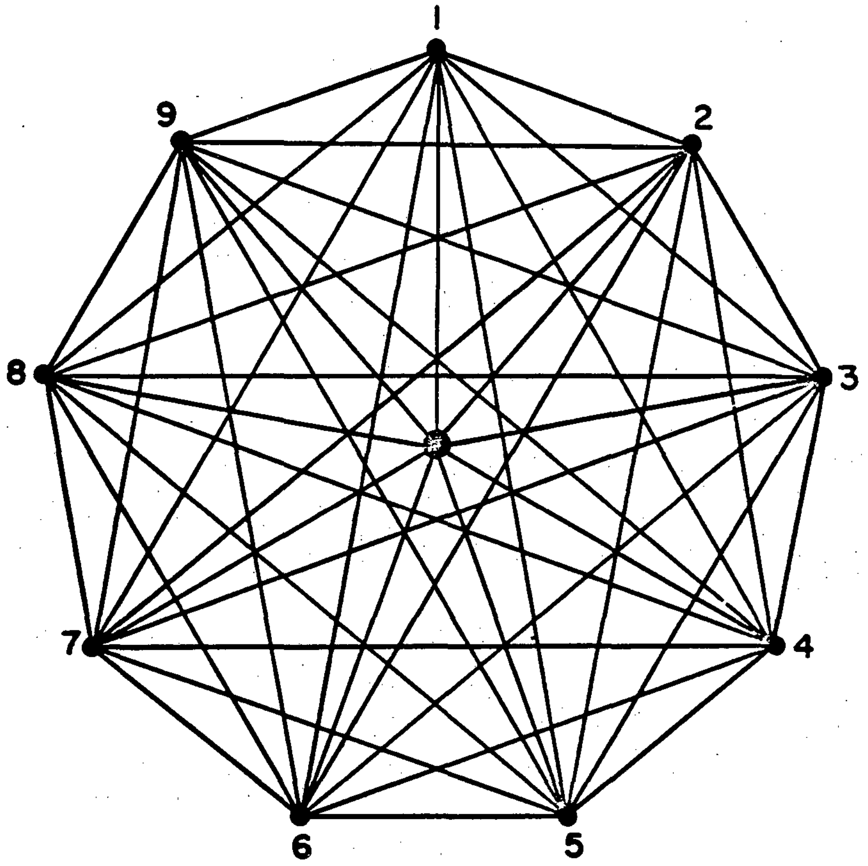

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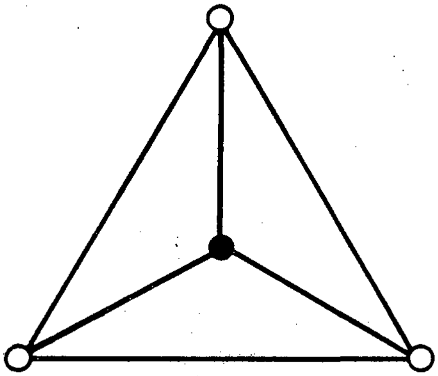
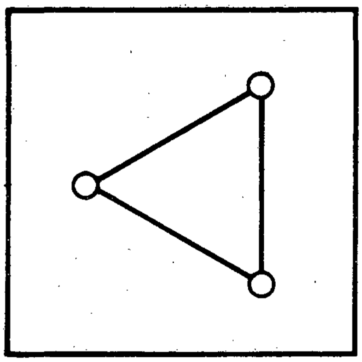


Q



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