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Operator and algebraic methods for NMR spectroscopy. II. NMR projection operators and spin functions

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We outline double coset and restricted character cycle index methods which generate the equivalence classes of NMR spin functions and the irreducible representations in the representation spanned by spin functions in any equivalence class. Elegant operator methods are developed by which the projection operators of NMR groups can be obtained in terms of the projection operators of composing groups. Thus, the projection operators of NMR groups of many molecules can be obtained without the knowledge of their character tables. Projection operators thus obtained are applied on the set of spin functions in an equivalence class of NMR spin functions (rather than the whole set of spin functions) which are generated by double coset methods to obtain symmetry-adapted NMR spin functions in the composite particle representation. Methods are illustrated with several examples of molecules containing as many as 2^{30} NMR spin functions. The methods developed here are quite general so that they can be applied to NMR of nuclei with multispin states and they do not require the character tables of NMR groups. The techniques outlined here are illustrated with 2, 2, 3, 3-tetramethyl butane for which the symmetry-adapted NMR spin couplings are obtained in the composite particle representation. The NMR Hamiltonian matrix of this molecule which is of order $2^{18} \times 2^{18}$ is factored into $2^6 \times 2^6$ matrix by the composite particle treatment. This is further factored into 8 1×1 matrices and 6 4×4, 4 2×2, and 3 8×8 matrices in the symmetry-adapted basis.

I. INTRODUCTION

A historical survey of applications of group theory to NMR spectroscopy can be found in an earlier paper of the present author[1] in this issue, hereafter to be referred to as I. We laid the basic algebraic foundations for generating the NMR spin species and enumerating the total number of equivalence classes of spin functions. Of course, the enumeration of the number of equivalence classes of nuclei and spin functions is the first step one needs to accomplish, in order to construct symmetry-adapted NMR spin functions in the composite particle representation or in the total representation (for dynamic NMR as a function of temperature). It is not enough if one knows just the number of equivalence classes to explicitly construct the symmetry-adapted NMR spin functions. We actually need to construct these equivalence classes. For this purpose we will outline a double coset technique here. Then one needs to know the irreducible representations contained in an equivalence class so that we can apply the corresponding projection operator on that equivalence class to construct the symmetry-adapted basis sets. We define and use restricted cycle indices (RCCI's) which generate the irreducible representations contained in each equivalence class without having to know the total character of the representation spanned by that class. The projection operators of NMR groups which are expressible as generalized wreath product groups are shown to be obtainable in terms of the projection operators of the composing groups in the generalized wreath product. The methods are illustrated with several examples of molecules containing as many as 2^{30} spin functions.

In Sec. II we develop double coset methods for the construction of equivalence classes of NMR spin functions. Section III develops RCCI (Restricted Character Cycle Index) methods for generating the irreducible representations contained in each equivalence class of spin functions. Section IV describes methods for the projection operators of NMR groups which in turn enable generation of symmetry-adapted spin functions corresponding to the irreducible representations in various equivalence classes. Finally, in Sec. V we give an example to illustrate the various methods by constructing the symmetry-adapted spin functions in the composite particle representation for the molecule 2, 2, 3, 3 tetramethyl butane. Readers are referred to I for the notations used in this paper.

II. DOUBLE COSETS AND NMR SPIN EQUIVALENCE CLASSES

Let n be the total number of nuclei. We know that two spin functions with different weights (cf. Sec. II B of I for the definition of weight of a spin function) can not be equivalent. Suppose the possible spin states of nuclei be k. (For example, $k = 3$ for a deuterium nucleus). Consider only the set F_w of spin functions with the same weight $w = w_1^{b_1} w_2^{b_2} \cdots w_k^{b_k}$, where $b_1, b_2, \ldots, b_k$ are the number of times first, 2nd, $\ldots$, kth spin state occurs in any function in the set F_w. Define the k-fold direct product group $S_{b_1} \times S_{b_2} \times \cdots \times S_{b_k}$ as the label subgroup of S_n and let us denote it as L. Let G be the NMR group which leaves the NMR spin Hamiltonian invariant. Let us consider a spin function f_w^1 as a standard spin function if in this function first b_1 nuclei take the first spin state (whose weight is w_1), the next b_2 nuclei take the second spin state (whose weight is w_2) etc. Then it can be easily seen that any spin function in F_w can be obtained by operating a permutation from S_n on f_w^1. Thus any element in S_n is a generator of spin functions in F_w. For any $s \in S_n$ the set LsG is known as the double coset[7] of L and G in S_n (cf. L is the label subgroup of S_n). G is also in general a subgroup of S_n. In some cases G is S_n itself if all the nuclei are magnetically equivalent. Of course, this is a trivial case and we are interested here

in more general cases. Two elements s_1 and s_2 are in the same double coset if $\exists\, g \in G$ and $l \in L$ such that

$$s_1 = l\, s_2\, g \quad .$$

If s_1 and s_2 are in the same double coset then they generate equivalent NMR spin functions in F_w. The relation defined above can be easily seen to be an equivalence relation. Thus a representative in each equivalence class is generated by an element in the set S of $= \{s_1, s_2, \ldots, s_k\}$ such that

$$S_n = \bigcup_{i=1}^{k} L s_i G, \quad (L s_i G) \cap (L s_j G) = \phi \ , \quad \text{if } i \ne j \ ,$$

where ϕ is the null set. The number of distinct representatives (k) was already enumerated in the earlier paper (I).

