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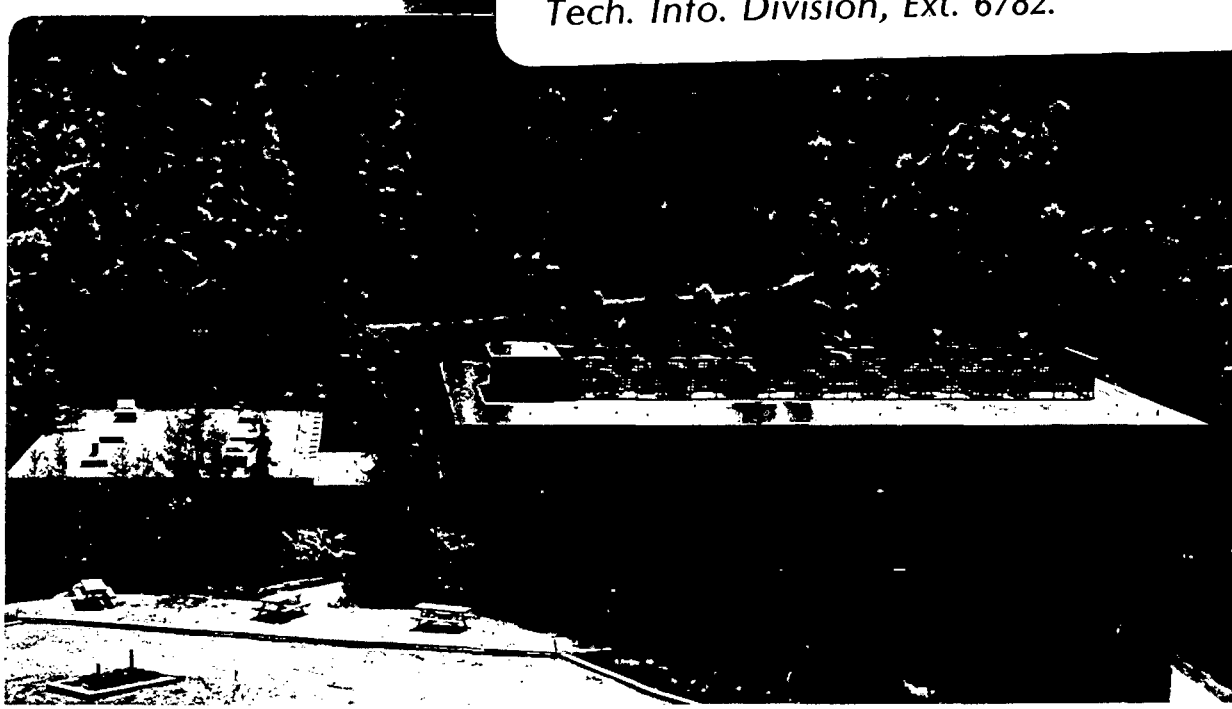

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NON-RIGID MOLECULAR GROUP THEORY AND ITS APPLICATIONS

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ABSTRACT

The use of generalized wreath product groups as representations of symmetry groups of non-rigid molecules is considered.

Generating function techniques are outlined for nuclear spin statistics and character tables of the symmetry groups of non-rigid molecules. Several applications of non-rigid molecular group theory to NMR spectroscopy, rovibronic splitting and nuclear spin statistics of non-rigid molecules, molecular beam deflection and electric resonance experiments of weakly bound Van der Waal complexes, isomerization processes, configuration interaction calculations and the symmetry of crystals with structural distortions are described.

1. INTRODUCTION

A molecule can be said to be non-rigid if it has an electronic potential surface with barriers that can be surmounted by large amplitude nuclear motions. The symmetry groups of such molecules should contain the permutations of nuclei induced by these rapid nuclear motions and inversion operations. Longuet-Higgins[1] formulated the permutation-inversion approach to the symmetry groups of non-rigid molecules. It is necessary that the symmetry groups of non-rigid molecules have the permutations induced by tunneling operations to interpret many experimental data obtained from their spectra. For example, the rotational spectra of these molecules exhibit a typical splitting attributed to tunneling among various possible conformational structures. The non-rigid molecular group theory has several applications in other areas of chemical physics such as NMR spectroscopy, spectroscopy of weakly bound Van der Waal complexes, molecular rearrangements, configuration interaction calculations, symmetry groups of crystals with distortions, chemical reactivity etc. Several of these applications will be considered in this article.

Since Longuet-Higgins[1] formulation of the symmetry groups of non-rigid molecules several other authors[2-67] have investigated the structure of these groups and many applications. Excellent reviews of these other schemes can be found in the articles of these authors in this volume and the review of Serre.[23] Since the space does not permit we will not go into the details of other schemes.

