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Graph theoretical characterization of NMR groups, nonrigid nuclear spin species and the construction of symmetry adapted NMR spin functions

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NMR group defined by Woodman is shown to be the generalized wreath product group of the NMR graph which is constructed with protons as vertices and edges representing nuclear couplings. The NMR graph can be expressed as a generalized composition of its quotient graph and various types. It is shown that the NMR group is the automorphism group of the NMR graph that preserves the coupling matrix defined here. Using the representation theory of generalized wreath product groups developed in an earlier paper of the present author, the character tables of NMR groups can be obtained. The character tables of certain NMR groups are presented. The quotient graph of the NMR graph is shown to be the composite particle graph. The automorphism group of the quotient NMR graph is the symmetry group of the composite particles, preserving the NMR coupling constants. An iterative algorithm is formulated for obtaining the automorphism group of the composite particle tree. A combinatorial approach is expounded for identifying the nuclear spin species of nonrigid and rigid molecules. The coalescence diagrams describing the effect of nonrigidity on nuclear spin species are introduced and obtained to exemplify the utility of the proposed method. It is shown that using the automorphism group of the quotient graph, the symmetry adapted composite particle spin functions can be constructed. We illustrate this method with 2,3-dimethylbutane. The nuclear spin Hamiltonian matrix of 2,3-dimethylbutane of order $2^{14} \times 2^{14}$ is reduced to a matrix of order 64×64 by the composite particle method. This matrix can be blocked in the symmetry adapted basis set constructed through the automorphism group of the quotient graph into 40 matrices of order 1×1 and 12 matrices of order 2×2 .

I. INTRODUCTION

Woodman^{1,2} defined the NMR group as the set of those permutations of the nuclei (protons) that leave the NMR Hamiltonian H_{NMR} , defined below, invariant.

$$H_{\text{NMR}} = \sum_i \nu_i I_{z_i} + \sum_{i,j} J_{ij} I_i \cdot I_j, \quad (1)$$

where ν_i is the chemical shift parameter of the i th nuclei, J_{ij} is the coupling constant between the nuclei i and j , I_{z_i} is the spin of the i th nuclei in the Z direction, $I_i \cdot I_j$ is the scalar product of the spin operators I_i and I_j . Woodman also obtained the character tables of certain specific NMR groups like the NMR group of ethane. Serre³ also obtained the character table of the NMR group of ethane using Mackey's theorems. The above definition of NMR group, however, does not explicitly express the NMR group as a permutation group. In this paper we give a diagrammatic approach to this problem. Representation of nuclear spin interactions by graphs enables us to identify the NMR groups systematically and elegantly. NMR graphs can be expressed as generalized composition of the NMR quotient graph and various types. The automorphism group of the generalized composition of the NMR graph is generalized wreath product group. Using the representation theory of generalized wreath product groups developed by the author,⁸ we can obtain the character tables of NMR groups.

Nevertheless, as commented by Woodman, the composite particle method is superior at every stage of NMR computations. The composite particle group is of much lower order. The character tables of composite particle groups can be, therefore, constructed more easily. We present a graph theoretical analog of the

composite particle method. The automorphism group of the composite particles can be constructed using an iterative algorithm that we present here.

In Sec. II, we discuss concepts related to NMR graphs. In Sec. III, we formulate a graph theoretical method of characterizing the NMR groups. Section IV uses the combinatorial theorem of Pólya for obtaining a generating function for the nuclear spin species. Using the generating function thus constructed, the nuclear spin species of both rigid and nonrigid molecules are obtained. The construction of the coalescence diagram is illustrated with propane in Sec. V. Section VI outlines the construction symmetry adapted composite NMR spin functions.

II. NMR GRAPHS

A. Preliminaries

Nuclear spin interactions can be represented by graphs, vertices representing nuclei and edges representing the nuclear-nuclear couplings. The NMR graph of a molecule modifies in accordance with the various approximations incorporated in the NMR Hamiltonian. For example, one may assume nearest-neighbor interactions, viz., the proton-proton interactions of protons attached only to adjacent or same carbon atoms. Such approximations often used in large molecules are not unreasonable since the coupling constant between two protons separated by a large distance is small. In general, the NMR group is dependent on the types of approximations incorporated in the NMR spin Hamiltonian.

By way of illustration, the NMR graph of the nuclear spin Hamiltonian of propane (^{12}C) which includes only nearest-neighbor interactions is shown in Fig. 1. If we replace ^{12}C nuclei by ^{13}C nuclei, and if we label ^{13}C nuclei 9, 10, and 11, the NMR graph modifies to the graph shown in Fig. 2.

Given a molecule to construct the NMR group, we

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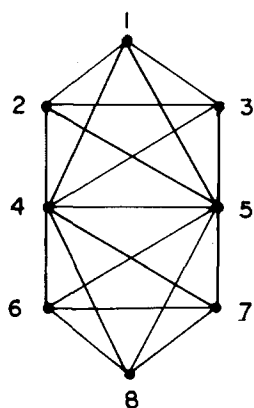
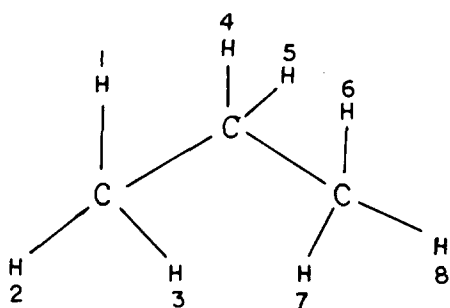


FIG. 1. NMR graph of propane (^{12}C) in the nearest-neighbor interaction.

must first know the classes of magnetically equivalent nuclei. The author⁴ gave a combinatorial solution to this problem using the theorem of Pólya.⁵ We first have to construct what is known as the cycle index of a permutation group and obtain a generating function using the theorem of Pólya. The cycle index of a permutation group is defined as

$$P_G(S_1, S_2, \dots) = \frac{1}{|G|} \sum_{g \in G} S_1^{b_1} S_2^{b_2} \dots, \quad (2)$$

where $S_1^{b_1} S_2^{b_2} \dots$ is a representation of a typical permutation $g \in G$ having b_1 cycles of length 1, b_2 cycles of length 2, etc. The group of permutations induced by internal rotations is the generalized wreath product group.⁴ The cycle index of the generalized wreath product can be found using a theorem described elsewhere.⁴ Let us assign a weight α_1 to protons and a weight α_2 to a group Z . Then the coefficient of $\alpha_1^{N-1} \alpha_2$ (where N is the number of nuclei whose magnetic equivalence is under consideration) in the configuration counting series obtained by replacing every cycle of length k in the cycle index of G by $\alpha_1^k + \alpha_2^k$, gives the number of classes of magnetically equivalent nuclei.⁴ For example, the cycle index for partitioning the eight protons of ^{12}C -propane into classes of magnetically equivalent nuclei is

$$P_G = \frac{1}{36} [S_1^8 + 4S_1^5 S_3 + 4S_1^2 S_3^2 + 3S_1^4 S_2 + 6S_2 S_6 + 12S_1^2 S_2^3 + 6S_1^2 S_6]. \quad (3)$$

The coefficient of $\alpha_1^7 \alpha_2$ in the expression obtained by replacing S_k in (3) by $\alpha_1^k + \alpha_2^k$ is

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

The two classes are $\{1, 2, 3, 6, 7, 8\}$ and $\{4, 5\}$. The permutations that permute magnetically nonequivalent nuclei cannot leave the NMR spin Hamiltonian invariant. Therefore, NMR groups contain only those permutations that permute the elements within the same class of magnetically equivalent nuclei. Note that, in general, all the nuclei in the same class of magnetically equivalent nuclei need not be coupled to the same extent among themselves or with other nuclei in the molecule. For example, the coupling constants J_{12} and J_{16} are not the same in propane. (In fact, in this case we have set $J_{16} = 0$). The nuclei 1, 2, and 3 of propane are magnetically equivalent and have identical coupling constants among themselves and with other nuclei. This motivates us to construct a quotient graph of NMR graph and express the NMR graph of a molecule as a product of its quotient graph and various "types".

B. NMR graph as a generalized composition

We start with certain definitions. The composition of two graphs Γ_1 and Γ_2 , denoted as $\Gamma_1[\Gamma_2]$, is obtained by replacing each vertex of Γ_1 by a copy of Γ_2 and each line of Γ_1 by the lines which join the corresponding copies of Γ_2 . The set of vertices of $\Gamma_1[\Gamma_2]$ is the Cartesian product of the vertices of Γ_1 and Γ_2 . Let (a_1, a_2) and (b_1, b_2) , $a_1, b_1 \in V(\Gamma_1)$ and $a_2, b_2 \in V(\Gamma_2)$ be two vertices in $\Gamma_1[\Gamma_2]$. $[V(\Gamma)]$ denotes the set of vertices of the graph Γ . (a_1, a_2) and (b_1, b_2) are adjacent in $\Gamma_1[\Gamma_2]$ if and only if either a_1, b_1 are adjacent in Γ_1 or $a_1 = b_1$ and a_2, b_2 are adjacent in Γ_2 . To illustrate, consider the NMR graph of ethane (^{12}C) shown in Fig. 3. The NMR graph of ethane can be expressed as a composition of the graph Q with T shown in Fig. 3.

A generalized composition of a graph Q with various "types" T_1, T_2, \dots is denoted as $Q[T_1, T_2, \dots]$. Given the classes of magnetically equivalent nuclei, we express the NMR graph as a generalized composition as follows. Construct a quotient graph Q by coalescing the magnetically equivalent nuclei attached to the same carbon atom into a single vertex. Let Y_i be the set of all such vertices in the quotient graph Q that are in the

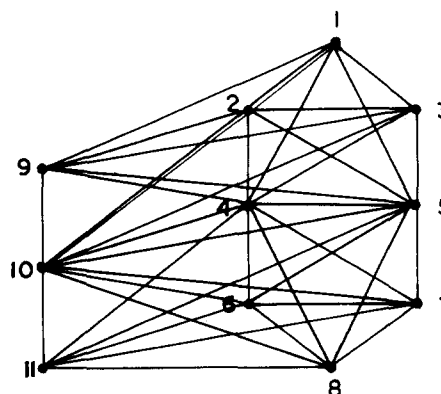


FIG. 2. NMR graph of propane (^{13}C) in the nearest-neighbor interaction. The vertices 9, 10, and 11 are ^{13}C carbon atoms.

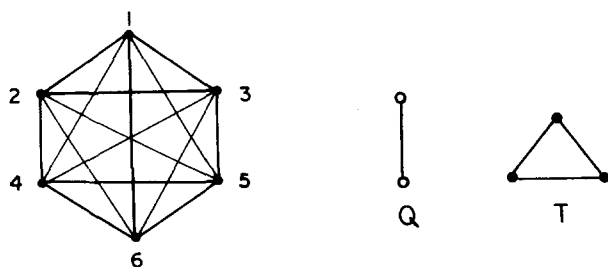


FIG. 3. NMR graph of ethane which is expressed as the composition of Q and T .

same magnetic equivalence class. Let T_i be the graph (hereafter referred to as a "type") that was coalesced into a vertex in Y_i . It can be seen that T_i has to be the same for all vertices in Y_i . Then the NMR graph can be expressed as the generalized composition $Q[T_1, T_2, \dots, T_t]$, where t is the number of types. It is obtained by replacing every vertex of Q in Y_i by a copy of the type T_i . Symbolically, $\Gamma = Q[y_{ir} - T_i]$, where Γ is the NMR graph, $y_{ir} \in Y_i$. The isomorphism thus introduced between y_{ir} and a copy of T_i is called a generalized composite isomorphism.

To illustrate, the NMR graph of ^{12}C -propane shown in Fig. 1 can be expressed as the generalized composition of Q with T_1 and T_2 shown in Fig. 4. The sets $Y_1 = \{1, 3\}$ and $Y_2 = \{2\}$ are obtained from the partitions of magnetically equivalent nuclei generated from Polya's theorem.

C. Graph theoretical analog of the composite particle method

An elegant method of exploiting the high symmetry of the NMR spin Hamiltonian of the nonrigid molecules is the composite particle method.⁶ The underlying principle in this method is that the coupling constants among a complete set of magnetically equivalent nuclei (set of magnetically equivalent nuclei that have identical coupling constants among themselves and with other nuclei in the system) do not affect the NMR spectrum. Hence, the complete set of magnetically equivalent nuclei can be thought of as a single composite particle and the simplified NMR Hamiltonian can be expressed in terms of these composite particles. The Hamiltonian H thus obtained is

$$H = \sum_G \nu_G I_{Z(G)} + \sum_{G \neq G'} J_{GG'} I_G \cdot I_{G'}, \quad (5)$$

where the symbols have the usual meaning; however, now, each "nucleus" G is a composite particle. Indeed the vertices of the quotient NMR graph of the generalized composition of NMR graph are the composite particles and the quotient graph is a diagrammatic representation of the composite particle spin Hamiltonian.