The number of elements in any double coset $L s G$ is given as

$$|L s G| = |L|\,|G| / |s^{-1} L s \cap G|$$

$$= |L|\,|G| / |L \cap s G s^{-1}| \ .$$

The number of elements in a double coset, in general, is not equal to the number of spin functions in an equivalence class. This is because two permutations in a double coset may generate the same spin function. Nevertheless, the number of elements in an equivalence class of spin functions corresponding to the double coset $L s G$ is given by

$$\frac{|L s G| \cdot |F_w|}{|S_n|} = \frac{|L s G|\,|F_w|}{n!} \ .$$

Equivalence classes of spin functions are thus generated by the representatives of various double cosets $L s_i G$ and the spin functions in each equivalence class are generated by the action of permutations in each double coset on the standard NMR spin function f_w^1. It is important to know the structure of equivalence classes of NMR spin functions, since two spin functions in different classes will not mix in a symmetry-adapted spin function. Consequently, projection operators need to be applied only on an equivalence class of spin functions rather than on the entire set of NMR spin functions.

III. RESTRICTED CHARACTER CYCLE INDICES (RCCI's) AND SYMMETRY SPECIES IN EQUIVALENCE CLASSES

Each equivalence class of NMR spin functions spans a reducible representation in the NMR group, in general. To obtain the irreducible representations contained in this representation using conventional methods, one needs the character of the representation spanned by the spin functions in the equivalence class of NMR spin functions. This process in turn requires the knowledge of all NMR spin functions in various equivalence classes and their transformation properties. Therefore, the conventional techniques are quite tedious for this purpose. In this section we introduce the concept of RCCI's which are generators of irreducible representations in each equivalence class. Define an RCCI corresponding to an equivalence class C and character χ of an irreducible representation Γ of G as

$$\mathrm{RCCI}^X(C) = \frac{1}{|G|} \sum_{g \in G} \chi(g)\, x_1^{C(b_1)}\, x_2^{C(b_2)} \cdots \ ,$$

where $C(b_1)$, $C(b_2)$ are the number of 1, 2 cycles, etc., generated within the equivalence class C when g is applied on C. It is possible to define such a cycle index restricted to C because NMR functions in two different equivalence classes do not mix by the operation of any g in G. In fact when one collects all the permutations of elements in G that are contained in C, we generate a new group G^1 which is in general a subgroup of G. This is precisely the site symmetry group defined by Flurry[2] when applied appropriately to NMR context. In general, when $|C| \ge n$, where n is the number of nuclei G^1 is isomorphic to G itself.

The number of times an irreducible representation Γ with character χ occurs in C is given by the coefficient of $\alpha_1^{|C|-1} \alpha_2$ in the G. F.$^X(C)$ shown below.

$$\mathrm{G.F.}^X(C) = \mathrm{GCCI}^X(C)(x_k \to \alpha_1^k + \alpha_2^k) \ .$$

Let us illustrate this with ^{19}F NMR of rigid PF$_5$. Let 1, 2, and 3 be equatorial nuclei and 4 and 5 be axial nuclei. Then, e.g., an equivalence class of spin functions whose representative is $\alpha\beta\alpha\alpha\alpha$ contains three spin functions. The NMR group of the rigid PF$_5$ molecule is $S_3 \times S_2$. The RCCI's corresponding to A_1, A_2, and E are shown below. The RCCI's corresponding to other representations are zero indicating that these representations do not appear in this class.

$$\mathrm{RCCI}^{A_1}(C) = \tfrac{1}{12}(2x_1^3 + 4x_3 + 6x_1 x_2) = \tfrac{1}{6}(x_1^3 + 2x_3 + 3x_1 x_2) \ ,$$

$$\mathrm{RCCI}^{A_2}(C) = \tfrac{1}{12}(2x_1^3 + 4x_3 - 6x_1 x_2) = \tfrac{1}{6}(x_1^3 + 2x_3 - 3x_1 x_2) \ ,$$

$$\mathrm{RCCI}^{E}(C) = \tfrac{1}{12}(4x_1^3 - 4x_3) = \tfrac{1}{3}(x_1^3 - x_3) \ .$$

The generating functions corresponding to these representations are shown below.

$$\mathrm{G.F.}^{A_1}(C) = \tfrac{1}{6}[(\alpha_1 + \alpha_2)^3 + 2(\alpha_1^3 + \alpha_2^3) + 3(\alpha_1 + \alpha_2)(\alpha_1^2 + \alpha_2^2)]$$

$$= \alpha_1^3 + \alpha_1^2 \alpha_2 + \alpha_1 \alpha_2^2 + \alpha_2^3 \ ,$$

$$\mathrm{G.F.}^{A_2}(C) = 0 \ ,$$

$$\mathrm{G.F.}^{E}(C) = \tfrac{1}{3}[(\alpha_1 + \alpha_2)^3 - (\alpha_1^3 + \alpha_2^3)] = \alpha_1^2 \alpha_2 + \alpha_1 \alpha_2^2 \ .$$

Collecting the coefficient of $\alpha_1^{|C|-1} \alpha_2 = \alpha_1^2 \alpha_2$ in all representations we immediately infer that the representations spanned by C are

$$\Gamma_C = A_1 + E \ .$$

Thus one can obtain Γ_C without having to know the character of Γ_C.