In this article we will first outline wreath product representation developed by the present author[41-44] for the symmetry groups of non-rigid molecules. Several applications to NMR spectroscopy, spectroscopy of weakly bound complexes, isomerization reactions, CI calculations and crystals with structural distortions are described with the intent of promoting further research along these directions.

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

A. Formulation

The present author showed that symmetry groups of non-rigid molecules which contain several internal rotors can be expressed as generalized wreath product groups.[41,44] We will briefly review the theory of generalized wreath product groups here with examples.

Let us start with an example of the non-rigid hydrazine molecule. The molecule in its equilibrium conformation contains only a two-fold axis of symmetry. This molecule is non-rigid in that twisting and inversion operations interconvert all the 16 possible conformations into one another. Consider the permutational subgroup of this molecule. All the permutation operations of the non-rigid molecule can be generated by a group product of much simpler groups, known as wreath product. Let us model this molecule by a particles-in-box model. Consider each nitrogen atom as a box and the protons attached to that atom as the two particles in the corresponding box (see Fig. 1). Then twisting

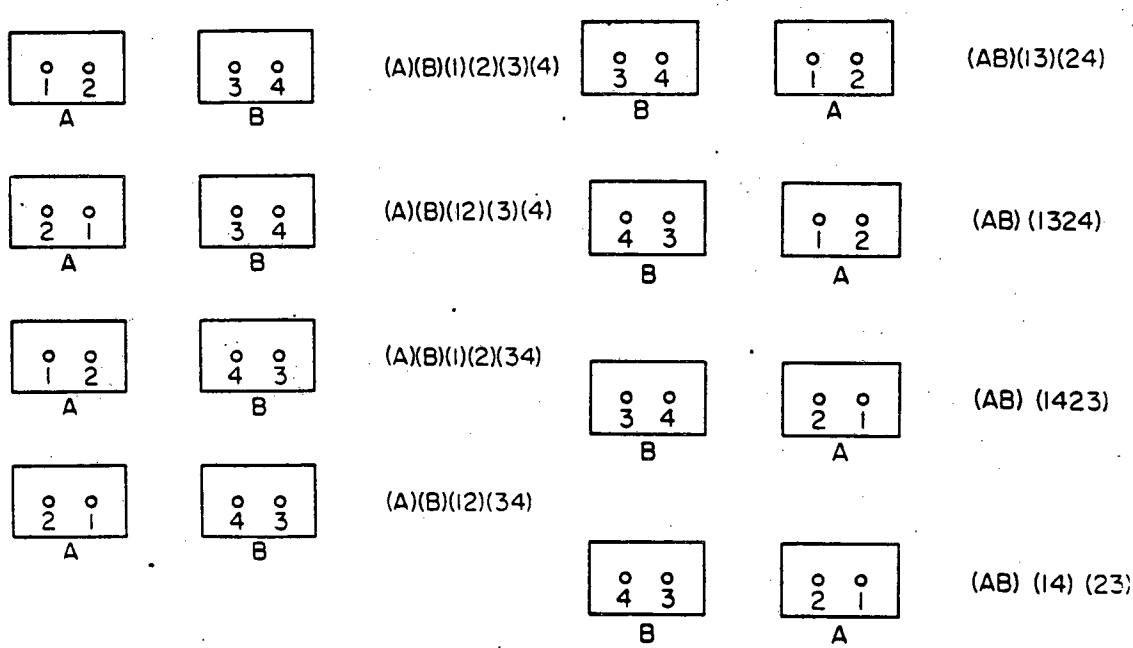

Figure 1. Particle-in-box model for the permutation group of the non-rigid N_2H_4. The permutation group of N_2H_4 is the wreath product of the group of boxes (S_2) and particles (S_2).

operation permutes the protons or the particles in each box. The two nitrogen atoms (and hence the protons attached to the nitrogen atoms) can be permuted by an operation preserving the rigid symmetry of the molecule. Consequently, we have two permutation groups namely, a permutation group G acting on the boxes in the particle-in-box model and a permutation group H acting on particles in each box. H can be called a torsion group if the particles in each box are permuted by torsion. The symmetry group of the non-rigid molecule will consist of permutations of particles in each box (torsional permutations), the permutations of the boxes, which in turn induce permutations of particles in all boxes and inversion operations. All the operations generated by permutations of particles in each box and the permutations of boxes are shown in Fig. 1. The resulting operations span a group of order 8. These operations can be generated by knowing the operations in the group G and H. The group of all particles in all the boxes is the wreath product of the group G with the group H, denoted as G[H]. In this example, G and H are both S_2, symmetric group of 2 objects containing 2! elements. Wreath product groups were first formulated by Pòlya[68] which he called Kranz groups. The order of G[H], $|G[H]|$ is given by (2.1).