III. GRAPH THEORETICAL CHARACTERIZATION OF NMR GROUPS

A. NMR groups at high temperature

Define the coupling matrix C of the NMR graph as a matrix whose ij th entry is J_{ij} (the coupling constant be-

tween the nuclei i and j) if the vertices i and j are connected in the NMR graph. Otherwise, C_{ij} is zero. (i) It is interesting that the NMR spin Hamiltonian has one-to-one correspondence with the coupling matrix C from the standpoint of permutational invariance. The automorphism group of a graph is defined as the set of permutations of the vertices of the graph that preserve the adjacency matrix A of a graph which is defined as follows:

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

The NMR group is the automorphism group of the NMR graph that preserves the coupling constants. Alternatively, the NMR group consists of those permutations whose permutation matrices P 's satisfy the following condition:

$$P C P^{-1} = C. \quad (6)$$

Let the group of such permutations be denoted as $\text{Aut}(\Gamma, C)$. For example, the permutation (123) preserves the coupling matrix of the NMR graph of ethane (Fig. 3). However, the permutation (35) does not preserve the coupling matrix since $J_{13} \neq J_{15}$. The coupling matrix of a NMR graph can be reduced to the adjacency matrix only when all the coupling constants are equal. In this special case, the NMR group is the automorphism group of the NMR graph, denoted as $\text{Aut}(\Gamma)$. In general $\text{Aut}(\Gamma, C)$ is not isomorphic to $\text{Aut}(\Gamma)$. For example, $\text{Aut}(\Gamma)$ of the NMR graph of ethane is S_6 , whereas $\text{Aut}(\Gamma, C)$ is the wreath product of S_2 with S_3 .

Let us try to find the automorphism group of the composition of two graphs Γ_1 and Γ_2 . Let G_1 and G_2 be the automorphism groups of Γ_1 and Γ_2 , respectively. Harary⁷ proved that the automorphism group of $\Gamma_1[\Gamma_2]$ is the wreath product $G_1[G_2]$ provided not both Γ_1 and Γ_2 are complete. If Γ_1 and Γ_2 are complete, then $\text{Aut}(\Gamma_1[\Gamma_2])$ is S_{mn} , if m and n are the number of vertices of Γ_1 and Γ_2 , respectively. However, $\text{Aut}(\Gamma_1[\Gamma_2], C)$ is always the wreath product $G_1[G_2]$ since the coupling constants among the nuclei attached to the same carbon atom are different from the coupling constants among the nuclei attached to different carbon atoms. For the general case, namely, $\text{Aut}(Q[T_1, T_2, \dots, T_t], C)$, we have the following theorem.

Theorem 1: $\text{Aut}(Q[T_1, T_2, \dots, T_t], C) = G[H_1, H_2, \dots, H_t]$, where G is the automorphism group of Q that preserves the coupling matrix restricted to Q , H_i being the automorphism group of T_i preserving the coupling matrix

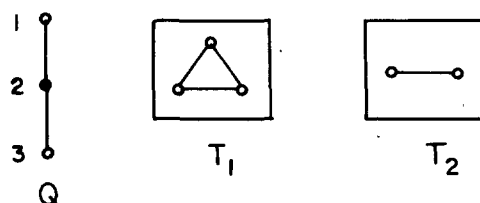


FIG. 4. Quotient graph Q and types T_1 and T_2 of the NMR graph of propane (^{12}C) shown in Fig. 1.

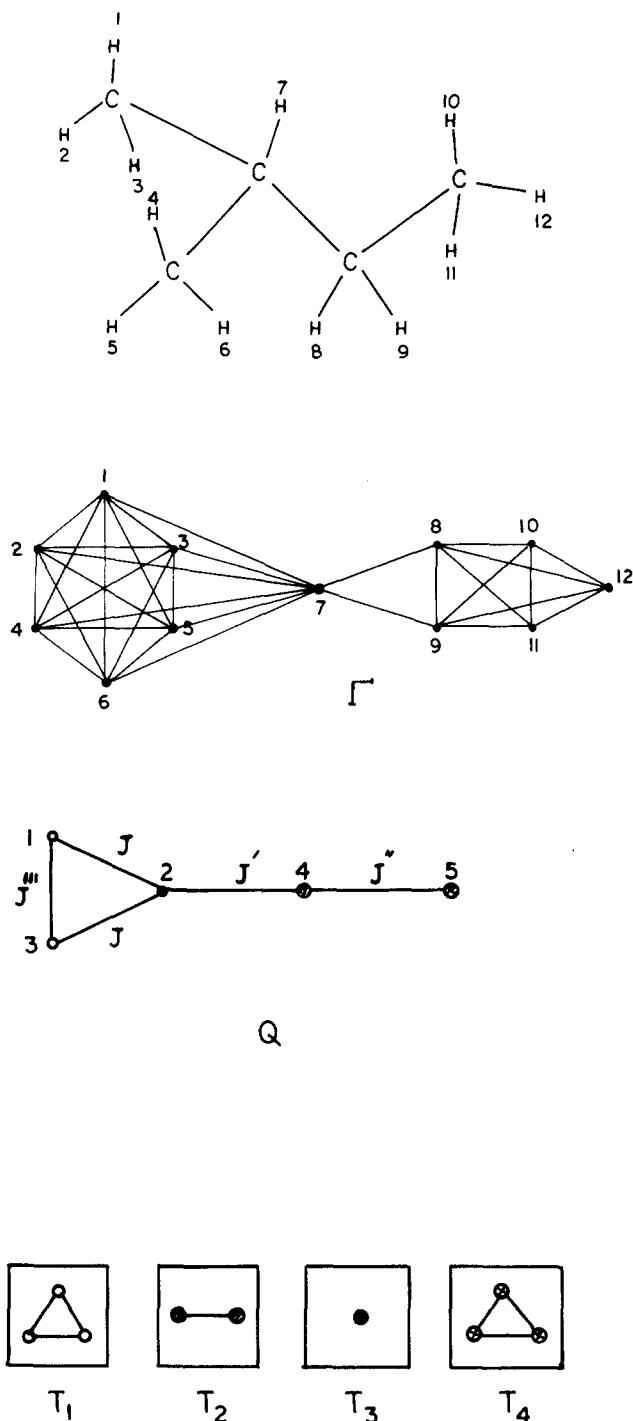


FIG. 5. The molecule 2 methylbutane, its NMR graph Γ , the quotient graph Q , and the various types. Interactions between the sets of nuclei $\{1, 2, 3\}$ and $\{4, 5, 6\}$ are included in the NMR graph. However, the inclusion or exclusion of these interactions does not affect the NMR group.

restricted to T_i . The symbol $G[H_1, H_2, \dots, H_t]$ is used for the generalized wreath product of G with the groups of H_1, H_2, \dots, H_t .

Proof: each isomorphism of $Q[T_1, T_2, \dots, T_t]$ that preserves the coupling matrix can be obtained by permuting the copies T_1, T_2, \dots, T_t with an element of $\text{Aut}(Q, C|_Q)$. Then we induce the generalized composite

isomorphism defined earlier on each separate representatives T_1, T_2, \dots, T_t . This process certainly preserves the coupling matrix. However, this is the construction of the generalized wreath product $G[H_1, H_2, \dots, H_t]$. Consequently, the result follows.

Let us illustrate the theorem with the molecule 2 methylbutane whose NMR graph Γ , the quotient graph Q and the various types are shown in Fig. 5. Note that we have included the interaction between the sets of nuclei $\{1, 2, 3\}$ and $\{4, 5, 6\}$. However, inclusion or exclusion of these interactions in particular, does not affect the NMR group. It can be seen from Polya's theorem that the classes of magnetically equivalent nuclei are $C_1 = \{1, 2, 3, 4, 5, 6\}$, $C_2 = \{8, 9\}$, $C_3 = \{7\}$, and $C_4 = \{10, 11, 12\}$. Hence, Q can be obtained by coalescing the set of vertices $\{1, 2, 3\}$, $\{4, 5, 6\}$, $\{8, 9\}$, $\{7\}$, $\{10, 11, 12\}$ each into a single vertex. Consequently, the Y sets of Q are $Y_1 = \{1, 3\}$, $Y_2 = \{4\}$, $Y_3 = \{2\}$, and $Y_4 = \{5\}$ (see Fig. 5). Thus, the NMR graph Γ is $Q[T_1, T_2, T_3, T_4]$. The coupling matrix restricted to Q is

$$C|_Q = \begin{bmatrix} 0 & J & J''' & 0 & 0 \\ J & 0 & J & J' & 0 \\ J''' & J & 0 & 0 & 0 \\ 0 & J' & 0 & 0 & J'' \\ 0 & 0 & 0 & J'' & 0 \end{bmatrix}.$$

$\text{Aut}(Q, C|_Q)$ can be seen to be $S_2(5)$ (a symmetric group containing $2!$ elements acting on five elements). The permutations are

$$(1)(2)(3)(4)(5), (13)(2)(4)(5).$$

The group H_1 acting on T_1 is S_3 ; H_2 acting on T_2 is S_2 ; H_3 acting on T_3 is E (group containing only the identity); and H_4 acting on T_4 is S_3 . Hence, the NMR group is

$$S_2(5)[S_3, S_2, E, S_3].$$

The order of this group is 864. There are 54 classes. Using the representation theory of the generalized wreath product groups developed in an earlier paper,⁸ we can obtain the character table. Table I shows molecules containing up to six carbon atoms and certain other molecules with their NMR quotient graphs, Y -set partitions, NMR groups, and their order. The quotient graphs shown in Table I reflect the type of approximation incorporated in the NMR spin Hamiltonian. Table II shows the conjugacy classes of the NMR group of 2 methylbutane and the character table is shown in Table III.

B. Effective NMR group

Since the coupling constants among a complete set of magnetically equivalent nuclei do not affect the NMR spectrum, Woodman² also defined an effective NMR group. The effective NMR group contains those permutations that leave the effective NMR spin Hamiltonian invariant where the effective NMR Hamiltonian is obtained by setting $J_{ij} = 0$ if i and j belong to a set of fully magnetically equivalent nuclei.

Define the effective NMR graph as the graph in which there are no edges between two completely equivalent

TABLE I. NMR quotient graphs, their Y -set partitions, and NMR groups of a series of molecules. The approximations incorporated in the NMR spin Hamiltonian are depicted by the NMR quotient graph.

Serial no.	Molecule	NMR quotient graph	Y -set partitions	NMR group	Order
1	ethane		$Y_1 = \{1, 2\}$	$S_2[S_3]$	72
2	propane		$Y_1 = \{1, 3\}$ $Y_2 = \{2\}$	$S_2[S_3, S_2]$	144
3	butane		$Y_1 = \{1, 4\}$ $Y_2 = \{2, 3\}$	$S_2[S_3, S_2]$	288
4	isobutane		$Y_1 = \{1, 3, 4\}$ $Y_2 = \{2\}$	$S_3[S_3]$	1 296
5	pentane		$Y_1 = \{1, 5\}$ $Y_2 = \{2, 4\}$ $Y_3 = \{3\}$	$S_2[S_3, S_2, S_2]$	576
6	isopentane		$Y_1 = \{1, 2\}$ $Y_2 = \{3\}$ $Y_3 = \{4\}$ $Y_4 = \{5\}$	$S_2[S_3, E, S_2, S_3]$	864
7	neopentane		$Y_1 = \{1, 2, 3, 4\}$ $Y_2 = \{5\}$	$S_4[S_3]$	31 104
8	hexane		$Y_1 = \{1, 6\}$ $Y_2 = \{2, 5\}$ $Y_3 = \{3, 4\}$	$S_2[S_3, S_2, S_2]$	1 152
9	2-methylpentane		$Y_1 = \{1, 2\}$ $Y_2 = \{3\}$ $Y_3 = \{4\}$ $Y_4 = \{5\}$ $Y_5 = \{6\}$	$S_2[S_3, E, S_2, S_2, S_3]$	1 728
10	3-methylpentane		$Y_1 = \{1, 5\}$ $Y_2 = \{2, 4\}$ $Y_3 = \{3\}$ $Y_4 = \{6\}$	$S_2[S_3, S_2, E, S_3]$	1 728
11	2,3-dimethylbutane		$Y_1 = \{1, 4, 5, 6\}$ $Y_2 = \{2, 3\}$	$(S_2[S_2])[S_3]$	10 368
12	2,2-dimethylbutane		$Y_1 = \{1, 2, 3\}$ $Y_2 = \{4\}$ $Y_3 = \{5\}$ $Y_4 = \{6\}$	$S_3[S_3, S_2, S_3]$	15 552
13	heptane		$Y_1 = \{1, 7\}$ $Y_2 = \{2, 6\}$ $Y_3 = \{3, 5\}$ $Y_4 = \{4\}$	$S_2[S_3, S_2, S_2, S_2]$	2 304
14	2-methylhexane		$Y_1 = \{1, 3\}$ $Y_2 = \{2\}$ $Y_3 = \{4\}$ $Y_4 = \{5\}$ $Y_5 = \{6\}$ $Y_6 = \{7\}$	$S_2[S_3, E, S_2, S_2, S_2, S_3]$	3 456

TABLE I (Continued)