IV. PROJECTION OPERATORS OF NMR GROUPS

In this section we show that the projection operators of NMR groups when they are wreath or generalized wreath products can be obtained in terms of the projection operators of the composing groups. We outline general methods so that special cases such as direct products of symmetric groups, etc., can be obtained as special cases of the techniques outlined in this section.

First we will outline Williamson's method[3,4] for the projection operators corresponding to characters of

one-dimensional representations (Abelian characters) of wreath products. Recall that D and R are sets of nuclei and spin states, respectively. $F = R^D$ is the set of spin functions (maps from D to R). Let V be a vector space of dimension $|R| = r$ and let $e_1, e_2, \ldots, e_r$ be a standard orthonormal basis of V. With each spin function $f \in F$ we can associate the tensor product

$$e_f = e_{f(1)} \otimes e_{f(2)} \otimes \cdots \otimes e_{f(d)} \, ,$$

where $d = |D|$. For a definition of outer tensor product (or simply outer product) see, e.g., Messiah.[5] The set of all possible such tensors e_f forms the basis for the dth tensor product of V, V^d. For a g in the NMR group G, we can define a permutation operator associated with g denoted as $P(g)$ by its action on e_f:

$$P(g) e_f = e_{gf} = e_{gf(1)} \otimes e_{gf(2)} \otimes \cdots \otimes e_{gf(d)}$$
$$= e_{f(g^{-1}1)} \otimes e_{f(g^{-1}2)} \otimes \cdots \otimes e_{f(g^{-1}d)} \, . \quad (4.1)$$

Let ω be a character of degree 1 (character of a one-dimensional representation). Then a projector on the tensor space V^d can be defined as

$$T_G^\omega = \frac{1}{|G|} \sum_{g \in G} \omega(g) P(g) \, . \quad (4.2)$$

Using the orthogonality property of characters it can be easily seen that T_G is idempotent (i.e., $T_G^2 = T_G$) and hence it is a projection operator. One can define such an operator for a wreath product $G[H]$ corresponding to an Abelian character ω as

$$T_{G[H]} = \frac{1}{|G[H]|} \sum_{l \in G[H]} \omega(l) P(l) \, , \quad (4.3)$$

where $P(l)$ is a permutation operator acting on the tensors in the tensor space V^d. However, to obtain the above operator by obtaining the character for each element l in the wreath product and the corresponding $P(l)$ and summing over all l is quite tedious since the number of elements in wreath products increase exponentially. We outline first a procedure for obtaining $T_{G[H]}^\omega$ in terms of projectors of G and H for one dimensional representations.

Recall that the set D of nuclei can be partitioned into sets of complete magnetic equivalence classes of nuclei. When all the equivalence classes of nuclei have the same number of nuclei, we have the case of wreath products. (When they are different, the group is generalized wreath product.) Since the equivalence class structure is identical we can simply denote an equivalence class by T. H is the permutation group acting on T such that the coupling constants restricted to T are left invariant. Let Q be the NMR diagram obtained by condensing each equivalence class T to a single vertex (composite particle) and G is the NMR group restricted to Q. Then the NMR group of the whole molecule is $G[H]$, and the order of $G[H]$ is $|G||H|^{|Y|}$, where Y is the set of vertices in Q. Recall from Sec. IV that an element in $G[H]$ can be denoted by $(g; \pi)$. Let λ be an Abelian character of H and χ be an Abelian character of G. Then a simple Abelian character of $G[H]$ (note that it is not an induced character) is defined by

$$\omega(g; \pi) = \bar{\lambda}(\pi) \chi(g) \, , \quad (4.4)$$

where

$$\bar{\lambda}(\pi) = \prod_{y \in Y} \lambda[\pi(y)] \, .$$

Note that $\bar{\lambda}$ is the character of $|Y|$-fold direct product of the representation corresponding to λ. Suppose T_H is the projector of λ in H and let $T_{G'}$ be defined as follows:

$$T_{G'}^\chi = \frac{1}{|G|} \sum_{g \in G} \omega(g; e) P(g; e) \, , \quad (4.5)$$

where

$$\omega(g; e) = \bar{\lambda}(e) \chi(g) \, .$$

Williamson[3,4] showed that

$$T_{G[H]}^\omega = T_H^{\bar{\lambda}Y} T_{G'}^\chi \, , \quad (4.6)$$

where H^Y is $|Y|$-fold direct product of H.

Let us illustrate this with an example before we proceed further. Consider the NMR group of the nonrigid hydrazine molecule which is $S_2[S_2]$. In all examples we will take $P(g)$ as simply the permutation representation of g. Consider the one-dimensional representation $([1^2] \# [1^2]) \otimes [2]'$ of this group. Then λ, $\bar{\lambda}$, and χ are the characters of $[1^2]$, $[1^2] \# [1^2]$, and $[2]$, respectively. The projectors corresponding to $[1^2]$, $[1^2] \# [1^2]$ and $[2]'$ are shown below:

$$T_{S_2}^{[1^2]} = \tfrac{1}{2}[e - (12)] \, , \quad (4.7)$$

$$T_{S_2 \times S_2}^{[1^2] \# [1^2]} = \tfrac{1}{4}[e - (12) - (34) + (12)(34)] \, , \quad (4.8)$$

$$T_{S_2}^{[2]'} = \tfrac{1}{2}[e + (13)(24)] \, . \quad (4.9)$$

Thus by Williamson's theorem the projector corresponding to $\Gamma = ([1^2] \# [1^2]) \otimes [2]'$ is

$$T_{S_2[S_2]}^\Gamma = T_{S_2 \times S_2}^{[1^2] \# [1^2]} \cdot T_{S_2}^{[2]'} = \tfrac{1}{8}[e - (12) - (34) + (12)(34)$$
$$+ (13)(24) - (1423) - (1324) + (14)(23)] \, . \quad (4.10)$$

Hence, we obtained the projector of a one-dimensional representation of $S_2[S_2]$ simply by knowing the projectors of S_2.