$$|G[H]| = |G|\cdot|H|^{|B|} \tag{2.1}$$

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

$$(g;\pi)(g';\pi') = (gg';\pi\pi'_g) \tag{2.2}$$

$$\pi'_g(i) = \pi'(g^{-1}i), \quad i\varepsilon B. \tag{2.3}$$

Products of two maps π and π' are defined by

$$\pi\pi'(i) = \pi(i)\pi'(i), \quad i\varepsilon D. \tag{2.4}$$

Let us illustrate this with the hydrazine example. Let g be identity (i.e., all the boxes are in their natural positions) and g' be a permutation of boxes denoted as (AB). Let π and π' be the maps shown below.

$$\pi(1) = (12) \qquad \pi'(1) = (1)(2)$$
$$\pi(2) = (34) \qquad \pi'(2) = (34) \tag{2.5}$$

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

$$\pi\pi'(1) = \pi(1)\pi'(1) = (12)$$
$$\pi\pi'(2) = \pi(2)\pi'(2) = (3)(4) \tag{2.6}$$

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

$$(g;\pi)(g';\pi') = ((AB);\pi\pi') \tag{2.7}$$

with $\pi\pi'$ defined by (2.6).

Define a group G' which is isomorphic to G as follows.

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

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

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

where

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

with e is the identity of G. Note that $H^* = H_1 \times H_2 \times \ldots \times H_b$ is simply b-fold direct product of b copies of the group H. The group H* is known as the basis group of G[H]. It can be shown that H* is an invariant subgroup of G[H]. Consequently, the permutation representation of G[H] = H*. G' is simply a semi-direct product of H* and G'. The fact that the symmetry groups of non-rigid molecules can be expressed as semidirect products was first noted by Altmann.[11] Serre[13] pointed out the use of Mackey's theorem for semi-direct products in the chemical contexts. Woodman[10,15] has also recognized the use of semi-direct product groups in representing the NMR groups of non-rigid molecules. Nevertheless, wreath product representation which is a special case of a semi-direct product representation is superior to semi-direct products in that several properties of G[H] can be simply obtained if the corresponding properties of G and

H are known. For example, conjugacy classes of $S_n[H]$ for any H (where S_n is the symmetric group of n objects) can be obtained from the conjugacy classes of S_n and H as shown by Kerber.[69] The irreducible representations of G[H] can be obtained from the irreducible representations of G and H. The generating functions for several problems concerning spectroscopy of non-rigid molecules can be obtained in terms of G and H. We will refer to G and H as composing groups in the rest of the manuscript.

Kerber and co-workers[69-71] have made significant contributions to the representation theory of wreath product groups. We will briefly review their methodology here.

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

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

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

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

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

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

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

with

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

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

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

Two representations F* and F*' are said to be equivalent if

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

where g acts on F* as

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

To illustrate for $G = C_2$, the representations $A_1 \# A_2$ and $A_2 \# A_1$ are equivalent by the above recipe. Let K be set of inequivalent representations among the possible representations F*. If one knows the representation matrices of $F^*(e;\pi)$ one can obtain the representation matrices of $F^*(g;\pi)$ by

$$\widetilde{F^*(g;\pi)} = f_{i_1 k_{g1^{-1}}} [\pi(1)]\, f_{i_2 k_{g2^{-1}}} [\pi(2)] \ldots f_{i_b k_{gb^{-1}}} [\pi(b)]$$

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

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

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

To illustrate consider the ferrocene molecule $(C_5H_5)_2Fe$. The barrier to rotation of the ferrocene rings (Fe atom is sandwiched between the rings) measured in the gas phase is only of the order of a kcal and thus this molecule is a non-rigid molecule. The rotation of the two (C_5H_5) rings can be described by the 5-fold cyclic group $\underset{\sim}{C}_5$. Thus the permutation group of the molecule is the wreath product $\underset{\sim}{C}_2[\underset{\sim}{C}_5]$, where $\underset{\sim}{C}_2$ is the group which switches the 2 ferrocene rings. The character table of $\underset{\sim}{C}_5$ can be trivially obtained. The conjugacy class structure of $C_2[C_5]$ can be easily obtained using the method outlined in the paper of the author.[44] In Table 1 we have shown all the irreducible representations and character table of $\underset{\sim}{C}_2[\underset{\sim}{C}_5]$.

Generalization of wreath product groups to generalized wreath product groups is possible. The simplest non-trivial example of such a system is shown in Fig. 2 in particle-in-box model. In Fig. 2, let G = {(A)(B)(C)(D), (AD)(BC)} be a

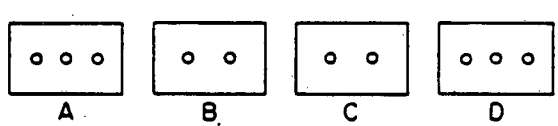

Figure 2. Particle-in-box model of a simplest non-trivial system with a generalized wreath product permutation group. This model represents the NMR group of butane.