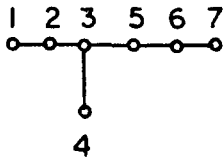
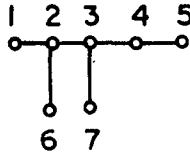
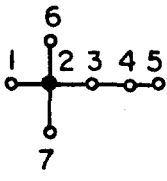
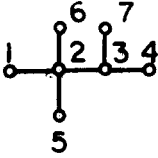
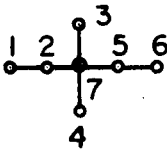
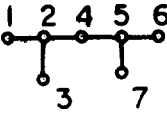
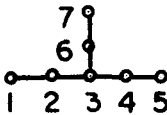
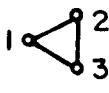
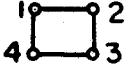
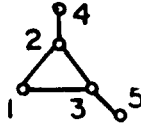
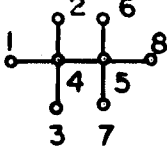
Serial no.	Molecule	NMR quotient graph	Y-set partitions	NMR group	Order
15	3-methylhexane		$Y_1 = \{1\}$ $Y_2 = \{2\}$ $Y_3 = \{3\}$ $Y_4 = \{4\}$ $Y_5 = \{5\}$ $Y_6 = \{6\}$ $Y_7 = \{7\}$	$E[S_3, S_2, E, S_3, S_2, S_2, S_3]$	1 728
16	2, 3-dimethylpentane		$Y_1 = \{1, 6\}$ $Y_2 = \{2\}$ $Y_3 = \{3\}$ $Y_4 = \{7\}$ $Y_5 = \{4\}$ $Y_6 = \{5\}$	$S_2[S_3, E, E, S_3, S_2, S_3]$	5 184
17	2, 2-dimethylpentane		$Y_1 = \{1, 6, 7\}$ $Y_2 = \{2\}$ $Y_3 = \{3\}$ $Y_4 = \{4\}$ $Y_5 = \{5\}$	$S_3[S_3, S_2, S_2, S_3]$	31 104
18	2, 2, 3-trimethylbutane		$Y_1 = \{1, 5, 6\}$ $Y_2 = \{2\}$ $Y_3 = \{3\}$ $Y_4 = \{4, 7\}$	$(S_3 \times S_2)$ $[S_3, E, S_3]$	93 312
19	3, 3-dimethylpentane		$Y_1 = \{1, 6\}$ $Y_2 = \{2, 5\}$ $Y_3 = \{3, 4\}$ $Y_4 = \{7\}$	$(S_2 \times S_2)$ $[S_3, S_2, S_3]$	20 736
20	2, 4-dimethylpentane		$Y_1 = \{1, 3, 6, 7\}$ $Y_2 = \{2, 5\}$ $Y_3 = \{4\}$	$(S_2[S_2])$ $[S_3, E, S_2]$	20 736
21	2-ethylpentane		$Y_1 = \{1, 5, 7\}$ $Y_2 = \{2, 4, 6\}$ $Y_3 = \{3\}$	$S_3[S_3, S_2, E]$	10 368
22	cyclopropane		$Y_1 = \{1, 2, 3\}$	$S_3[S_2]$	48
23	cyclobutane		$Y_1 = \{1, 2, 3, 4\}$	$S_4[S_2]$	384
24	1, 2-dimethylcyclopropane		$Y_1 = \{1\}$ $Y_2 = \{2, 3\}$ $Y_3 = \{4, 5\}$	$S_2[S_2, E, S_3]$	144
25	2, 2, 3, 3-tetramethylbutane		$Y_1 = \{1, 2, 3, 6, 7, 8\}$ $Y_2 = \{4, 5\}$	$(S_2[S_3]) [S_3]$	3 359 232

TABLE II. Conjugacy classes of the NMR group of 2-methylbutane, in the same order as given in Table III.

Serial no.	Conjugacy class	Order	Serial no.	Conjugacy class	Order
1	E	1	28	(8, 9)	1
2	(1, 2)	6	29	(1, 2)(8, 9)	6
3	(1, 2, 3)	4	30	(1, 2, 3)(8, 9)	4
4	(1, 2)(4, 5)	9	31	(1, 2)(4, 5)(8, 9)	9
5	(1, 2, 3)(4, 5, 6)	4	32	(1, 2, 3)(4, 5, 6)(8, 9)	4
6	(1, 2)(4, 5, 6)	12	33	(12)(4, 5, 6)(8, 9)	12
7	(1, 4)(2, 5)(3, 6)	6	34	(1, 4)(2, 5)(8, 9)(3, 6)	6
8	(1, 5, 3, 4, 2, 6)	12	35	(1, 5, 3, 4, 2, 6)(8, 9)	12
9	(1, 5)(2, 6, 3, 4)	18	36	(1, 5)(2, 6, 3, 4)(8, 9)	18
10	(10, 11)	3	37	(8, 9)(10, 11)	3
11	(1, 2)(10, 11)	18	38	(1, 2)(8, 9)(10, 11)	18
12	(1, 2, 3)(10, 11)	12	39	(1, 2, 3)(8, 9)(10, 11)	12
13	(1, 2)(4, 5)(10, 11)	27	40	(1, 2)(4, 5)(8, 9)(10, 11)	27
14	(1, 2, 3)(4, 5, 6)(10, 11)	12	41	(1, 2, 3)(4, 5, 6)(10, 11)	12
15	(1, 2)(4, 5, 6)(10, 11)	36	42	(1, 2)(4, 5, 6)(8, 9)(10, 11)	36
16	(1, 4)(2, 5)(3, 6)(10, 11)	18	43	(1, 4)(2, 5)(3, 6)(8, 9)(10, 11)	18
17	(1, 5, 3, 4, 2, 6)(10, 11)	36	44	(1, 5, 3, 4, 2, 6)(8, 9)(10, 11)	36
18	(1, 5)(2, 6, 3, 4)(10, 11)	54	45	(1, 5)(2, 6, 3, 4)(8, 9)(10, 11)	54
19	(10, 11, 12)	2	46	(8, 9)(10, 11, 12)	2
20	(1, 2)(10, 11, 12)	12	47	(1, 2)(8, 9)(10, 11, 12)	12
21	(1, 2, 3)(10, 11, 12)	8	48	(1, 2, 3)(8, 9)(10, 11, 12)	8
22	(1, 2)(4, 5)(10, 11, 12)	18	49	(1, 2)(4, 5)(8, 9)(10, 11, 12)	18
23	(1, 2, 3)(4, 5, 6)(10, 11, 12)	8	50	(1, 2, 3)(4, 5, 6)(8, 9)(10, 11, 12)	8
24	(1, 2)(4, 5, 6)(10, 11, 12)	24	51	(1, 2)(4, 5, 6)(8, 9)(10, 11, 12)	24
25	(1, 4)(2, 5)(3, 6)(10, 11, 12)	12	52	(1, 4)(2, 5)(3, 6)(8, 9)(10, 11, 12)	12
26	(1, 5, 3, 4, 2, 6)(10, 11, 12)	24	53	(1, 5, 3, 4, 2, 6)(8, 9)(10, 11, 12)	24
27	(1, 5)(2, 6, 3, 4)(10, 11, 12)	36	54	(1, 5)(2, 6, 3, 4)(8, 9)(10, 11, 12)	36

nuclei. For example, the effective NMR graph of ^{12}C butane is shown in Fig. 6. This effective NMR graph corresponds to the effective NMR Hamiltonian which includes only the nearest-neighbor interactions. The quotient graph Q and the types T_1 and T_2 are also shown in Fig. 6. The sets Y_1 and Y_2 are $Y_1 = \{1, 4\}$ and $Y_2 = \{2, 3\}$. The group $\text{Aut}(Q, C|_Q)$ is $S_2(4)$ containing the permutations (1)(2)(3)(4) and (14)(23). The groups $H_1 = S_3$ and $H_2 = S_2$. Hence, the effective NMR group of the NMR graph in Fig. 6 is $S_2[S_3, S_2]$. The order of this group is $2 \times 6^2 \times 2^2 = 288$. If we include all the interactions (including the non-nearest-neighbor interactions), the NMR graph modifies to the one shown in Fig. 7. In this case, the NMR group is $E[S_8, S_4]$ which is isomorphic to $S_8 \times S_4$. The order of this group is $6!4! = 17280$. Thus one can see that the effect of inclusion or exclusion of various types of interactions on the NMR group using this simple and elegant graph theoretical technique.

C. NMR groups at low temperature

At very low temperature, molecules are essentially rigid and, therefore, no longer there will be high permutational symmetry in the NMR spin Hamiltonian. In this section we try to throw light on the effect of non-rigidity on the NMR groups. Consider ^{12}C -propane at low temperature. The point group of rigid propane molecule is C_{2v} . To find the classes of magnetically equivalent nuclei one constructs the cycle index of the group C_{2v} acting on the eight protons of ^{12}C -propane. The cycle index can be seen to be

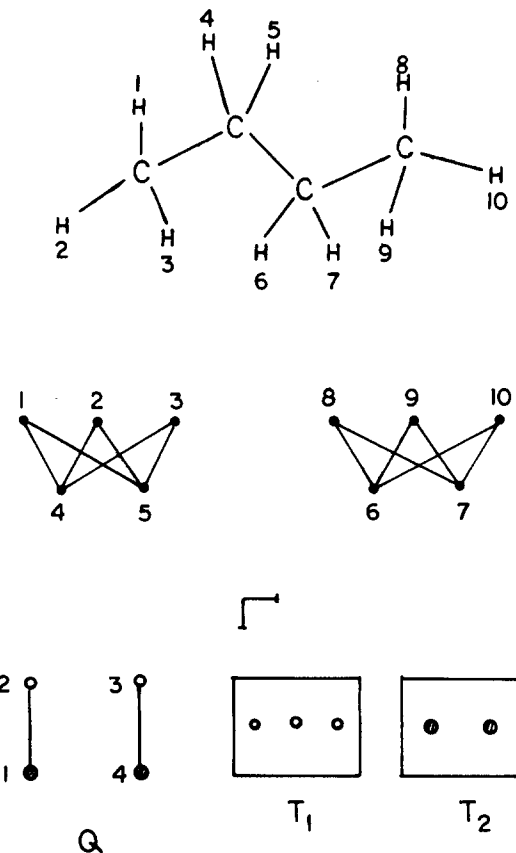


FIG. 6. Effective NMR graph Γ of butane (^{12}C) within the spirit of nearest-neighbor interactions. The quotient graph Q and the types T_1 and T_2 are also shown.

TABLE III. Character table of the NMR group of 2 methylbutane.