We will now develop here a method to obtain the projection operators of any representation (not only one-dimensional) in terms of the projectors of the composing group. Let us obtain a more general irreducible matrix representation projector rather than just the character projector. Of course, the character projector can always be obtained by taking the trace of matrix projectors. Nevertheless, matrix projectors are needed especially for higher dimensional representations since character projectors can generate only one component of the symmetry-adapted functions for higher dimensional representations. A matrix projector can be defined in terms of the matrix $\Gamma(g)$ of an irreducible representation Γ corresponding to the operation g in the group G. Such a projector for a group G and irreducible representation Γ can be defined as

$$T_G^\Gamma = \frac{\dim(\Gamma)}{|G|} \sum_{g \in G} \Gamma(g) P(g) \, , \quad (4.11)$$

where $P(g)$ for the present purpose is simply a permutation representation of g. Then we show here that the projectors of generalized wreath products can be ob-

tained in terms of just the projectors of the composing groups. Consider an irreducible representation Γ of $G[H_1, H_2, \ldots, H_t]$ of the form

$$\Gamma = (\#_i F_i^{m_i^*} \otimes F')\uparrow G[H_1, H_2, \ldots, H_t] \ .$$

Let us consider first the case when the inertia group of $\#F_i^{m_i^*}$ is $G[H_1, H_2, \ldots, H_t]$. In this case $\Gamma = (\#_i F_i^{m_i^*} \otimes F')$. Let the projection operator of the representation $F_i^{m_i^*}$ $= F_{i1} \# F_{i2} \# \cdots \# F_{im_i} = F_i^*$, (where $m_i = |Y_i|$) in the group $H_i^{|Y_i|}$ be defined as

$$T^{F_i^*} = \frac{1}{|H_i^{|Y_i|}|} \sum_{h \in H_i^{|Y_i|}} \Gamma(h) P(h) \ . \tag{4.12}$$

Note that the above projector is simply the $|Y_i|$-fold product of the projector of H_i corresponding to a representation F_{ij} with the products of irreducible matrices understood as Kronecker products. Thus $T^{F_i^*}$ can be obtained trivially. The projector corresponding to $\#_i F_i^{m_i^*}$ is also simply the product of various projectors $T^{F_i^*}$.

In symbols,

$$T^\Delta = T^{F_1^*} \cdot T^{F_2^*} \cdots \ , \tag{4.13}$$

where

$$\Delta = \#_i F_i^{m_i^*} \ .$$

Define a new operator $\underline{T^\Delta}$ as the operator obtained by permuting the columns of the matrices in the Kronecker products of the matrices of $F_i^{m_i^*}$ as determined by the action of g^{-1} on the columns. This was illustrated in great details by the present author in the development of the representation theory of these groups in an earlier paper.[6] We will illustrate this procedure with an appropriate example after we complete this discussion. The projector corresponding to F' in the inertia factor group G' is shown below

$$T^{F'} = \frac{1}{|G'|} \sum_{g' \in G'} \Gamma(g') P(g') \ .$$

We then have the following result for the projector of T^Γ

$$T^\Gamma = \underline{T^\Delta} \otimes T^{F'} \ , \tag{4.14}$$

where $\otimes$ stands for inner product. While forming the product of the projectors one takes the inner product of the corresponding representation. We will now illustrate the above procedure with examples. Consider the representation

$$\Gamma_{14} = G_5 = \underline{[2,1]} \# \underline{[2,1]} \# \underline{[2]} \# \underline{[2]} \otimes \underline{[2]}'$$

of the NMR group of butane (cf. Table III of I). For this case $F_{11} = [2,1]$, $F_{12} = [2,1]$, $F_{21} = [2]$, and $F_{22} = [2]$. The projection operators corresponding to these representations are shown below

$$T^{F_{11}} = \frac{2}{6} \left\{ \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} E + \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}(123) \right.$$
$$+ \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}(132) + \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}(13)$$
$$\left. + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}(23) + \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}(12) \right\} \ , \tag{4.15}$$

$$T^{F_{12}} = \frac{2}{6} \left\{ \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} E + \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}(8,9,10) \right.$$
$$+ \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}(8,10,9) + \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}(8,10)$$
$$\left. + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}(9,10) + \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}(8,9) \right\} \ , \tag{4.16}$$

$$T^{F_{21}} = \tfrac{1}{2} [[1]E + [1](45)] \ , \tag{4.17}$$

$$T^{F_{22}} = \tfrac{1}{2} [[1]E + [1](67)] \ . \tag{4.18}$$

The projector corresponding to $[2]'$ is below

$$T^{[2]'} = \tfrac{1}{2} [[1]E + [1](18)(29)(3,10)(46)(57)] \ . \tag{4.19}$$

The projection operator of $\Gamma = \underline{[2,1]} \# \underline{[2,1]} \# \underline{[2]} \# \underline{[2]} \otimes \underline{[2]}'$ is obtained by simply "multiplying" Eqs. (4.15)–(4.19). While multiplying the matrix corresponding to E in $T^{[2]'}$ with the other matrices in Eq. (4.15), etc., one takes the Kronecker product of matrices in Eqs. (4.15)–(4.18). However, when one multiplies the second element of the projector in Eq. (4.19) {i.e., $[1](18)(29)(3,10)(46)(57)$} with elements in the other projector the second and third column of the matrix obtained by Kronecker product of matrices in Eqs. (4.15)–(4.18) need to be permuted. Of course, one can easily multiply the projectors to generate 288 elements of the NMR group of butane and the corresponding matrices. We will only give examples of two terms for the sake of illustration. The permutation $(123)(8,9,10)(45)(67)$ is a term in the projector thus obtained. Let us find the matrix corresponding to this operator in the resulting 4×4 projector. The matrix of this operation is