TABLE 1

The character table of the rotational subgroup of the non-rigid ferrocene molecule

Γ	e	$\{e;C_5,C_5^2\}$	$\{e;C_5^2,C_5^3\}$	$\{e;C_5^3,C_5^4\}$	$\{e;C_5^4,C_5\}$	$\{e;e,C_5\}$	$\{e,e,C_5^2\}$	$\{e;e,C_5^3\}$	$\{e;e,C_5^4\}$	$\{e;C_5,C_5^2\}$	$\{e;C_5,C_5^3\}$	$\{e;C_5,C_5^4\}$	$\{e;C_5^2,C_5^3\}$	$\{e;C_5^2,C_5^4\}$	$\{e;C_5^3,C_5^4\}$	$\{(12);e,e\}$	$\{(12);C_5,e\}$	$\{(12);C_5^2,e\}$	$\{(12);C_5^3,e\}$	$\{(12);C_5^4,e\}$
Order	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	5	5	5	5	5
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1
E_1	1	ε^2	ε^*	ε	ε^{2*}	ε	ε^2	ε^{2*}	ε^*	ε^{2*}	ε^*	1	1	ε	ε^2	1	ε	ε^2	ε^{2*}	ε^*
	1	ε^{2*}	ε	ε^*	ε^2	ε^*	ε^{2*}	ε^2	ε	ε^2	ε	1	1	ε^*	ε^{2*}	1	ε^*	ε^{2*}	ε^2	ε
E_2	1	ε^2	ε^*	ε	ε^{2*}	ε	ε^2	ε^{2*}	ε^*	ε^{2*}	ε^*	1	1	ε	ε^2	-1	$-\varepsilon$	$-\varepsilon^2$	$-\varepsilon^{2*}$	$-\varepsilon^*$
	1	ε^{2*}	ε	ε^*	ε^2	ε^*	ε^{2*}	ε^2	ε	ε^2	ε	1	1	ε^*	ε^{2*}	-1	$-\varepsilon^*$	$-\varepsilon^{2*}$	$-\varepsilon^2$	$-\varepsilon$
E_3	1	ε	ε^{2*}	ε^2	ε^*	ε^2	ε^*	ε	ε^{2*}	ε	ε^{2*}	1	1	ε^2	ε^*	1	ε^2	ε^*	ε^*	ε^{2*}
	1	ε^*	ε^2	ε^{2*}	ε	ε^{2*}	ε	ε^*	ε^2	ε^*	ε^2	1	1	ε^{2*}	ε	1	ε^{2*}	ε	ε	ε^2
E_4	1	ε	ε^{2*}	ε^2	ε^*	ε^2	ε^*	ε	ε^{2*}	ε	ε^{2*}	1	1	ε^2	ε^*	-1	$-\varepsilon^2$	$-\varepsilon^*$	$-\varepsilon^*$	$-\varepsilon^{2*}$
	1	ε^*	ε^2	ε^{2*}	ε	ε^{2*}	ε	ε^*	ε^2	ε^*	ε^2	1	1	ε^{2*}	ε	-1	$-\varepsilon^{2*}$	$-\varepsilon$	$-\varepsilon$	$-\varepsilon^2$
E_5	2	2	2	2	2	C	C^2	C^2	C	C	C^2	C^2	C	C^2	C	0	0	0	0	0
E_6	2	2	2	2	2	C^2	C	C	C^2	C^2	C	C	C^2	C	C^2	0	0	0	0	0

$\varepsilon = \exp(\frac{2\pi i}{5})$

$C^k = \varepsilon^k + \varepsilon^{-k}$

Table I (continued)