Conjugacy class order	1	6	4	9	4	12	6	12	18	3	18	12	27	12	36	18	36	54	2	12	8	18	8	24	12	24	36
Γ_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	+1	-1	-1	-1	1	1	1	1	1	1	-1	-1	-1	1	1	1	1	1	1	-1	-1	-1
Γ_3	1	-1	1	1	1	-1	-1	-1	-1	1	-1	1	1	1	-1	-1	-1	-1	1	-1	1	1	1	-1	-1	-1	1
Γ_4	1	-1	1	1	1	-1	1	1	-1	1	-1	1	1	1	-1	1	1	-1	1	-1	1	1	1	-1	1	1	-1
Γ_5	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	1	1	1
Γ_6	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	1	1	1	-1	-1	-1
Γ_7	1	-1	1	1	1	-1	-1	-1	-1	1	-1	1	-1	-1	-1	1	1	1	-1	1	-1	1	1	1	-1	-1	1
Γ_8	1	-1	1	1	1	-1	1	1	-1	-1	1	-1	-1	-1	1	-1	-1	1	1	-1	1	1	1	-1	1	1	-1
Γ_9	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_{10}	1	1	1	1	1	1	-1	-1	-1	1	1	1	1	1	1	-1	-1	-1	1	1	1	1	1	1	-1	-1	-1
Γ_{11}	1	-1	1	1	1	-1	-1	-1	-1	1	1	-1	1	1	1	-1	-1	-1	1	1	-1	1	1	1	-1	-1	1
Γ_{12}	1	-1	1	1	1	-1	1	1	-1	1	-1	1	1	1	-1	1	1	-1	1	-1	1	1	1	-1	1	1	-1
Γ_{13}	1	+1	1	1	1	+1	1	1	+1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	+1	1	1	1	+1	1	1	+1
Γ_{14}	1	+1	1	1	1	+1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	+1	1	1	1	+1	-1	-1	-1
Γ_{15}	1	-1	1	1	1	-1	-1	-1	-1	+1	-1	-1	-1	-1	-1	+1	1	1	-1	1	-1	1	1	-1	-1	-1	+1
Γ_{16}	1	-1	1	1	1	-1	1	1	-1	-1	1	-1	-1	-1	1	-1	-1	1	1	-1	1	1	1	-1	1	1	-1
Γ_{17}	2	2	2	2	2	2	2	2	2	0	0	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1	-1	-1	-1
Γ_{18}	2	2	2	2	2	2	-2	-2	-2	0	0	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1	-1	1	1
Γ_{19}	2	-2	2	2	2	-2	-2	-2	-2	0	0	0	0	0	0	0	0	0	0	-1	1	-1	-1	-1	1	1	-1
Γ_{20}	2	-2	2	2	2	-2	2	2	-2	0	0	0	0	0	0	0	0	0	0	-1	1	-1	-1	-1	1	1	-1
Γ_{21}	2	2	2	2	2	2	2	2	2	0	0	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1	-1	-1	-1
Γ_{22}	2	2	2	2	2	2	-2	-2	-2	0	0	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1	-1	1	1
Γ_{23}	2	-2	2	2	2	-2	-2	-2	-2	0	0	0	0	0	0	0	0	0	0	-1	1	-1	-1	-1	1	1	-1
Γ_{24}	2	-2	2	2	2	-2	2	2	-2	0	0	0	0	0	0	0	0	0	0	-1	1	-1	-1	-1	1	-1	-1
Γ_{25}	2	0	2	-2	2	0	0	0	0	0	2	0	-2	2	0	0	0	0	0	2	0	2	-2	2	0	0	0
Γ_{26}	2	0	2	-2	2	0	0	0	0	-2	0	-2	2	-2	0	0	0	0	0	2	0	2	-2	2	0	0	0
Γ_{27}	2	0	2	-2	2	0	0	0	0	2	0	2	-2	2	0	0	0	0	0	2	0	2	-2	2	0	0	0
Γ_{28}	2	0	2	-2	2	0	0	0	0	-2	0	-2	2	-2	0	0	0	0	0	2	0	2	-2	2	0	0	0
Γ_{29}	4	0	4	-4	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-2	0	-2	2	-2	0	0	0
Γ_{30}	4	0	4	-4	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-2	0	-2	2	-2	0	0	0
Γ_{31}	4	0	-2	0	1	0	2	-1	0	4	0	-2	0	1	0	2	-1	0	4	0	-2	0	1	0	2	-1	0
Γ_{32}	4	0	-2	0	1	0	2	-1	0	4	0	-2	0	1	0	2	-1	0	4	0	-2	0	1	0	2	-1	0
Γ_{33}	4	0	-2	0	1	0	2	-1	0	4	0	-2	0	1	0	2	-1	0	4	0	-2	0	1	0	2	-1	0
Γ_{34}	4	0	-2	0	1	0	2	-1	0	4	0	-2	0	1	0	2	-1	0	4	0	-2	0	1	0	2	-1	0
Γ_{35}	4	0	-2	0	1	0	-2	1	0	4	0	-2	0	1	0	-2	1	0	4	0	-2	0	1	0	-2	1	0
Γ_{36}	4	0	-2	0	1	0	-2	1	0	4	0	-2	0	1	0	-2	1	0	4	0	-2	0	1	0	-2	1	0
Γ_{37}	4	0	-2	0	1	0	-2	1	0	4	0	-2	0	1	0	-2	1	0	4	0	-2	0	1	0	-2	1	0
Γ_{38}	4	0	-2	0	1	0	-2	1	0	4	0	-2	0	1	0	-2	1	0	4	0	-2	0	1	0	-2	1	0
Γ_{39}	4	2	1	0	-2	-1	0	0	0	4	2	1	0	-2	-1	0	0	0	4	2	1	0	-2	-1	0	0	0
Γ_{40}	4	2	1	0	-2	-1	0	0	0	4	2	1	0	-2	-1	0	0	0	4	2	1	0	-2	-1	0	0	0
Γ_{41}	4	2	1	0	-2	-1	0	0	0	4	2	1	0	-2	-1	0	0	0	4	2	1	0	-2	-1	0	0	0
Γ_{42}	4	2	1	0	-2	-1	0	0	0	4	2	1	0	-2	-1	0	0	0	4	2	1	0	-2	-1	0	0	0
Γ_{43}	4	-2	1	0	-2	1	0	0	0	4	-2	1	0	-2	1	0	0	0	4	-2	1	0	-2	1	0	0	0
Γ_{44}	4	-2	1	0	-2	1	0	0	0	4	-2	1	0	-2	1	0	0	0	4	-2	1	0	-2	1	0	0	0
Γ_{45}	4	-2	1	0	-2	1	0	0	0	4	-2	1	0	-2	1	0	0	0	4	-2	1	0	-2	1	0	0	0
Γ_{46}	4	-2	1	0	-2	1	0	0	0	4	-2	1	0	-2	1	0	0	0	4	-2	1	0	-2	1	0	0	0
Γ_{47}	8	0	-4	0	2	0	4	-2	0	0	0	0	0	0	0	0	0	0	0	-4	0	2	0	-1	0	-2	1
Γ_{48}	8	0	-4	0	2	0	4	-2	0	0	0	0	0	0	0	0	0	0	0	-4	0	2	0	-1	0	-2	1
Γ_{49}	8	0	-4	0	2	0	4	-2	0	0	0	0	0	0	0	0	0	0	0	-4	0	2	0	-1	0	-2	1
Γ_{50}	8	0	-4	0	2	0	4	-2	0	0	0	0	0	0	0	0	0	0	0	-4	0	2	0	-1	0	-2	1
Γ_{51}	8	4	2	0	-4	-2	0	0	0	0	0	0	0	0	0	0	0	0	0	-4	-2	-1	0	2	1	0	0
Γ_{52}	8	4	2	0	-4	-2	0	0	0	0	0	0	0	0	0	0	0	0	0	-4	-2	-1	0	2	1	0	0
Γ_{53}	8	-4	2	0	-4	2	0	0	0	0	0	0	0	0	0	0	0	0	0	-4	2	-1	0	2	-1	0	0
Γ_{54}	8	-4	2	0	-4	2	0	0	0	0	0	0	0	0	0	0	0	0	0	-4	2	-1	0	2	-1	0	0

$$P_G = \frac{1}{4}(S_1^8 + 2S_1^2 S_2^3 + S_2^4) \quad (7)$$

The coefficient of $\alpha_1^7 \alpha_2$ obtained from the above expression by replacing every S_k with $\alpha_1^k + \alpha_2^k$ is

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

The three classes are $C_1 = \{1, 6\}$, $C_2 = \{4, 5\}$, and $C_3 = \{2, 3, 8, 7\}$. Now one can construct the NMR graph and

its quotient graph successively. The vertices of Q are partitioned into the Y sets, $Y_1 = \{1, 5\}$, $Y_2 = \{2, 6\}$, and $Y_3 = \{3\}$. The graphs, thus constructed are shown in Fig. 8. The automorphism group of Q preserving the coupling matrix restricted to Q is $S_2(5)$ which contains the permutations (1)(2)(3)(4)(5) and (15)(24)(3). The groups H_1 , H_2 , and H_3 are E , S_2 , and S_2 , respectively. Hence, the NMR group of propane at low temperature is the generalized wreath product $S_2[E, S_2, S_2]$. The or-

TABLE III (Continued)

Conjugacy class order	1	6	4	9	4	12	6	12	18	3	18	12	27	12	36	18	36	54	2	12	8	18	8	24	12	24	36
Γ_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	1	-1	-1	-1	1	1	1	1	1	1	-1	-1	-1	1	1	1	1	1	1	-1	-1	-1
Γ_3	1	-1	1	1	1	-1	-1	-1	1	1	-1	1	1	1	1	-1	-1	-1	1	+1	-1	1	1	1	-1	-1	-1
Γ_4	1	-1	1	1	1	-1	1	1	-1	1	-1	1	1	1	1	-1	1	1	-1	+1	-1	+1	1	1	-1	1	-1
Γ_5	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	1	1	1
Γ_6	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	1	1	1	-1	-1	-1
Γ_7	1	-1	1	1	1	-1	-1	-1	1	-1	1	-1	-1	-1	1	1	1	1	-1	1	-1	1	1	1	-1	-1	-1
Γ_8	1	-1	1	1	1	-1	1	1	-1	-1	1	-1	-1	-1	1	-1	-1	1	1	-1	1	1	1	1	-1	1	-1
Γ_9	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
Γ_{10}	-1	-1	-1	-1	-1	-1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1	-1	-1	-1	-1	-1	-1	-1	1	1
Γ_{11}	-1	1	-1	-1	-1	1	1	1	-1	-1	1	-1	-1	-1	1	1	1	-1	-1	1	-1	-1	-1	1	1	1	-1
Γ_{12}	-1	1	-1	-1	-1	1	-1	-1	1	-1	+1	-1	-1	-1	+1	-1	-1	+1	-1	1	-1	-1	-1	1	-1	-1	1
Γ_{13}	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	+1	1	1	1	+1	1	1	+1	-1	-1	-1	-1	-1	-1	-1	-1	-1
Γ_{14}	-1	-1	-1	-1	-1	-1	1	1	+1	+1	1	+1	+1	+1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	+1
Γ_{15}	-1	+1	-1	-1	-1	+1	+1	1	-1	+1	-1	+1	+1	+1	-1	-1	-1	1	-1	1	-1	-1	-1	1	+1	+1	-1
Γ_{16}	-1	1	-1	-1	-1	1	-1	-1	1	1	-1	1	1	1	-1	1	1	-1	-1	1	-1	-1	-1	1	-1	-1	1
Γ_{17}	2	2	2	2	2	2	2	2	2	0	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1	-1	-1	-1	-1
Γ_{18}	2	2	2	2	2	2	-2	-2	-2	0	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1	-1	1	1	1
Γ_{19}	2	-2	2	2	2	-2	-2	-2	2	0	0	0	0	0	0	0	0	0	-1	1	-1	-1	-1	1	1	1	-1
Γ_{20}	2	-2	2	2	2	-2	2	2	-2	0	0	0	0	0	0	0	0	0	-1	1	-1	-1	-1	1	-1	-1	1
Γ_{21}	-2	-2	-2	-2	-2	-2	-2	-2	-2	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1
Γ_{22}	-2	-2	-2	-2	-2	-2	2	2	2	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	-1	-1	-1
Γ_{23}	-2	2	-2	-2	-2	2	2	2	-2	0	0	0	0	0	0	0	0	0	1	-1	1	1	1	-1	-1	-1	1
Γ_{24}	-2	2	-2	-2	-2	2	-2	-2	2	0	0	0	0	0	0	0	0	0	1	-1	1	1	1	-1	-1	-1	1
Γ_{25}	2	0	2	-2	2	0	0	0	0	2	0	2	-2	2	0	0	0	0	2	0	2	-2	2	0	0	0	0
Γ_{26}	2	0	2	-2	2	0	0	0	0	-2	0	-2	2	-2	0	0	0	0	2	0	2	-2	2	0	0	0	0
Γ_{27}	-2	0	-2	2	-2	0	0	0	0	-2	0	-2	2	-2	0	0	0	0	-2	0	-2	2	-2	0	0	0	0
Γ_{28}	-2	0	-2	2	-2	0	0	0	0	2	0	2	-2	2	0	0	0	0	-2	0	-2	2	-2	0	0	0	0
Γ_{29}	+4	0	4	-4	4	0	0	0	0	0	0	0	0	0	0	0	0	0	-2	0	-2	2	-2	0	0	0	0
Γ_{30}	-4	0	-4	4	-4	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	2	-2	2	0	0	0	0
Γ_{31}	4	0	-2	0	1	0	2	-1	0	4	0	-2	0	1	0	2	-1	0	4	0	-2	0	1	0	2	-1	0
Γ_{32}	4	0	-2	0	1	0	2	-1	0	-4	0	2	0	-1	0	-2	1	0	4	0	-2	0	1	0	2	-1	0
Γ_{33}	-4	0	2	0	-1	0	-2	1	0	-4	0	2	0	-1	0	-2	1	0	-4	0	2	0	-1	0	-2	1	0
Γ_{34}	-4	0	2	0	-1	0	-2	1	0	4	0	-2	0	1	0	2	-1	0	-4	0	2	0	-1	0	-2	1	0
Γ_{35}	4	0	-2	0	1	0	-2	1	0	4	0	-2	0	1	0	-2	1	0	4	0	-2	0	1	0	-2	1	0
Γ_{36}	4	0	-2	0	1	0	-2	1	0	-4	0	2	0	-1	0	2	-1	0	4	0	-2	0	1	0	-2	1	0
Γ_{37}	-4	0	2	0	-1	0	2	-1	0	-4	0	2	0	-1	0	2	-1	0	-4	0	2	0	-1	0	2	-1	0
Γ_{38}	-4	0	2	0	-1	0	2	-1	0	4	0	-2	0	1	0	-2	1	0	-4	0	2	0	-1	0	2	-1	0
Γ_{39}	4	2	1	0	-2	-1	0	0	0	4	2	1	0	-2	-1	0	0	0	4	2	1	0	-2	-1	0	0	0
Γ_{40}	4	2	1	0	-2	-1	0	0	0	-4	-2	-1	0	2	1	0	0	0	4	2	1	0	-2	-1	0	0	0
Γ_{41}	-4	-2	-1	0	2	1	0	0	0	-4	-2	-1	0	2	1	0	0	0	-4	-2	-1	0	2	1	0	0	0
Γ_{42}	-4	-2	-1	0	2	1	0	0	0	4	2	1	0	-2	-1	0	0	0	-4	-2	-1	0	2	1	0	0	0
Γ_{43}	4	-2	1	0	-2	1	0	0	0	4	-2	1	0	-2	1	0	0	0	4	-2	1	0	-2	1	0	0	0
Γ_{44}	4	-2	1	0	-2	1	0	0	0	-4	2	-1	0	2	-1	0	0	0	4	-2	1	0	-2	1	0	0	0
Γ_{45}	-4	2	-1	0	2	-1	0	0	0	-4	2	-1	0	2	-1	0	0	0	-4	+2	-1	0	2	-1	0	0	0
Γ_{46}	-4	2	-1	0	2	-1	0	0	0	4	-2	1	0	-2	1	0	0	0	-4	2	-1	0	2	-1	0	0	0
Γ_{47}	8	0	-4	0	2	0	4	-2	0	0	0	0	0	0	0	0	0	0	-4	0	2	0	-1	0	-2	1	0
Γ_{48}	-8	0	4	0	-2	0	-4	2	0	0	0	0	0	0	0	0	0	0	4	0	-2	0	1	0	2	-1	0
Γ_{49}	8	0	-4	0	2	0	-4	2	0	0	0	0	0	0	0	0	0	0	-4	0	2	0	-1	0	2	-1	0
Γ_{50}	-8	0	4	0	-2	0	4	-2	0	0	0	0	0	0	0	0	0	0	4	0	-2	0	1	0	-2	1	0
Γ_{51}	8	4	2	0	-4	-2	0	0	0	0	0	0	0	0	0	0	0	0	-4	-2	-1	0	2	1	0	0	0
Γ_{52}	-8	-4	-2	0	4	2	0	0	0	0	0	0	0	0	0	0	0	0	4	2	1	0	-2	-1	0	0	0
Γ_{53}	8	-4	2	0	-4	2	0	0	0	0	0	0	0	0	0	0	0	0	-4	2	-1	0	2	-1	0	0	0
Γ_{54}	-8	4	-2	0	4	-2	0	0	0	0	0	0	0	0	0	0	0	0	4	-2	1	0	-2	1	0	0	0