$$\begin{array}{ccccc} (123) & (8,9,10) & (45) & (67) & E \end{array}$$
$$\left\{ \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} [1] \quad [1] \right\} \otimes [1]'$$

$$= \begin{bmatrix} 1/4 & -\sqrt{3}/4 & -\sqrt{3}/4 & 3/4 \\ \sqrt{3}/4 & 1/4 & -3/4 & -\sqrt{3}/4 \\ \sqrt{3}/4 & -3/4 & 1/4 & -\sqrt{3}/4 \\ 3/4 & +\sqrt{3}/4 & \sqrt{3}/4 & 1/4 \end{bmatrix} (123)(8,9,10)(45)(67) \ . \tag{4.20}$$

Another example that will be considered is the matrix corresponding to $(123)(8,10,9)(18)(29)(3,10)(46)(57)$

$$(123) \qquad\qquad (8,10,9) \qquad E \quad E \qquad (18)(29)(3,10)(46)(57)$$

$$\begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix} [1] \quad [1] \Big\} \otimes \qquad [1]'$$

$$= \begin{bmatrix} 1/4 & \sqrt{3}/4 & -\sqrt{3}/4 & -3/4 \\ -\sqrt{3}/4 & 1/4 & 3/4 & -\sqrt{3}/4 \\ +\sqrt{3}/4 & 3/4 & 1/4 & \sqrt{3}/4 \\ -3/4 & \sqrt{3}/4 & -\sqrt{3}/4 & 1/4 \end{bmatrix} [(19)(2,10)(38)(46)(57)]$$

$$= \begin{bmatrix} 1/4 & -\sqrt{3}/4 & \sqrt{3}/4 & -3/4 \\ -\sqrt{3}/4 & 3/4 & 1/4 & -\sqrt{3}/4 \\ \sqrt{3}/4 & 1/4 & 3/4 & \sqrt{3}/4 \\ -3/4 & -\sqrt{3}/4 & \sqrt{3}/4 & 1/4 \end{bmatrix} (19)(2,10)(38)(46)(57) \ . \qquad (4.21)$$

In practice however, we do not need all the matrix operators to construct the symmetry-adapted NMR spin functions. Using the character projector one component of the symmetry-adapted spin function can be easily obtained. The other components can be obtained by just knowing the matrices of dim(Γ) operations. Then by applying these operations and matrices on the first component the other components can be easily obtained by solving dim(Γ) linear equations.

In general when the inertia group is not isomorphic to the NMR group of the molecule, the representations of the NMR group are the representations of the inertia group induced to the NMR group. There does not seem to be any simple procedure (as outlined above) to obtain the projectors of these representations in terms of the projectors of the composing groups. Of course, one can obtain the character of an induced representation with well-known methods as outlined in an earlier paper of the author[6] and then construct the projector. Nevertheless, there is a simple solution when the inertia factor is the identity group. We outline this procedure below.

Let the representations in $K = \{\#_i F_i^{m*i}\}$ be equivalent and let the inertia factor corresponding to any representation be the identity group. The character projection operator corresponding to any representation k in K is simply the product of the character projectors of the composing representations in k. In symbols, if P^F represents a character projector corresponding to the representation F then

$$P^k = \prod_i \prod_j P^{F_{ij}} \ . \qquad (4.22)$$

Then the character projector of

$$\Gamma = (\#_i F_i^{m*i}) \dagger G[H_1, H_2, \ldots, H_t]$$

is simply given by Eq. (4.23),

$$P^\Gamma = \sum_{k \in K} P^k \ , \qquad (4.23)$$

where summation runs over all equivalent representations in K. The above result is quite useful for several chemically interesting systems for which $G = S_2$, since in this case the inertia factor is either S_2' or just the group containing only the identity. Since for both these cases procedures outlined in this section are applicable, for such systems the projectors can be trivially obtained. Examples of such systems are linear alkanes, or molecules which have internal rotors which have C_{2v} symmetry when internal rotors are replaced by a single particle (composite particle).