Γ	e	$\{e;c_5,c_5\}$	$\{e;c_5^2,c_5^2\}$	$\{e;c_5^3,c_5^3\}$	$\{e;c_5^4,c_5^4\}$	$\{e;e,c_5\}$	$\{e;e,c_5^2\}$	$\{e;e,c_5^3\}$	$\{e;e,c_5^4\}$	$\{e;c_5,c_5^2\}$	$\{e;c_5,c_5^3\}$	$\{e;c_5,c_5^4\}$	$\{e;c_5^2,c_5^3\}$	$\{e;c_5^2,c_5^4\}$	$\{e;c_5^3,c_5^4\}$	$\{(12);e,e\}$	$\{(12);c_5,e\}$	$\{(12);c_5^2,e\}$	$\{(12);c_5^3,e\}$	$\{(12);c_5^4,e\}$
Order	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	5	5	5	5	5
G_1	2	2ε	$2\varepsilon^2$	$2\varepsilon^{2*}$	$2\varepsilon^*$	$1+\varepsilon$	$1+\varepsilon^2$	$1+\varepsilon^{2*}$	$1+\varepsilon^*$	$\varepsilon+\varepsilon^2$	$\varepsilon+\varepsilon^{2*}$	c	c^2	$\varepsilon^*+\varepsilon^2$	$\varepsilon^*+\varepsilon^{2*}$	0	0	0	0	0
	2	$2\varepsilon^*$	$2\varepsilon^{2*}$	$2\varepsilon^2$	2ε	$1+\varepsilon^*$	$1+\varepsilon^{2*}$	$1+\varepsilon^2$	$1+\varepsilon$	$\varepsilon^*+\varepsilon^{2*}$	$\varepsilon^*+\varepsilon^2$	c^2	c	$\varepsilon+\varepsilon^{2*}$	$\varepsilon+\varepsilon^2$	0	0	0	0	0
G_2	2	$2\varepsilon^2$	$2\varepsilon^*$	2ε	$2\varepsilon^{2*}$	$1+\varepsilon^2$	$1+\varepsilon^*$	$1+\varepsilon$	$1+\varepsilon^{*2}$	$\varepsilon^*+\varepsilon^2$	$\varepsilon+\varepsilon^2$	c^2	c	$\varepsilon^{2*}+\varepsilon$	$\varepsilon+\varepsilon^{2*}$	0	0	0	0	0
	2	$2\varepsilon^{*2}$	2ε	$2\varepsilon^*$	$2\varepsilon^2$	$1+\varepsilon^{2*}$	$1+\varepsilon$	$1+\varepsilon^*$	$1+\varepsilon^2$	$\varepsilon+\varepsilon^{2*}$	$\varepsilon^*+\varepsilon^{2*}$	c	c^2	$\varepsilon^2+\varepsilon^*$	$\varepsilon^*+\varepsilon^2$	0	0	0	0	0
G_3	2	$2\varepsilon^{2*}$	2ε	$2\varepsilon^*$	$2\varepsilon^2$	$\varepsilon+\varepsilon^2$	$\varepsilon^2+\varepsilon^*$	$\varepsilon+\varepsilon^{2*}$	$\varepsilon^*+\varepsilon^{2*}$	2	$1+\varepsilon^2$	c	c^2	2	$1+\varepsilon$	0	0	0	0	0
	2	$2\varepsilon^2$	$2\varepsilon^*$	2ε	$2\varepsilon^{2*}$	$\varepsilon^*+\varepsilon^{2*}$	$\varepsilon+\varepsilon^{2*}$	$\varepsilon^*+\varepsilon^2$	$\varepsilon+\varepsilon^2$	2	$1+\varepsilon^{2*}$	c^2	c	2	$1+\varepsilon^*$	0	0	0	0	0
G_4	2	$2\varepsilon^*$	$2\varepsilon^{2*}$	$2\varepsilon^2$	2ε	$\varepsilon+\varepsilon^{2*}$	$\varepsilon+\varepsilon^2$	$\varepsilon^*+\varepsilon^{2*}$	$\varepsilon^*+\varepsilon^2$	$1+\varepsilon^2$	2	c^2	c	$1+\varepsilon^*$	2	0	0	0	0	0
	2	2ε	$2\varepsilon^2$	$2\varepsilon^{2*}$	$2\varepsilon^*$	$\varepsilon^*+\varepsilon^2$	$\varepsilon^*+\varepsilon^{2*}$	$\varepsilon+\varepsilon^2$	$\varepsilon+\varepsilon^{2*}$	$1+\varepsilon^{2*}$	2	c	c^2	$1+\varepsilon$	2	0	0	0	0	0

permutation group of boxes. Note that G does not permute boxes containing different number of particles. Equivalently, the cycle products of G can be divided in to disjoints sets. When the cycle products of a group can be divided in to more than one disjoint set it is known as an intransitive group. The cyclic group $\underline{C}_5$ of 5 objects is an example of a transitive group and the group G shown above is intransitive. The cycle products of G can be divided into the disjoint sets $Y_1 = \{A,D\}$, $Y_2 = \{B,C\}$. Alternatively G does not permute elements in different Y sets. Let H_i be the group acting on particles in the boxes belonging to the set Y_i (let $1 \le i \le t$). Let G be the intransitive group acting on the boxes such that the boxes can be divided into disjoint sets $Y_1, Y_2, \ldots, Y_t$. Then the group of all the particles in all the boxes is the generalized wreath product group $G[H_1, H_2, \ldots, H_t]$ defined below.

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

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

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

with

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

One can easily see that

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

The representation theory of wreath product groups can be extended to generalized wreath product groups as shown by the present author.[44] We will briefly review this here. Let $|Y_i| = m_i$. Then $G[H_1,H_2,\ldots,H_t]$ has the following permutation representations.

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

where

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

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

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

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

where F' is a representation of G'_{F^*}. The tilde symbol has the same meaning as in the representation theory of wreath product groups. F^*'s are chosen from K.