der of this group is 16. This group is isomorphic to D_{4h} and, hence, the character table can be readily obtained. It is also interesting to find the effective NMR group of propane at low temperature. The effective NMR graph, the quotient graph, and the various types are shown in Fig. 9. The automorphism group of Q is $\{(1)(2)(3)(4)(5), (15)(24)(3)\}$. The effective NMR group and the NMR graph are the same in this special case.

D. Iterative algorithm for characterizing the automorphism group of the quotient NMR graph

In this section an iterative algorithm is presented for characterizing the automorphism group of the quotient NMR graph. Let us start with a nontrivial example, namely 2, 2, 5, 5 tetramethyl, 3, 3, 4, 4 tetra isopropylhexane whose quotient NMR graph within the spirit of

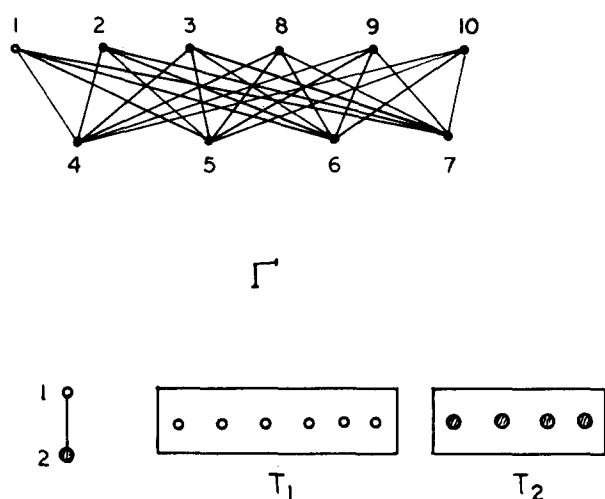


FIG. 7. The effective NMR graph Γ , the quotient graph Q , and the types T_1 and T_2 of butane (^{12}C) when all the nuclear interactions are included.

nearest-neighbor interaction is shown in Fig. 10. Let the vertices of degree greater than 1 be considered as distinguishable from the other vertices of degree 1. Such distinguishable vertices of degree more than 1 can be called roots.

For example, the vertices 2, 3, 11, 12, 4, 15, 18, 5 are the roots of the NMR quotient graph shown in Fig. 10. The vertices of degree 1 together with their edges to the root can be called the corresponding types. Let Y_i be the set of all roots possessing the same type T_i . Then, the NMR quotient graph Q shown in Fig. 10 can be broken down further in the following sense into types and quotient graph Q_1 shown in Fig. 11. The Y sets are

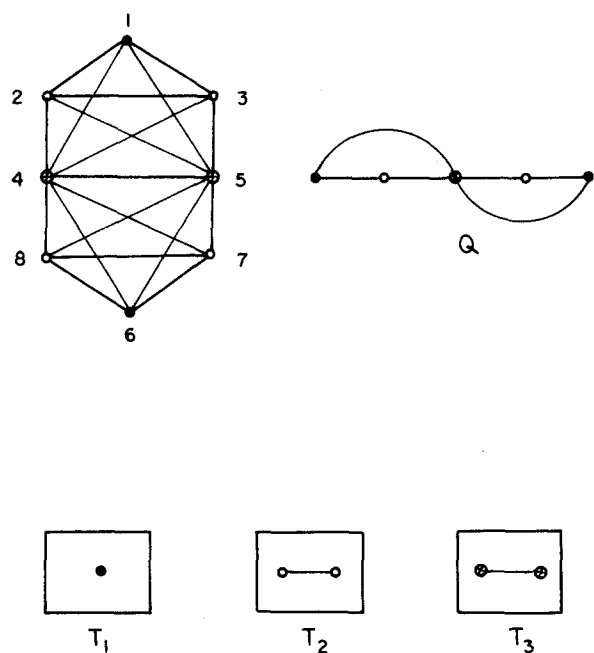


FIG. 8. NMR graph Γ , the quotient graph Q , and the types T_1 , T_2 , and T_3 of propane (^{12}C) at low temperatures when the molecule is essentially rigid.

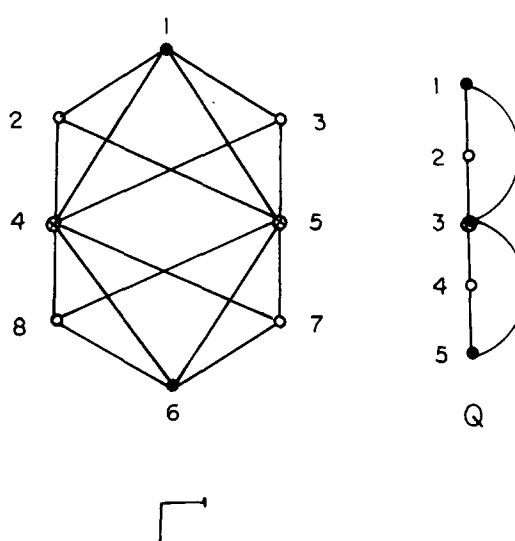


FIG. 9. Effective NMR graph, its quotient graph and types of propane (^{12}C) at low temperatures.

given as follows: $Y_1 = \{2, 3, 6, 7\}$, $Y_2 = \{1, 8\}$, $Y_3 = \{4, 5\}$. The graph Q can be constructed from Q_1 by attaching each vertex of Q_1 contained in the set Y_1 and a copy of the type T_i . Such a product was formulated by the author⁴ in the context of isomer enumeration, and it can be called a root-to-root product. In symbols,

$$Q = Q_1 \cdot (T_{11}, T_{12}, T_{13}) .$$

This process of breaking down the graph Q into quotient graphs and types can be iterated until one obtains a quotient graph Q_n in the n th stage which is unbranched. In the present example, this is achieved at the second iteration. Q_2 and the corresponding types are shown in Fig.

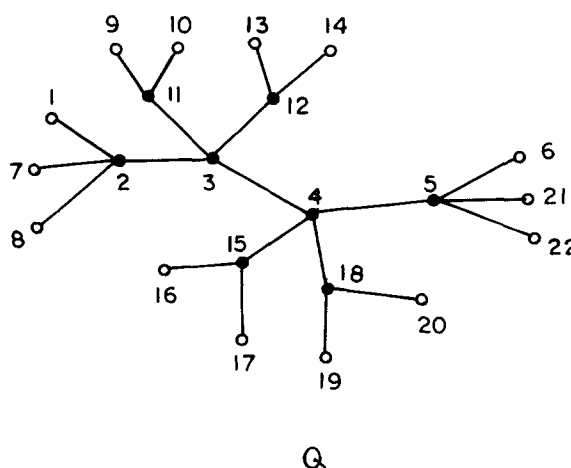


FIG. 10. NMR quotient graph Q of 2,2,5,5-tetramethyl 3,3,4,4-tetra-isopropylhexane in the approximation of nearest-neighbor interaction.

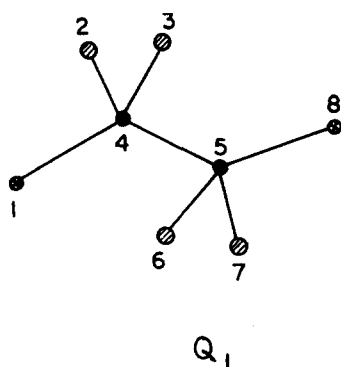


FIG. 11. Root-to-root quotient tree Q_1 of Q and the types T_1 , T_2 , and T_3 . Q can be obtained from Q_1 , T_1 , T_2 , and T_3 by attaching the root of Q_1 in the set Y_i and the root of a copy of the type T_i .

12, with $Y_1 = \{1, 2\}$. The automorphism graph of Q_n , the unbranched graph, is either S_2 or a group containing only the identity. At every stage of iteration, the automorphism group of Q_i , G_i , is given as follows:

$$G_i = G_{i+1}[H_{i+1,1}, H_{i+2,2} \dots],$$

with $G_n = E$ or S_2 . Thus G , the automorphism group of Q is an iterative generalized wreath product. For the present example, $G = (S_2[S_2])[S_2, S_3, E]$.

IV. COMBINATORIAL METHOD OF IDENTIFYING NUCLEAR SPIN SPECIES OF NONRIGID MOLECULES

In this section we offer a combinatorial method of partitioning nuclear spin functions into equivalence classes. Longuet-Higgins⁹ found the nuclear spin species of certain nonrigid molecules like $\text{CH}_3 \cdot \text{BF}_2$, hydrazine, etc. However, Longuet-Higgins did not give a method for partitioning the spin functions into classes. An organized method for this problem is certainly warranted since a molecule containing N protons has 2^N spin distributions. We shall use the combinatorial theorem of Pólya and theorem 1 in Ref. 4.

Let the vertices of the quotient graph Q be partitioned into Y sets. Let G be the automorphism group of the quotient graph Q and let H_i be the group acting on the type T_i . Let us define the generalized cycle index of Q as follows:



FIG. 12. Result of second iteration of the root-to-root product algorithm. Q_1 is the root-to-root product of Q_2 and T_{21} .

$$Z_Q = \frac{1}{|G|} \sum_{g \in G} S_{ijl}^{C_{ijl}(g)}, \quad (9)$$

where $C_{ijl}(g)$ denotes the number of j cycles of g in the set Y_l . The suffix l which is equal to i is retained through all the operations carried out to obtain the cycle index of the generalized wreath product groups in order to preserve the identity of the set from which it is constructed. Let Z_{il} be the cycle index of H_i . Let Z_{ijl} be obtained by replacing every cycle length k by S_{kjl} in Z_{il} . (The first two suffixes on the S variables are the products.) Then the cycle index of the NMR group $G[H_1, H_2, \dots, H_t]$ acting on the protons is

$$Z(G[H_1, H_2, \dots, H_t]) = Z_Q[S_{ijl} - Z_{ijl}]. \quad (10)$$

For a detailed discussion on the cycle index of the generalized wreath product groups, see Ref. 4.