We will now give an example to illustrate Eq. (4.23). Consider the eight dimensional representation $K_1(\Gamma_{16})$ in Table III of I. It is of the form

$$K_1 = [2, 1] \# [2, 1] \# [2] \# [1^2] \dagger S_2[S_3, S_2] \ .$$

There are only two representations in the set K of equivalent representations and they are

$$K = \{[2, 1] \# [2, 1] \# [2] \# [1^2] \ , \quad [2, 1] \# [2, 1] \# [1^2] \# [2]\} \ .$$

They are equivalent since the permutation (14)(23) of the four carbon atoms of butane transforms them into one another. If we denote these representations by k_1 and k_2 then

$$P^{k_1} = \tfrac{2}{6}\{2E - (123) - (132)\} \cdot \tfrac{2}{6} \cdot \{2E - (8,9,10) - (8,10,9)\}$$
$$\cdot \tfrac{1}{2}\{E + (45)\} \cdot \tfrac{1}{2} \cdot \{E - (67)\} \ , \qquad (4.24)$$

$$P^{k_2} = \tfrac{2}{6}[2E - (123) - (132)] \cdot \tfrac{2}{6}[2E - (8,9,10) - (8,10,9)]$$
$$\cdot \tfrac{1}{2}[E - (45)] \cdot \tfrac{1}{2}[E + (67)] \ . \qquad (4.25)$$

Adding Eqs. (4.24) and (4.25) we obtain the projector of Γ_{16} shown below.

$$P^{\Gamma_{16}} = P^{k_1} + P^{k_2} = \tfrac{8}{288}[8E - 4(123) - 4(132) - 4(8,9,10) - 4(8,10,9) + 2(123)(8,9,10) + 2(123)(8,10,9) + 2(132)(8,9,10)$$
$$+ 2(132)(8,10,9) - 8(45)(67) + 4(123)(45)(67) + 4(132)(45)(67) + 4(8,9,10)(45)(67) + 4(8,10,9)(45)(67)$$
$$- 2(123)(8,9,10)(45)(67) - 2(123)(8,10,9)(45)(67) - 2(132)(8,9,10)(45)(67) - 2(132)(8,10,9)(45)(67)] \ . \qquad (4.26)$$

Thus we have shown here that the projection operators of NMR group of butane (or 2, 2, 3, 3, 4, 4, 5, 5 octamethyl hexane in the composite particle representation) can be obtained without knowing their character tables. Consider

TABLE I. Symmetry-adapted spin functions of $2,2,3,3$ tetramethyl butane in the composite particle representation. Q stands for the quartet state of methyl protons ($^4A_1$) and D for the doublet set (^2E). The last four classes are obtained by changing D to Q and Q to D and hence they are not shown here.

Representative of class C	$|C|$	Γ	SASF
QQQQQQ	1	A_1	QQQQQQ
QQQQQD	6	A_1	$\frac{1}{\sqrt{6}}$ [QQQQQD + QQQQDQ + QQQDQQ + QQDQQQ + QDQQQQ + DQQQQQ]
		A_2	$\frac{1}{\sqrt{6}}$ [QQQQQD + QQQQDQ + QQQDQQ − QQDQQQ − QDQQQQ − DQQQQQ]
		G_3	$\frac{1}{\sqrt{6}}$ [2QQQQQD − QQQQDQ − QQQDQQ] $\frac{1}{\sqrt{2}}$ [QQQDQQ − QQQQDQ] $\frac{1}{\sqrt{6}}$ [2DQQQQQ − QDQQQQ − QQDQQQ] $\frac{1}{\sqrt{2}}$ [QQDQQQ − QDQQQQ]
DDQQQQ	6	A_1	$\frac{1}{\sqrt{6}}$ [QDDQQQ + DQDQQQ + DDQQQQ + QQQQDD + QQQDQD + QQQDDQ]
		A_2	$\frac{1}{\sqrt{6}}$ [QDDQQQ + DQDQQQ + DDQQQQ − QQQQDD − QQQDQD − QQQDDQ]
		G_3	$\frac{1}{\sqrt{6}}$ [2DDQQQQ − DQDQQQ − QDDQQQ] $\frac{1}{\sqrt{2}}$ [DQDQQQ − QDDQQQ] $\frac{1}{\sqrt{6}}$ [2QQQDDQ − QQQDQD − QQQQDD] $\frac{1}{\sqrt{2}}$ [QQQDQD − QQQQDD]
DQQDQQ	9	A_1	$\frac{1}{\sqrt{9}}$ [DQQDQQ + QDQDQQ + QQDDQQ + DQQQDQ + QDQQDQ + QQDQDQ + DQQQQD + QDQQQD + QQDQQD]
		G_1	$\frac{1}{\sqrt{6}}$ [4DQQDQQ − 2QDQDQQ − 2QQDDQQ − 2DQQQDQ − 2DQQQQD + QDQQDQ + QDQQQD + QQDQDQ + QQDQQD] $\frac{1}{\sqrt{12}}$ [2QDQDQQ − 2QQDDQQ − QDQQDQ − QDQQQD + QQDQDQ + QQDQQD] $\frac{1}{\sqrt{12}}$ [2DQQQDQ − 2DQQQQD + QQDQQD + QDQQQD − QQDQDQ − QDQQDQ] $\frac{1}{2}$ [QDQQDQ − QQDQDQ − QDQQQD + QQDQQD]
		G_3	$\frac{1}{6}$ [4DQQDQQ + QDQDQQ + QQDDQQ + DQQQDQ + DQQQQD − 2QDQQDQ − 2QDQQQD − 2QQDQDQ − 2QQDQQD] $\frac{1}{\sqrt{12}}$ [2QDQQDQ − 2QQDQQD + QDQDQQ − QQDDQQ + DQQQDQ − DQQQQD] $\frac{1}{2}$ [DQQQQD − QQDDQQ − QDQDQQ + DQQQDQ] $\frac{1}{\sqrt{12}}$ [2QDQQQD − 2QQDQDQ + DQQQQD + QQDDQQ + QDQDQQ − DQQQDQ]

TABLE I (*Continued*)