We conclude this subsection with the note that the symmetry group of the system shown in Fig. 2 is the generalized wreath product $S_2[S_3, S_2]$ if $H_1 = S_3$ acts on the particles in boxes A and D and $H_2 = S_2$ acts on particles in boxes B and C. This is an example of the NMR group of the non-rigid butane molecule as we will show in a latter section.

B. Generalized Character Cycle Indices (GCCI's)

Define a generalized character cycle index (GCCI) of a group G corresponding to character χ as

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

where $x_1^{b_1} x_2^{b_2} \ldots x_n^{b_n}$ is a representation of the permutation $g \in G$ which generates b_1 cycles of length 1, b_2 cycles of length 2 etc. on its action on a set D of objects. The GCCI corresponding to the totally symmetric representation is the well-known cycle index of a group G defined by Pólya.[68] These polynomials are quite useful in generating the nuclear spin species and nuclear spin statistical weights of rovibronic levels as shown by the present author. We will demonstrate the usefulness and applications of this in spectroscopy of non-rigid molecules in the next section. In this section we will show how GCCIs of generalized wreath product group $G[H_1, H_2, \ldots, H_t]$ can be obtained in terms of GCCI's of G, H_1, H_2, ...etc. Let the inertia factor of $F^* = F_1^{m_1*} \# F_2^{m_2*} \# \ldots \# F_t^{m_t*}$ be G'_{F^*}. Then a GCCI of G'_{F^*} corresponding to a character χ is given by

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

where $C_{ij}(g)$ is the number of j-cycles of g in the set Y_i. Note that the product $x_1^{b_1} x_2^{b_2} \ldots x_n^{b_n}$ in the GCCI can be cast into the form $\prod_i \prod_j x_{ij}^{C_{ij}(g)}$ since

any $g \varepsilon G$ permutes only elements within a Y-set. Let λ_k be the character of F_i in the m_i-fold outer product $F_i^{m_i *}$. Let the corresponding GCCI be defined as follows.

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

Define $Z_{ij}^{\lambda_k}$ as follows.

$$Z_{ij}^{\lambda_k} = Z_i^{\lambda_k}(x_\ell \rightarrow x_{\ell j})$$

where the subscript ℓj on the x variable is a product. The arrow stands for replacing x_ℓ in $Z_i^{\lambda_k}$ by $x_{\ell j}$. A GCCI of an irreducible representation $\Gamma = (\#_i F_i^{m_i *} \otimes F') \uparrow G[H_1, H_2, \ldots H_t]$ is given by

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

It is obtained by replacing every x_{ij} by $Z_{ij}^{\lambda_k}$ in $P^{\chi}_{G', F*}$ if this j cycle in Y_i is constituted by j copies of the representation whose character is λ_k. Thus all the GCCI's of $G[H_1, H_2, \ldots H_t]$ can be obtained in terms of the GCCI's of G, H_1, $H_2, \ldots H_t$.

Several illustrative examples of this technique can be found in the papers of the present author.[52,53,72]

The GCCI's obtained with this technique are also partial generators of their character tables of non-rigid molecules as shown by the author.[65]

3. ROVIBRONIC SPLITTING AND NUCLEAR SPIN STATISTICS OF NON-RIGID MOLECULES

A non-rigid molecule tunnels between the various possible conformational rigid structures. As a consequence of this tunneling process a given rotational level (and hence a rovibronic level) splits into finer levels which can be called tunneling splitting. Tunneling-splitting is a function of barrier and the nature of potential energy surface. In order to calculate the splitting, one first needs to correlate the rovibronic levels of the rigid molecule to the non-rigid molecule. Watson[6] showed that the symmetry species of the rovibronic level of a molecule can be correlated to non-rigid molecule by the use of induced representation. The symmetry group of the molecule in its equilibrium geometry is, in general, a subgroup of the non-rigid molecule. An irreducible representation of the rigid molecule can be extended (induced) to the symmetry group of the non-rigid molecule. The concept of induced representations has been dealt by Altmann[32] in great details and the readers are referred to his

work and the recent book of Bunker.[73]

The nuclear spin statistical weights of the split levels govern the intensity patterns of transitions among these levels. For a molecule containing b_1 nuclei with a_1 spin states, b_2 nuclei with a_2 spin states..., the total number of nuclear spin functions can be seen to be $a_1^{b_1} a_2^{b_2} \ldots$. One needs the character of the representation spanned by these nuclear spin functions in the molecular symmetry group in order to find the nuclear spin statistical weights. It is very tedious to find the character of the representation spanned by nuclear spin functions using their transformation properties, since they are numerous in number. The present author developed generating function techniques for the nuclear spin statistics of both rigid and non-rigid molecules of any symmetry.[52,53] Further, the author has developed computer programs which generate the nuclear spin species and spin statistical weights.[58,59] The input for this program is the set of GCCI's which can be obtained for non-rigid molecules very elegantly without having to know their character tables as shown in Sec 2B. We will review this method here.