Let D be the set of all protons (or any nucleus possessing magnetic moment). Let R be a set representing nuclear spin states of the elements in D . For instance, a proton can have two spin states, namely, α or β . To each spin state in R , let us assign a weight. A spin distribution of the nuclei in the set D is an assignment of possible spin states in R to each nucleus in the set D . Consequently, every spin distribution of nuclei can be envisaged as a mapping from D to R . Two spin distributions are equivalent if the maps which correspond to them are transformable into each other by a permutation of the generalized wreath product. Hence, spin distributions that are equivalent belong to the same class. Thus the generalized wreath product divides the spin distributions into equivalence classes. The number of classes of spin distributions is given by

$$N = Z(G[H_1, H_2, \dots, H_t])(S_{1k} - |R|). \quad (11)$$

Let the weight assigned to an element $r_i \in R$ which is an image of an element in Y_i be α_{ii} . Then a generating function for the classes of spin distributions is as follows:

$$F = Z(G[H_1, H_2, \dots, H_t]) \left[S_{1k} - \sum_i \alpha_{ii}^k \right]. \quad (12)$$

By way of illustration, consider the nonrigid propane. The Y sets are $Y_1 = \{1, 2, 3, 6, 7, 8\}$ and $Y_2 = \{4, 5\}$. The cycle index of the corresponding generalized wreath product is

$$\begin{aligned} Z(S_2[S_3, S_2]) = & \frac{1}{144} [S_{11}^6 S_{21}^2 + 4 S_{11}^3 S_{13} S_{21}^2 + 12 S_{11} S_{12} S_{13} S_{21}^2 + 6 S_{11}^4 S_{12} S_{21}^2 + 4 S_{13}^2 S_{21}^2 + 9 S_{11}^2 S_{12}^2 S_{21}^2 + S_{11}^6 S_{22} \\ & + 4 S_{11}^3 S_{13} S_{22} + 12 S_{11} S_{12} S_{13} S_{22} + 6 S_{11}^4 S_{12} S_{22} + 4 S_{13}^2 S_{22} + 9 S_{11}^2 S_{12}^2 S_{22} + 6 S_{21}^3 S_{12}^2 + 12 S_{21}^2 S_{16} \\ & + 18 S_{21}^2 S_{12} S_{14} + 6 S_{12}^3 S_{22} + 12 S_{22} S_{16} + 18 S_{22} S_{14} S_{12}] \end{aligned} \quad (13)$$

Hence, the number of classes of spin distribution is

$$N = \frac{1}{144} [2^8 + 4 \times 2^6 + 12 \times 2^5 + 6 \times 2^7 + 4 \times 2^4 + 9 \times 2^6 + 2 \times 2^6 + 4 \times 2^3 \times 2 \times 2 + 12 \times 2^4 + 6 \times 2^4 \times 2^2 + 4 \times 2^2 \times 2 + 9 \times 2^2 \times 2^2 \times 2 + 6 \times 2^2 \times 2^3 + 12 \times 2^2 \times 2 + 18 \times 2^2 \times 2 \times 2 + 6 \times 2 \times 2^3 + 12 \times 2^2 + 18 \times 2^3] = 30. \quad (14)$$

Let α_i be the weight associated with the spin state α whose preimage is an element in the set Y_i . Similarly let β_i be the weight assigned to the spin state β whose preimage is an element in the set Y_i . Then replacing S_{ik} with $\alpha_i^k + \beta_i^k$, we obtain the following results. Let $P_1(\alpha_1, \beta_1)$ be

$$P_1(\alpha_1, \beta_1) = (\alpha_1 + \beta_1)^6 + 4(\alpha_1 + \beta_1)^3(\alpha_1^3 + \beta_1^3) + 12(\alpha_1 + \beta_1)(\alpha_1^2 + \beta_1^2)(\alpha_1^3 + \beta_1^3) + 6(\alpha_1 + \beta_1)^4(\alpha_1^2 + \beta_1^2) + 4(\alpha_1^3 + \beta_1^3)^2 + 9(\alpha_1 + \beta_1)^2(\alpha_1^2 + \beta_1^2)^2. \quad (15)$$

Let $P_2(\alpha_1, \beta_1)$ be

$$P_2(\alpha_1, \beta_1) = (\alpha_1^2 + \beta_1^2)^3 + 2(\alpha_1^6 + \beta_1^6) + 3(\alpha_1^2 + \beta_1^2)(\alpha_1^4 + \beta_1^4). \quad (16)$$

Then the generating function for the classes of spin distributions of propane is given by

$$F = \frac{1}{144} [P_1(\alpha_1, \beta_1)(\alpha_2 + \beta_2)^2 + (\alpha_2^2 + \beta_2^2)P_1(\alpha_1, \beta_1) + 6(\alpha_2 + \beta_2)^2P_2(\alpha_1, \beta_1) + 6(\alpha_2^2 + \beta_2^2)P_2(\alpha_1, \beta_1)] \quad (17)$$

This, on simplification, yields

$$F = \alpha_1^6 \alpha_2^2 + \alpha_1^5 \beta_1 \alpha_2^2 + 2\alpha_1^4 \beta_1^2 \alpha_2^2 + 2\alpha_1^3 \beta_1^3 \alpha_2^2 + 2\alpha_1^2 \beta_1^4 \alpha_2^2 + \alpha_1 \beta_1^5 \alpha_2^2 + \beta_1^6 \alpha_2^2 + \alpha_1^6 \alpha_2 \beta_2 + \alpha_1^5 \beta_1 \alpha_2 \beta_2 + 2\alpha_1^4 \beta_1^2 \alpha_2 \beta_2 + 2\alpha_1^3 \beta_1^3 \alpha_2 \beta_2 + 2\alpha_1^2 \beta_1^4 \alpha_2 \beta_2 + \alpha_1 \beta_1^5 \alpha_2 \beta_2 + \beta_1^6 \alpha_2 \beta_2 + \alpha_1^6 \beta_2^2 + \alpha_1^5 \beta_1 \beta_2^2 + 2\alpha_1^4 \beta_1^2 \beta_2^2 + 2\alpha_1^3 \beta_1^3 \beta_2^2 + 2\alpha_1^2 \beta_1^4 \beta_2^2 + \alpha_1 \beta_1^5 \beta_2^2 + \beta_1^6 \beta_2^2. \quad (18)$$

When the group acting on the set D contains only the identity, the generating function corresponds to the possible spin distributions (not the equivalence classes of spin distributions). This is trivially obtained and can be seen to be

$$F' = (\alpha_1 + \beta_1)^6 (\alpha_2 + \beta_2)^2. \quad (19)$$

This expression on simplification reduces to

$$F' = \alpha_1^6 \alpha_2^2 + 6\alpha_1^5 \beta_1 \alpha_2^2 + 15\alpha_1^4 \beta_1^2 \alpha_2^2 + 20\alpha_1^3 \beta_1^3 \alpha_2^2 + 15\alpha_1^2 \beta_1^4 \alpha_2^2 + 6\alpha_1 \beta_1^5 \alpha_2^2 + \beta_1^6 \alpha_2^2 + 2\alpha_1^6 \alpha_2 \beta_2 + 12\alpha_1^5 \beta_1 \alpha_2 \beta_2 + 30\alpha_1^4 \beta_1^2 \alpha_2 \beta_2 + 40\alpha_1^3 \beta_1^3 \alpha_2 \beta_2 + 30\alpha_1^2 \beta_1^4 \alpha_2 \beta_2 + 12\alpha_1 \beta_1^5 \alpha_2 \beta_2 + 2\beta_1^6 \alpha_2 \beta_2 + \alpha_1^6 \beta_2^2 + 6\alpha_1^5 \beta_1 \beta_2^2 + 15\alpha_1^4 \beta_1^2 \beta_2^2 + 20\alpha_1^3 \beta_1^3 \beta_2^2 + 15\alpha_1^2 \beta_1^4 \beta_2^2 + 6\alpha_1 \beta_1^5 \beta_2^2 + \beta_1^6 \beta_2^2. \quad (20)$$

In physical sense F' and F are generating functions for spin distributions and the equivalence classes of spin distributions, respectively. Using the character table of the NMR group of propane obtained in an earlier paper,⁸ (cf. Table IV) each equivalence class of spin distributions (as given by F) can be decomposed into irreducible representations of $S_2[S_3, S_2]$. Using the notation of irreducible representations of $S_2[S_3, S_2]$ shown in Ref. 8 we obtain the symmetry species of the proton nuclear spin functions at high temperature when the molecule is nonrigid. They are shown in Table IV. When one groups the spin functions belonging to the same symmetry species, we obtain the following proton species at high temperature: 9A_1 , 7A_1 , 5A_1 , 3A_1 , 1A_1 , 7A_2 , 5A_2 , 3A_2 , 1A_2 , 5G_1 , 3G_1 , 1G_1 , 5G_2 , 3G_2 , 1G_2 , 5G_3 , 3G_3 , 1G_3 , ${}^7A'_1$, ${}^5A'_1$, ${}^3A'_1$, ${}^1A'_1$, ${}^5G'_1$, ${}^3G'_1$, ${}^1G'_1$, ${}^5G'_2$, ${}^3G'_2$, and ${}^1G'_3$.

V. EFFECT OF NONRIGIDITY ON NUCLEAR SPIN SPECIES AND THE CONSTRUCTION OF COALESCENCE DIAGRAMS

To understand the effect of nonrigidity on nuclear spin species, one has to know the corresponding nuclear spin species when the molecule is rigid. In general, as we shall show here, the effect of nonrigidity is to coalesce the nuclear spin species of the rigid molecule into degenerate spin species belonging to an irreducible representation of higher dimension.

Let us illustrate the effect of nonrigidity on nuclear

spin species using propane (${}^{12}\text{C}$) as an example. As shown earlier (cf. Sec. IIID), the NMR group of propane at low temperature is the generalized wreath product $S_2[E, S_2, S_2]$ with appropriately chosen Y sets (cf. Sec. IIID), and it is isomorphic to D_{4h} . The character table of this group is shown in Table V with appropriate symmetry species. This group $S_2[E, S_2, S_2]$ is a subgroup of the NMR group of propane at high temperature which is $S_2[S_3, S_2]$. The nuclear spin species of propane at high temperature were already found in Sec. IV. Each nuclear spin species of propane at high temperature thus belongs to an irreducible representation of $S_2[S_3, S_2]$. This irreducible representation decomposes into a set of irreducible representations in the subgroup $S_2[E, S_2, S_2]$. To exemplify this concept, consider the species G_2 . The species G_2 has the following character as a reducible representation of $S_2[E, S_2, S_2]$:

D_{4h}	E	(23)	(16)(27)(38)	(16)(2738)	(23)(78)	(45)	(23)(45)	(16)(27)(38)(45)	(2738)(16)(45)	(23)(78)(45)
G_2	4	0	-2	0	0	4	0	-2	0	0

Thus, G_2 as a reducible representation of $S_2[E, S_2, S_2]$ decomposes into the following irreducible representations:

$$G_2 = A_2^+ + B_1^+ + E^+$$

Thus, for example, the nuclear spin species 3G_2 of non-rigid propane will split into species ${}^3A_2^+$, ${}^3B_1^+$, and ${}^3E^+$ at low temperature when the molecule is rigid. Conversely, the nuclear spin species ${}^3A_2^+$, ${}^3B_1^+$, and ${}^3E^+$ of the rigid propane will coalesce into a degenerate species 3G_2 when the molecule becomes nonrigid. In this way the effect of nonrigidity on the nuclear spin species can be found and pictorially represented by a diagram which we shall call the coalescence diagram for the obvious reason. Such a diagram for the molecule propane is shown in Fig. 13. The nuclear spin species at low temperature can also be alternatively obtained by generating a combinatorial

TABLE IV. Symmetry species of propane at high temperature.

Serial no.	Class	M_z	Symmetry species
1	$\alpha\alpha\alpha\alpha\alpha\alpha$	4	A_1
2	$\alpha\alpha\alpha\alpha\alpha\beta$	3	$A_1 + A_2 + G_3$
3	$\alpha\beta\beta\alpha\alpha\alpha$	2	$A_1 + A_2 + G_3$
4	$\alpha\alpha\beta\alpha\alpha\beta$	2	$A_1 + G_1 + G_3$
5	$\alpha\alpha\alpha\alpha\beta\beta\beta$	1	$A_1 + A_2$
6	$\alpha\alpha\beta\alpha\alpha\beta\beta$	1	$A_1 + A_2 + G_1 + G_2 + 2G_3$
7	$\beta\alpha\alpha\alpha\beta\beta\beta$	0	$A_1 + A_2 + G_3$
8	$\beta\beta\alpha\alpha\beta\beta\alpha$	0	$A_1 + G_1 + G_3$
9	$\beta\beta\beta\alpha\alpha\beta\beta\alpha$	-1	$A_1 + A_2 + G_3$
10	$\beta\beta\beta\alpha\alpha\beta\beta\beta$	-2	A_1
11	$\alpha\alpha\alpha\alpha\beta\alpha\alpha\alpha$	3	$A_1 + A_1'$
12	$\alpha\alpha\alpha\alpha\beta\alpha\alpha\beta$	2	$A_1 + A_2 + G_3 + A_1' + A_2' + G_3'$
13	$\alpha\beta\beta\alpha\beta\alpha\alpha\alpha$	1	$A_1 + A_2 + G_3 + A_1' + A_2' + G_3'$
14	$\alpha\alpha\beta\alpha\beta\alpha\alpha\beta$	1	$A_1 + G_1 + G_3 + A_1' + G_1' + G_3'$
15	$\alpha\alpha\alpha\alpha\beta\beta\beta\beta$	0	$A_1 + A_2 + A_1' + A_2'$
16	$\alpha\alpha\beta\alpha\beta\alpha\beta\beta$	0	$A_1 + A_2 + G_1 + G_2 + 2G_3 + A_1' + A_2' + G_1' + G_2' + 2G_3'$
17	$\beta\alpha\alpha\alpha\beta\beta\beta\beta$	-1	$A_1 + A_2 + G_3 + A_1' + A_2' + G_3'$
18	$\beta\beta\alpha\alpha\beta\beta\beta\alpha$	-1	$A_1 + G_1 + G_3 + A_1' + G_1' + G_3'$
19	$\beta\beta\beta\alpha\beta\beta\beta\alpha$	-2	$A_1 + A_2 + G_3 + A_1' + A_2' + G_3'$
20	$\beta\beta\beta\alpha\beta\beta\beta\beta$	-3	$A_1 + A_1'$
21	$\alpha\alpha\alpha\beta\beta\alpha\alpha\alpha$	2	A_1
22	$\alpha\alpha\alpha\beta\beta\alpha\alpha\beta$	1	$A_1 + A_2 + G_3$
23	$\alpha\beta\beta\beta\beta\alpha\alpha\alpha$	0	$A_1 + A_2 + G_3$
24	$\alpha\alpha\beta\beta\beta\alpha\alpha\beta$	0	$A_1 + G_1 + G_3$
25	$\alpha\alpha\alpha\beta\beta\beta\beta\beta$	-1	$A_1 + A_2$
26	$\alpha\alpha\beta\beta\beta\alpha\beta\beta$	-1	$A_1 + A_2 + G_1 + G_2 + 2G_3$
27	$\beta\alpha\alpha\beta\beta\beta\beta\beta$	-2	$A_1 + A_2 + G_3$
28	$\beta\beta\alpha\beta\beta\beta\beta\alpha$	-2	$A_1 + G_1 + G_3$
29	$\beta\beta\beta\beta\beta\beta\beta\alpha$	-3	$A_1 + A_2 + G_3$
30	$\beta\beta\beta\beta\beta\beta\beta\beta$	-4	A_1

TABLE V. Character table of NMR group of propane at low temperature.