Representative of class C	$|C|$	Γ	SASF
DDQQQD	18	A_1	$\frac{1}{\sqrt{18}}$ [DDQQQD + DDQDQQ + DDQQDQ + DQDQQD + DQDDQQ + DQDQDQ + QDDQQD + QDDDQQ + QDDQDQ + QQDDDQ + DQQDDQ + QDQDDQ + QQDDQD + DQQDQD + QDQDQD + QQDQDD + DQQQDD + QDQQDD]
		A_2	$\frac{1}{\sqrt{18}}$ [DDQQQD + DDQDQQ + DDQQDQ + DQDQQD + DQDDQQ + DQDQDQ + QDDQQD + QDDDQQ + QDDQDQ − QQDDDQ − DQQDDQ − QDQDDQ − QQDDQD − DQQDQD − QDQDQD − QQDQDD − DQQQDD − QDQQDD]
		G_1	$\frac{1}{\sqrt{72}}$ [4DDQQQD − 2QDDQQD − 2DQDQQD − 2DDQDQQ − 2DDQQDQ + QDDDQQ + QDDQDQ + DQDDQQ + DQDQDQ + 4QQDDDQ + QDQDQD + QDQQDD + DQQQDD + DQQDQD − 2QQDQDD − 2DQQDDQ − 2QQDDQD − 2QDQDDQ]
			$\frac{1}{2\sqrt{6}}$ [2QDDQQD − 2DQDQQD + 2DQQDDQ − 2QDQDDQ − QDDDQQ − QDDQDQ + DQDDQQ + DQDQDQ + QDQDQD + QDQQDD − DQQQDD − DQQDQD]
			$\frac{1}{2\sqrt{6}}$ [2QQDQDD − 2QQDDQD + 2DDQDQQ − 2DDQQDQ − DQQQDD − QDQQDD + DQQDQD + QDQDQD + DQDQDQ + QDDQDQ − QDDDQQ − DQDDQQ]
			$\frac{1}{2\sqrt{2}}$ [DQQQDD + QDDDQQ − QDQQDD − QDDQDQ − DQQDQD − DQDDQQ + QDQDQD + DQDQDQ]
		G_2	$\frac{1}{\sqrt{72}}$ [4DDQQQD − 2QDDQQD − 2DQDQQD − 2DDQDQQ − 2DDQQDQ + QDDDQQ + QDDQDQ + DQDDQQ + DQDQDQ − 4QQDDDQ − QDQDQD − QDQQDD − DQQQDD − DQQDQD + 2QQDQDD + 2DQQDDQ + 2QQDDQD + 2QDQDDQ]
			$\frac{1}{2\sqrt{6}}$ [2QDDQQD − 2DQDQQD − 2DQQDDQ + 2QDQDDQ − QDDDQQ − QDDQDQ + DQDDQQ + DQDQDQ − QDQDQD − QDQQDD + DQQQDD + DQQDQD]
			$\frac{1}{2\sqrt{6}}$ [2QQDQDD − 2QQDDQD − 2DDQDQQ + 2DDQQDQ − DQQQDD − QDQQDD + DQQDQD + QDQDQD − DQDQDQ − QDDQDQ + QDDDQQ + DQDDQQ]
			$\frac{1}{2\sqrt{2}}$ [DQQQDD − QDDDQQ − QDQQDD + QDDQDQ − DQQDQD + DQDDQQ + QDQDQD − DQDQDQ]
		G_3	$\frac{1}{6}$ [4DDQQQD + QDDQQD + DDQDQQ + DDQQDQ + DQDQQD − 2QDDDQQ − 2QDDQDQ − 2DQDDQQ − 2DQDQDQ]
			$\frac{1}{\sqrt{12}}$ [2QDDDQQ − 2DQDQDQ + QDDQDQ + DDQDQQ − DDQQDQ − DQDQQD]
			$\frac{1}{2}$ [DQDQDQ − DDQQQD + DQDDQQ − QDDQQD]
			$\frac{1}{\sqrt{12}}$ [2DDQQDQ + DQDQDQ + DDQQQD − DQDDQQ − QDDQQD − 2QDDDQQ]
		G_3	$\frac{1}{6}$ [4QQDDDQ + DQQDDQ + QQDQDD + QQDDQD + QDQDDQ − 2DQQQDD − 2DQQDQD − 2QDQQDD − 2QDQDQD]
			$\frac{1}{\sqrt{12}}$ [2DQQQDD − 2QDQDQD + DQQDDQ + QQDQDD − QQDDQD − QDQDDQ]
			$\frac{1}{2}$ [QDQDQD − QQDDDQ + QDQQDD − DQQDDQ]
			$\frac{1}{\sqrt{12}}$ [2QQDDQD + QDQDQD + QQDDDQ − QDQQDD − DQQDDQ − 2DQQQDD]
QQQDDD	2	A_1	$\frac{1}{\sqrt{2}}$ [QQQDDD + DDDQQQ]
		A_2	$\frac{1}{\sqrt{2}}$ [QQQDDD − DDDQQQ]

the representation $\Gamma = [2,1] \# [3] \# [1^3] \uparrow S_3[S_3]$ of the NMR group of Boron trimethyl (or isobutane). The inertia group of $[2,1] \# [3] \# [1^3]$ is just $S_3 \times S_3 \times S_3$ so that the inertia factor is the identity group. The set K of equivalent representations is

$$K = \{[2,1] \# [3] \# [1^3],\ [2,1] \# [1^3] \# [3],\ [3] \# [2,1] \# [1^3],\ [3] \# [1^3] \# [2,1],\ [1^3] \# [2,1] \# [3],\ [1^3] \# [3] \# [2,1]\}.$$