Let D be the set of nuclei and R be the set of the nuclear spin states of nuclei in D. Then nuclear spin functions can be conceived of as maps from D to R. Let the symmetry group of the non-rigid molecule be M and let the GCCI's of G be denoted as $GCCI_M^{\chi}$. With each element $r \varepsilon R$, let us associate a weight $w(r)$, which is used to book keep the number of various spin states in a given spin function. The weight of a spin function is the product of the weights of the spin states in the spin function. If the spin function contains b_1 spin states with the same weight w_1, b_2 spin states with the weight w_2 etc., then its weight is $w_1^{b_1} w_2^{b_2} \ldots$. The author showed that a generating function for nuclear spin species can be obtained by the following substitution using a theorem of Williamson[74a] and Merris.[74b]

$$G.F.^{\chi} = GCCI_M^{\chi} \left[x_k \rightarrow \sum_{r \varepsilon R} (w(r))^k\right]$$

It is obtained by replacing every x_k in $GCCI_M^{\chi}$ by $\sum_{r \varepsilon R} (w(r))^k$. The coefficient of a typical term $w_1^{b_1} w_2^{b_2} \ldots$ in $G.F.^{\chi}$ gives the number of times the irreducible representation Γ (whose character is χ) occurs in the representation spanned by nuclear spin functions. Consequently, Γ^{spin}, the representation spanned by spin functions can be obtained without having to know the character of Γ^{spin}. The author has illustrated this technique with several examples.

We will conclude this section with an example of non-rigid $B(CH_3)_3$ molecule. The molecule in its equilibrium geometry possesses $\underset{\sim}{C}_{3h}$ symmetry and the symmetry group of the non-rigid molecule is $D_{3h}[\underset{\sim}{C}_3]$. The character table of this group

was obtained by Longuet-Higgins. The nuclear spin statistical weights of the levels split by tunneling were obtained by the present author using generating function techniques. The symmetric top rotational levels in C_{3h} symmetry can be correlated to the split levels of non-rigid molecule. We show in Fig. 3 the splitting pattern and statistical weights of the 2 lowest levels of $^{11}B(CD_3)_3$.

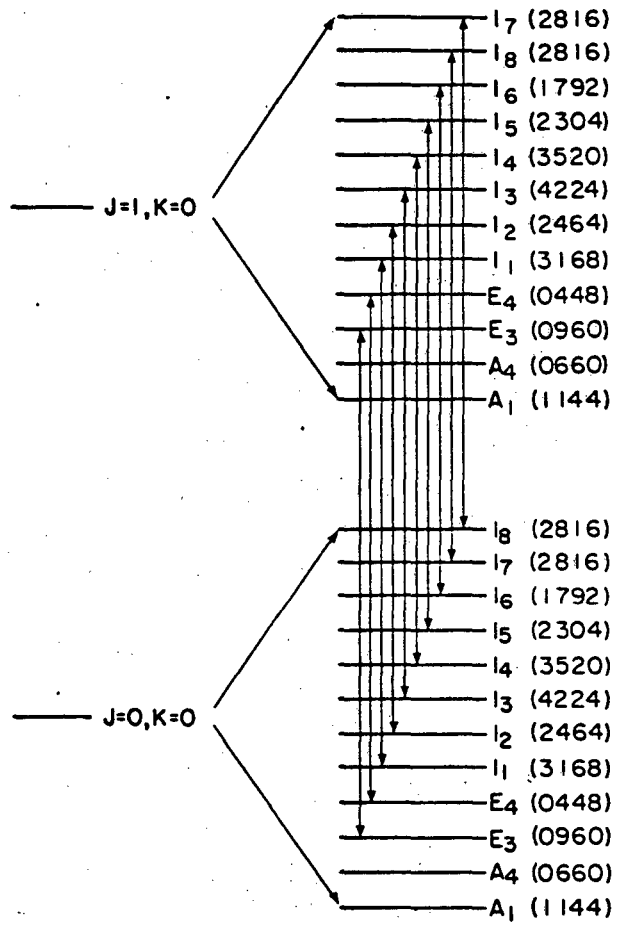

Figure 3. Tunneling-splitting, allowed transitions and nuclear spin statistics of non-rigid $^{11}B(CD_3)_3$. Figure shows only the two lowest levels.