Conjugacy class	E	(23)	(16)(27)(38)	(16)(2738)	(23)(78)	(45)	(23)(45)	(16)(27)(38)(45)	(16)(2738)(45)	(23)(78)(45)
Order	1	2	2	2	1	1	2	2	2	1
A_1^+	1	1	1	1	1	1	1	1	1	1
A_2^+	1	-1	-1	1	1	1	-1	-1	1	1
B_1^+	1	1	-1	-1	1	1	1	-1	-1	1
B_2^+	1	-1	1	-1	1	1	-1	1	-1	1
E^+	2	0	0	0	-2	2	0	0	0	-2
A_1^-	1	1	1	1	1	-1	-1	-1	-1	-1
A_2^-	1	-1	-1	1	1	-1	1	1	-1	-1
B_1^-	1	1	-1	-1	1	-1	-1	1	1	-1
B_2^-	1	-1	1	-1	1	-1	1	-1	1	-1
E^-	2	0	0	0	-2	-2	0	0	0	2

generating function using the group $S[E, S_2, S_2]$ proceeding along the lines of Sec. IV. The splitting of nuclear spin species may be observed experimentally even at room temperature using a dynamic NMR spectrometer.

VI. CONSTRUCTION OF SYMMETRY ADAPTED SPIN FUNCTIONS

The history of employing group theory to simplify nuclear-nuclear spin interactions goes back to Wilson.¹⁰ The composite particle method of treating the nuclear spin interactions of nonrigid molecule is much superior to treating the nuclei as individual species. In this section we show the use of (generalized) wreath products in obtaining the symmetry adapted composite particle spin functions.

Consider the molecule 2,3 dimethylbutane. The quotient NMR graph Q and the various types are shown in Fig. 14. In the composite particle method, the quotient graph is used for constructing the symmetry adapted spin functions instead of the complete NMR graph. The composite particle state of a particle in the set Y_i is determined by the spin state of the particles in the type T_i . For example, the composite particle states of the particles 1, 4, 5, and 6 in Q are determined by the type T_1 (Fig. 14). The type T_1 contains three protons. The symmetry group of this type is S_3 . One finds the equivalence classes of spin distributions of three nuclei in T_1 induced by S_3 . Classifying each equivalence class into a spin species one can see that 4A_1 and 2E are the nuclear spin species of the protons in the type T_1 . These species correspond to a quartet (Q) and a doublet (D), respectively. Thus, each composite particle in the set $Y_1 = \{1, 4, 5, 6\}$ can take two possible states, namely, Q or D . Since the type T_2 contains just a proton, its spin state is either α or β .

To find the symmetry adapted spin functions, first one finds the automorphism group of the quotient graph of

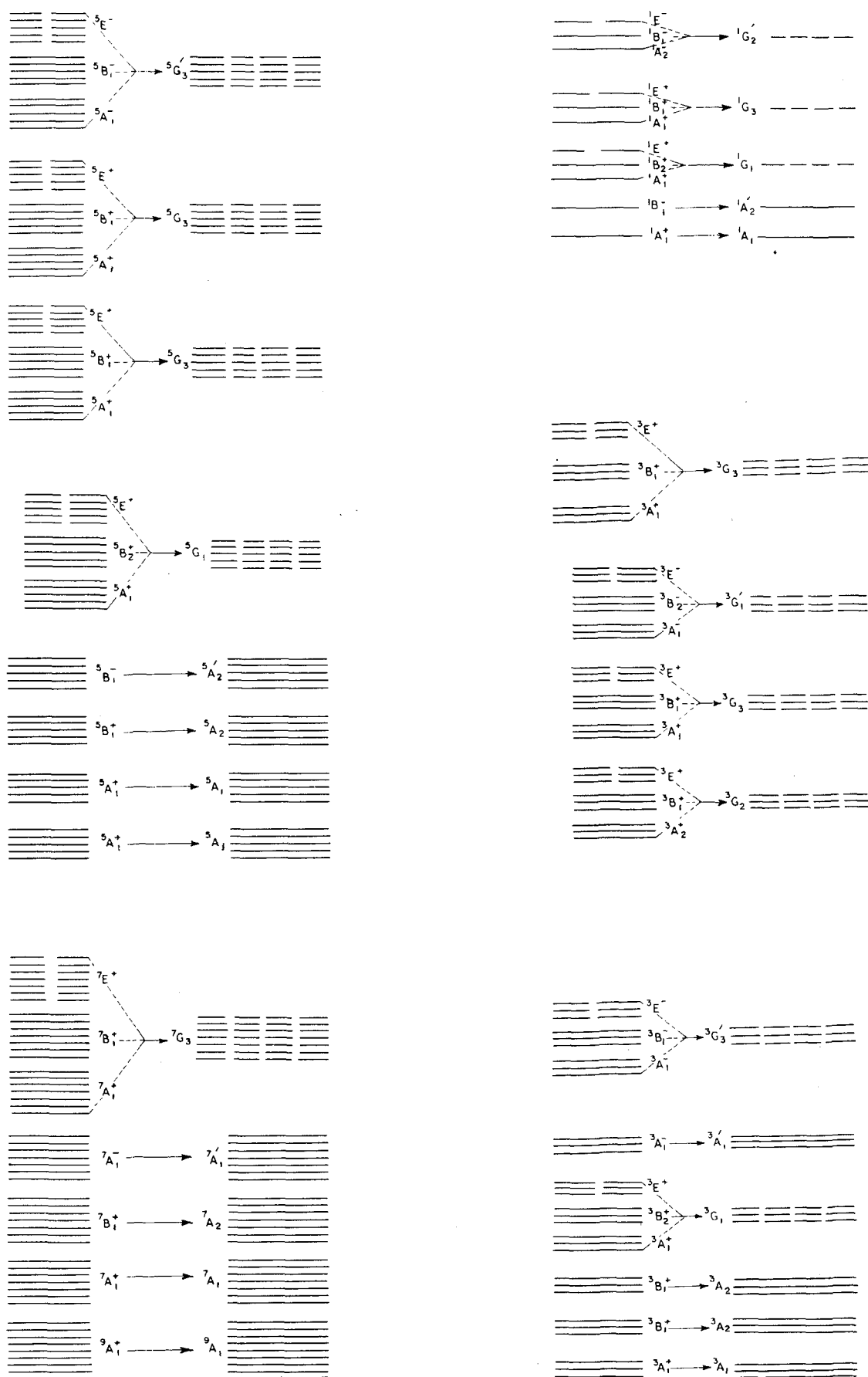


FIG. 13. Coalescence diagram of propane. The spin species on the left-hand side correspond to low temperature, and the spin species on the right-hand side correspond to high temperature.

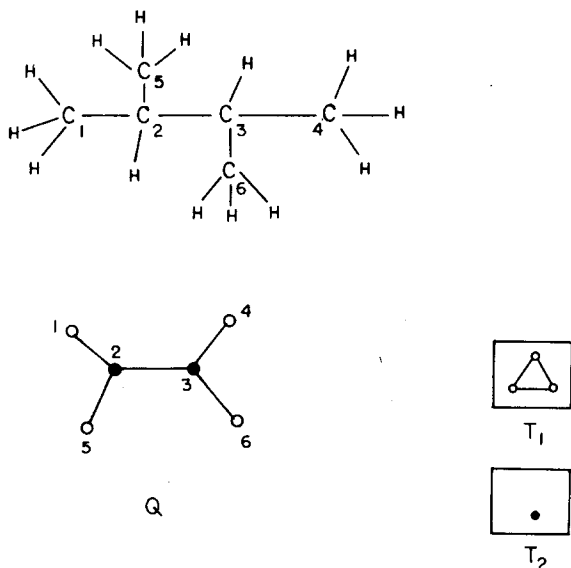


FIG. 14. Quotient NMR graph Q and the various types of the molecule 2,3 dimethylbutane. The symmetry adapted spin functions (SASF) of this molecule are shown in Table VI.

Q . This can be found by the iterative algorithm described earlier (cf. Sec. IIID). The automorphism group of Q can be seen to be $S_2[S_2]$. The automorphism group of the quotient graph partitions the spin distribution of composite particles into equivalence classes. These classes, in turn, can be determined by the use of generating functions described earlier. The cycle index of $S_2[S_2]$ acting on the vertices of Q can be seen to be

$$Z(S_2[S_2]) = \frac{1}{8} [S_{11}^4 S_{21}^2 + 2S_{11}^2 S_{12} S_{21}^2 + S_{12}^2 S_{21}^2 + 2S_{12}^2 S_{22} + 2S_{14} S_{22}] \quad (21)$$

The number of classes of composite particle spin functions is given by

$$N = Z(S_2[S_2])(S_{ik} \rightarrow |R_i|) \quad (22)$$

where $|R_i|$ denotes the number of composite particle states of the particles in the set Y_i . In this example, all the composite particles can take two states and hence

$$N = \frac{1}{8} [2^6 + 2 \times 2^5 + 2^4 + 2 \times 2^3 + 2 \times 2^2] = 21 \quad (23)$$

A generating function for the equivalence classes of composite particle spin distributions can be obtained by replacing S_{1k} with $\alpha_1^k + \beta_1^k$ and S_{2k} with $\alpha_2^k + \beta_2^k$, where α_1 and β_1 are the weights assigned to the states Q and D , respectively; α_2 and β_2 are the weights associated with the states α and β of the particles in the set Y_2 . Thus, the generating function is given by Eq. (24).

$$F = \frac{1}{8} [(\alpha_1 + \beta_1)^4 + 2(\alpha_1 + \beta_1)^2(\alpha_2^2 + \beta_2^2) + (\alpha_2^2 + \beta_2^2)^2] \times (\alpha_2 + \beta_2)^2 + 2\{(\alpha_1^2 + \beta_1^2)^2 + (\alpha_1^4 + \beta_1^4)\}(\alpha_2^2 + \beta_2^2) \quad (24)$$

Equation (24), on simplification, reduces to Eq. (25):

$$F = \alpha_1^4 \alpha_2^2 + \alpha_1^3 \beta_1 \alpha_2^2 + 2\alpha_1^2 \beta_1^2 \alpha_2^2 + \alpha_1 \beta_1^3 \alpha_2^2 + \beta_1^4 \alpha_2^2 + \alpha_1^4 \alpha_2 \beta_2 + 2\alpha_1^3 \beta_1 \alpha_2 \beta_2 + 3\alpha_1^2 \beta_1^2 \alpha_2 \beta_2 + 2\alpha_1 \beta_1^3 \alpha_2 \beta_2 + \beta_1^4 \alpha_2 \beta_2 + \alpha_1^3 \beta_1 \beta_2^2 + 2\alpha_1^2 \beta_1^2 \beta_2^2 + \alpha_1 \beta_1^3 \beta_2^2 + \beta_1^4 \beta_2^2 \quad (25)$$

A generating function for the possible composite particle spin distributions (not the equivalence classes of spin distributions) is obtained by letting the group acting on Q to be the group containing only the identity. It is given by Eq. (26).

$$F' = (\alpha_1 + \beta_1)^4 (\alpha_2 + \beta_2)^2 \quad (26)$$

Equation (26), on simplification, yields Eq. (27):

$$F' = \alpha_1^4 \alpha_2^2 + 4\alpha_1^3 \beta_1 \alpha_2^2 + 6\alpha_1^2 \beta_1^2 \alpha_2^2 + 4\alpha_1 \beta_1^3 \alpha_2^2 + \beta_1^4 \alpha_2^2 + 2\alpha_1^4 \alpha_2 \beta_2 + 8\alpha_1^3 \beta_1 \alpha_2 \beta_2 + 12\alpha_1^2 \beta_1^2 \alpha_2 \beta_2 + 8\alpha_1 \beta_1^3 \alpha_2 \beta_2 + 2\beta_1^4 \alpha_2 \beta_2 + \alpha_1^4 \beta_2^2 + 4\alpha_1^3 \beta_1 \beta_2^2 + 6\alpha_1^2 \beta_1^2 \beta_2^2 + 4\alpha_1 \beta_1^3 \beta_2^2 + \beta_1^4 \beta_2^2 \quad (27)$$

The coefficient of a typical term $\alpha_1^{b_1} \beta_1^{b_2} \alpha_2^{b_3} \beta_2^{b_4}$ in (27) and (25) give the number of composite particle spin functions and the number of classes of composite particle spin functions, respectively, containing b_1 states of the type Q , b_2 states of the type D , b_3 states of the type α and b_4 states of the type β . The spin functions belonging to the same equivalence class transform among themselves under the action of permutations of the automorphism group of the quotient graph. The character table of $S_2[S_2]$ has already been obtained in Ref. 8. (cf. Table II. Let us identify the five representations by the species A_1 , B_1 , E , B_2 , and A_2 in the order shown in Table II of Ref. 8. The symmetry species of each class can be obtained by examining the transformation properties of all the functions in the same class. The reducible representation of all the functions in the same class is then broken into the irreducible representations of the automorphism group of the composite particle graph. The projection operator¹¹ which corresponds to each symmetry species is then applied on the spin functions belonging to that species. Normalizing the resulting function will yield a symmetry adapted composite particle spin function. Table VI shows a representative composite particle spin function in each class, the symmetry species of the functions in that class and the symmetry adapted spin function which corresponds to the respective species.