Thus p^{ki}'s are as follows. In the expressions shown below for convenience all the elements in a conjugacy class of S_3 are simply represented by a summation sign:

$$P^{k_1} = \tfrac{2}{6}[2E - \textstyle\sum(123)] \cdot \tfrac{1}{6}[E + \textstyle\sum(45) + \textstyle\sum(456)] \cdot \tfrac{1}{6}[E - \textstyle\sum(78) + \textstyle\sum(789)],\tag{4.27}$$

$$P^{k_2} = \tfrac{2}{6}[2E - \textstyle\sum(123)] \cdot \tfrac{1}{6}[E - \textstyle\sum(45) + \textstyle\sum(456)] \cdot \tfrac{1}{6}[E + \textstyle\sum(78) + \textstyle\sum(789)],\tag{4.28}$$

$$P^{k_3} = \tfrac{1}{6}[E + \textstyle\sum(12) + \textstyle\sum(123)] \cdot \tfrac{2}{6}[2E - \textstyle\sum(456)] \cdot \tfrac{1}{6}[E - \textstyle\sum(78) + \textstyle\sum(789)],\tag{4.29}$$

$$P^{k_4} = \tfrac{1}{6}[E + \textstyle\sum(12) + \textstyle\sum(123)] \cdot \tfrac{1}{6}[E - \textstyle\sum(45) + \textstyle\sum(456)] \cdot \tfrac{2}{6}[2E - \textstyle\sum(789)],\tag{4.30}$$

$$P^{k_5} = \tfrac{1}{6}[E - \textstyle\sum(12) + \textstyle\sum(123)] \cdot \tfrac{2}{6}[2E - \textstyle\sum(456)] \cdot \tfrac{1}{6}[E + \textstyle\sum(78) + \textstyle\sum(789)],\tag{4.31}$$

$$P^{k_6} = \tfrac{1}{6}[E - \textstyle\sum(12) + \textstyle\sum(123)] \cdot \tfrac{1}{6}[E + \textstyle\sum(45) + \textstyle\sum(456)] \cdot \tfrac{2}{6}[2E - \textstyle\sum(789)].\tag{4.32}$$

Thus

$$P^\Gamma = P^{k_1} + P^{k_2} + P^{k_3} + P^{k_4} + P^{k_5} + P^{k_6}$$

is given by Eq. (4.33),

$$P^\Gamma = \frac{12}{6^4}[12E + 6\textstyle\sum(123) - 4\textstyle\sum(12)(45) + 2\textstyle\sum(12)(45)(789) - 6\textstyle\sum(123)(456)(789)].\tag{4.33}$$

In Eq. (4.33) the summations are over conjugacy classes of $S_3[S_3]$. Thus, note that the projectors of $S_3[S_3]$, a group of order 6^4 were simply obtained in terms of the projectors of S_3.

V. CONSTRUCTION OF SYMMETRY-ADAPTED SPIN FUNCTIONS

We will conclude this paper with a complete example. Consider the molecule 2, 2, 3, 3 tetramethyl butane. As pointed out in earlier sections, the composite particle representation is much superior at every stage of NMR computations since it requires less storage, the NMR group is much smaller, etc. The protons of the methyl groups in this molecule span a $^4A_1$ and ^2E species in the group S_3. We will simply denote these by Q (quartet) and D (doublet), respectively. Then in the composite particle representation one replaces each methyl group in the molecule by a single composite particle nucleus with two spin states namely, Q or D. Then the problem is factored into a Hamiltonian of the interaction of these particles. The resulting composite particle NMR group is $S_2[S_3]$ of order 72. All the projectors of this group can be obtained simply in terms of the projectors of S_2 and S_3 by procedures in Sec. IV. First, one obtains the equivalence class structure of the composite particle spin functions using the double coset analysis. The resulting equivalence class structure is shown in Table I in the first two columns where the first column gives a representative in the equivalence class obtained by double cosets and the second column gives the number of spin functions in the equivalence class. Using the restricted character cycle indices (RCCI's) the irreducible representations in each class are generated. They are shown in the third column. The projection operator corresponding to each irreducible representation is then applied on the elements of that class to generate the symmetry-adapted NMR spin functions. The spin functions thus obtained for each symmetry species are shown in the last column of Table I. The original NMR Hamiltonian matrix of this molecule is of order $2^{18} \times 2^{18}$. This is factored into $2^6 \times 2^6$ matrix in the composite particle representation. This matrix is further factored into 8 1×1 matrices, 6 4×4, 4 2×2 and 3 8×8 matrices in the symmetry-adapted basis sets shown in Table I.

[1] K. Balasubramanian, J. Chem. Phys. 78, 6369 (1983).
[2] R. L. Flurry, Theor. Chim. Acta 31, 221 (1973).
[3] S. G. Williamson, J. Comb. Theory 8, 162 (1970).
[4] S. G. Williamson, J. London Math. Soc. 3, 411 (1971).
[5] A. Messiah, Quantum Mechanics (Wiley, New York, 1958), Vol. 1, pp. 252–254.
[6] K. Balasubramanian, J. Chem. Phys. 72, 665 (1980).
[7] E. Ruch, W. Hasselbarth, and B. Richler, Theor. Chim. Acta 19, 288 (1970).