The original NMR spin Hamiltonian of 2,3 dimethylbutane is of order $2^{14} \times 2^{14}$. This matrix can be reduced to a matrix of order 64×64 by the composite particle method. This matrix in turn, can be blocked in to 40 1×1 matrices and 12 2×2 matrices in the basis of symmetry adapted composite particle spin functions.

In this paper a rigorous graph theoretical approach was developed for characterizing the NMR spin Hamiltonian. This, in turn, made it possible to characterize the NMR group which was shown to be the automorphism group of the NMR graph. We further showed that the NMR graph can be expressed as a generalized composition of a quotient graph and various types. The quotient graph diagrammatically represented the interaction of composite particles. A combinatorial approach was outlined for obtaining a generating function for the equivalence classes of nuclear spin distribution and the effect of nonrigidity on nuclear spin species was described in terms of the coalescence diagram that we introduced here. It was demonstrated that using the automorphism group of the quotient NMR graph, symmetry adapted

TABLE VI. Symmetry adapted spin functions (SASF) of the composite particles of 2,3 dimethylbutane in the group $S_2[S_2]$.

Serial no.	Class	No. of functions in the class	Symmetry species	SASF
1	$DD\beta\beta DD$	1	A_1	$DD\beta\beta DD$
2	$QD\beta\beta DD$	4	A_1	$\frac{1}{2}(QD\beta\beta DD + DQ\beta\beta DD + DD\beta\beta QD + DD\beta\beta DQ)$
			B_1	$\frac{1}{2}(QD\beta\beta DD + DQ\beta\beta DD - DD\beta\beta QD - DD\beta\beta DQ)$
			E	$\begin{cases} (1/\sqrt{2})(QD\beta\beta DD - DQ\beta\beta DD) \\ (1/\sqrt{2})(DD\beta\beta QD - DD\beta\beta DQ) \end{cases}$
3	$QQ\beta\beta DD$	2	A_1	$(1/\sqrt{2})(QQ\beta\beta DD + DD\beta\beta QQ)$
			B_1	$(1/\sqrt{2})(QQ\beta\beta DD - DD\beta\beta QQ)$
4	$QD\beta\beta QD$	4	A_1	$\frac{1}{2}(QD\beta\beta QD + QD\beta\beta DQ + DQ\beta\beta QD + DQ\beta\beta DQ)$
			B_2	$\frac{1}{2}(QD\beta\beta QD + DQ\beta\beta DQ - DQ\beta\beta QD - QD\beta\beta DQ)$
			E	$\begin{cases} (1/\sqrt{2})(QD\beta\beta QD - DQ\beta\beta DQ) \\ (1/\sqrt{2})(QD\beta\beta DQ - DQ\beta\beta QD) \end{cases}$
5	$QQ\beta\beta QD$	4	A_1	$\frac{1}{2}(QQ\beta\beta QD + QQ\beta\beta DQ + QD\beta\beta QQ + DQ\beta\beta QQ)$
			B_1	$\frac{1}{2}(QQ\beta\beta DQ + QQ\beta\beta QD - QD\beta\beta QQ - DQ\beta\beta QQ)$
			E	$\begin{cases} (1/\sqrt{2})(QQ\beta\beta QD - QQ\beta\beta DQ) \\ (1/\sqrt{2})(QD\beta\beta QQ - DQ\beta\beta QQ) \end{cases}$
6	$QQ\beta\beta QQ$	1	A_1	$QQ\beta\beta QQ$
7	$DD\alpha\beta DD$	2	A_1	$(1/\sqrt{2})(DD\alpha\beta DD + DD\beta\alpha DD)$
			B_1	$(1/\sqrt{2})(DD\alpha\beta DD - DD\beta\alpha DD)$
8	$QD\alpha\beta DD$	4	A_1	$\frac{1}{2}(QD\alpha\beta DD + DQ\alpha\beta DD + DD\beta\alpha QD + DD\beta\alpha DQ)$
			B_1	$\frac{1}{2}(QD\alpha\beta DD - DD\beta\alpha QD + QD\alpha\beta DD - DD\beta\alpha DQ)$
			E	$\begin{cases} (1/\sqrt{2})(QD\alpha\beta DD - DQ\alpha\beta DD) \\ (1/\sqrt{2})(DD\beta\alpha QD - DD\beta\alpha DQ) \end{cases}$
9	$DD\alpha\beta QD$	4	A_1	$\frac{1}{2}(DD\alpha\beta QD + DD\alpha\beta DQ + QD\beta\alpha DD + DQ\beta\alpha DD)$
			B_1	$\frac{1}{2}(DD\alpha\beta QD - QD\beta\alpha DD + DD\alpha\beta DQ - DQ\beta\alpha DD)$
			E	$\begin{cases} (1/\sqrt{2})(DD\alpha\beta QD - DD\alpha\beta DQ) \\ (1/\sqrt{2})(QD\beta\alpha DD - DQ\beta\alpha DD) \end{cases}$
10	$QQ\alpha\beta DD$	2	A_1	$(1/\sqrt{2})(QQ\alpha\beta DD + DD\beta\alpha QQ)$
			B_1	$(1/\sqrt{2})(QQ\alpha\beta DD - DD\beta\alpha QQ)$
11	$QD\alpha\beta QD$	8	A_1	$(1/\sqrt{8})(QD\alpha\beta QD + DQ\alpha\beta QD + QD\alpha\beta DQ + DQ\alpha\beta DQ + QD\beta\alpha QD + DQ\beta\alpha DQ + DQ\beta\alpha QD + QD\beta\alpha DQ)$
			A_2	$(1/\sqrt{8})(QD\alpha\beta QD - DQ\alpha\beta QD - QD\alpha\beta DQ + DQ\alpha\beta DQ - QD\beta\alpha QD - DQ\beta\alpha DQ + DQ\beta\alpha QD + QD\beta\alpha DQ)$
			B_1	$(1/\sqrt{8})(QD\alpha\beta QD + DQ\alpha\beta QD + QD\alpha\beta DQ + DQ\alpha\beta DQ - QD\beta\alpha QD - DQ\beta\alpha DQ - DQ\beta\alpha QD - QD\beta\alpha DQ)$
			B_2	$(1/\sqrt{8})(QD\alpha\beta QD - DQ\alpha\beta QD - QD\alpha\beta DQ + DQ\alpha\beta DQ + QD\beta\alpha QD + DQ\beta\alpha DQ - DQ\beta\alpha QD - QD\beta\alpha DQ)$
			E	$\begin{cases} \frac{1}{2}(QD\alpha\beta QD + DQ\alpha\beta QD - DQ\alpha\beta DQ - QD\alpha\beta DQ) \\ \frac{1}{2}(QD\beta\alpha QD + QD\beta\alpha DQ - DQ\beta\alpha DQ - DQ\beta\alpha QD) \end{cases}$
			E	$\begin{cases} \frac{1}{2}(QD\alpha\beta QD + QD\alpha\beta DQ - DQ\alpha\beta DQ - DQ\alpha\beta QD) \\ \frac{1}{2}(QD\beta\alpha QD + DQ\beta\alpha QD - DQ\beta\alpha DQ - QD\beta\alpha DQ) \end{cases}$
			E	$\begin{cases} \frac{1}{2}(QD\alpha\beta QD + QD\alpha\beta DQ - DQ\alpha\beta DQ - DQ\alpha\beta QD) \\ \frac{1}{2}(QD\beta\alpha QD + DQ\beta\alpha QD - DQ\beta\alpha DQ - QD\beta\alpha DQ) \end{cases}$
12	$QQ\beta\alpha DD$	2	A_1	$(1/\sqrt{2})(QQ\beta\alpha DD + DD\alpha\beta QQ)$
			B_1	$(1/\sqrt{2})(QQ\beta\alpha DD - DD\alpha\beta QQ)$

TABLE VI (Continued)

Serial no.	Class	No. of functions in the class	Symmetry species	SASF
13	$QQ\alpha\beta QD$	4	A_1	$\frac{1}{2}(QQ\alpha\beta QD + QQ\alpha\beta DQ + QD\beta\alpha QQ + DQ\beta\alpha QQ)$
			B_1	$\frac{1}{2}(QQ\alpha\beta QD + QQ\alpha\beta DQ - QD\beta\alpha QQ - DQ\beta\alpha QQ)$
			E	$\frac{1}{\sqrt{2}}(QQ\alpha\beta QD - QQ\alpha\beta DQ)$
				$\frac{1}{\sqrt{2}}(QD\beta\alpha QQ - DQ\beta\alpha QQ)$
14	$QQ\beta\alpha QD$	4	A_1	$\frac{1}{2}(QQ\beta\alpha QD + QQ\beta\alpha DQ + QD\alpha\beta QQ + DQ\alpha\beta QQ)$
			B_1	$\frac{1}{2}(QQ\beta\alpha QD + QQ\beta\alpha DQ - QD\alpha\beta QQ - DQ\alpha\beta QQ)$
			E	$\frac{1}{\sqrt{2}}(QQ\beta\alpha QD - QQ\beta\alpha DQ)$
				$\frac{1}{\sqrt{2}}(QD\alpha\beta QQ - DQ\alpha\beta QQ)$
15	$QQ\alpha\beta QQ$	2	A_1	$\frac{1}{\sqrt{2}}(QQ\alpha\beta QQ + QQ\beta\alpha QQ)$
			B_1	$\frac{1}{\sqrt{2}}(QQ\alpha\beta QQ - QQ\beta\alpha QQ)$
16	$DD\alpha\alpha DD$	1	A_1	$DD\alpha\alpha DD$
17	$DQ\alpha\alpha DD$	4	A_1	$\frac{1}{2}(DQ\alpha\alpha DD + QD\alpha\alpha DD + DD\alpha\alpha QD + DD\alpha\alpha DQ)$
			B_1	$\frac{1}{2}(DQ\alpha\alpha DD + QD\alpha\alpha DD - DD\alpha\alpha QD - DD\alpha\alpha DQ)$
			E	$\frac{1}{\sqrt{2}}(DQ\alpha\alpha DD - QD\alpha\alpha DD)$
				$\frac{1}{\sqrt{2}}(DD\alpha\alpha QD - DD\alpha\alpha DQ)$
18	$QQ\alpha\alpha DD$	2	A_1	$\frac{1}{\sqrt{2}}(QQ\alpha\alpha DD + DD\alpha\alpha QQ)$
			B_1	$\frac{1}{\sqrt{2}}(QQ\alpha\alpha DD - DD\alpha\alpha QQ)$
19	$QD\alpha\alpha QD$	4	A_1	$\frac{1}{2}(QD\alpha\alpha QD + DQ\alpha\alpha QD + QD\alpha\alpha DQ + DQ\alpha\alpha DQ)$
			B_2	$\frac{1}{2}(QD\alpha\alpha QD - DQ\alpha\alpha QD - QD\alpha\alpha DQ + DQ\alpha\alpha DQ)$
			E	$\frac{1}{\sqrt{2}}(QD\alpha\alpha QD - DQ\alpha\alpha DQ)$
				$\frac{1}{\sqrt{2}}(DQ\alpha\alpha QD - QD\alpha\alpha DQ)$
20	$QQ\alpha\alpha QD$	4	A_1	$\frac{1}{2}(QQ\alpha\alpha QD + QD\alpha\alpha QD + QD\alpha\alpha QQ + DQ\alpha\alpha QQ)$
			B_1	$\frac{1}{2}(QQ\alpha\alpha QD - QD\alpha\alpha QQ + QD\alpha\alpha DQ - DQ\alpha\alpha QQ)$
			E	$\frac{1}{\sqrt{2}}(QQ\alpha\alpha QD - QD\alpha\alpha DQ)$
				$\frac{1}{\sqrt{2}}(QD\alpha\alpha QQ - DQ\alpha\alpha QQ)$
21	$QQ\alpha\alpha QQ$	1	A_1	$QQ\alpha\alpha QQ$

composite particle spin functions can be constructed and, thus, one can elegantly effect the simplification of NMR computations. Reference 12 describes the effect of non-rigidity on the NMR spectrum using graphical methods.

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