4. APPLICATIONS TO MOLECULAR BEAM DEFLECTION AND ELECTRIC RESONANCE EXPERIMENTS OF WEAKLY BOUND VAN DER WAAL COMPLEXES

Klemperer and co-workers[75] have shown that it is possible to synthesize weakly bound complexes of several molecules like H_2O, HF, NH_3 etc. by a supersonic expansion. The Van der Waal complexes thus formed are non-rigid in that the weak bonds can be broken and made. Further, in dimers like $(NH_3)_2$ the protons of each unit rotate around the hydrogen bond and the umbrella inversion of protons are quite rapid. Molecular beam deflection and resonance experiments of these complexes reveal significant details about the dipole moment and structure

of these polymers. The microwave spectra of these complexes show a typical tunneling-splitting consistent with a model of a non-rigid complex. The tunneling-splitting is dependent on barrier heights and is quite large for these complexes. Hyperfine splittings of Stark transitions are consistent with spin species obtained using the non-rigid molecular groups of these molecules. Muenter and co-workers have studied Ammonic dimers[75] using molecular beam deflection and electric resonance experiments.

Dyke and co-workers[56] have recognized the use of wreath product groups in representing the symmetry of these complexes. All the permutation groups of these complexes are wreath products. The PI groups are either semi-direct product of P and I groups or direct product of P and I groups depending on the presence of inversion operation in the molecular symmetry group. To illustrate the PI groups of $(H_2O)_2$, $(NH_3)_2$ and $(C_6H_6)_2$ are $S_2[S_2] \times I$, $S_2[S_3] \times I$, $S_2[D_6] \wedge I$, where the symbol $\wedge$ is used to denote a semi-direct product.

5. APPLICATIONS OF NON-RIGID MOLECULAR GROUP THEORY TO NMR SPECTROSCOPY

The early applications of group theory to simplifying NMR spin Hamiltonian are due to McConne, McLean and Reilley[76] and Wilson.[77] Soon after the development of symmetry groups of non-rigid molecules by Longuet-Higgins, Woodman[10,15] showed that NMR groups of these molecules can be expressed as semi-direct product groups. He further showed that the composite particle representation is much superior to the total representation at every stage of NMR computation since the NMR Hamiltonian is much simpler in this representation. Flurry and co-workers[36,40,46] developed the unitary group treatment for the NMR problem. The present author[45] showed that the NMR group of any molecule can be obtained by a diagrammatic technique by representing the NMR spin Hamiltonian by an interaction diagram known as NMR graph.

The NMR spin Hamiltonian is of the form

$$H_{NMR} = \sum_i \nu_i I_{Zi} + \sum_{i<j}\sum J_{ij} \vec{I}_i \cdot \vec{I}_j .$$

where ν_i is the chemical shift of the ith nucleus and J_{ij} is the coupling constant between the nuclei i and j. The NMR group is defined as the set of permutations of nuclei that leave the NMR spin Hamiltonian invariant. In symbols, a permutation of the nuclei is in the NMR group if the corresponding permutation matrix P satisfies

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

The present author showed that a diagrammatic representation of H_{NMR} can be obtained by representing nuclei as vertices and edges by the coupling constants. Such a diagram is shown in Fig. 4 for $B(CH_3)_3$ where the center is the ^{11}B nucleus.

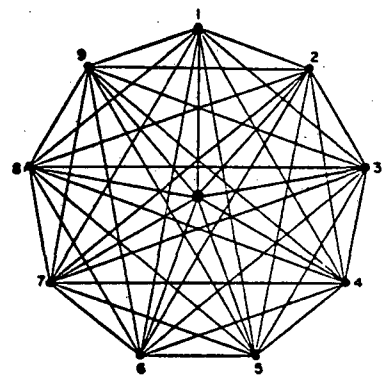

Figure 4. NMR graph of $^{11}B(CH_3)_3$. This is the interaction diagram of all the nuclear spins.

The NMR graph in Fig. 4 can be expressed as a composition of a graph Q and T shown in Fig. 5. That is, the graph in Fig. 4 can be obtained by replacing

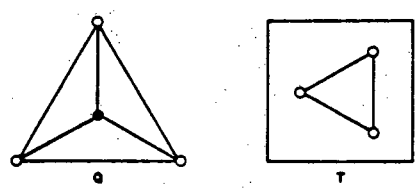

Figure 5. The NMR graph in Fig. 5 expressed as a composition of Q and T in this figure. The graph in Fig. 4 is obtainable by replacing every open vertex of Q by a copy of T.

every vertex of Q in Fig. 5 by a copy of T. In particle-in-box analogy vertices in Q are the boxes and the vertices in T are the particles in boxes. The group S_3 preserves the couplings restricted to Q and T. Consequently, the NMR group of $B(CH_3)_3$ is the wreath product $S_3[S_3]$. Figure 2 shows the particle-in-box picture for the NMR group of butane which is the generalized wreath product $S_2[S_3,S_2]$.

Flurry and co-workers[36,40,46,51] have developed the unitary group treatment for the NMR problem using the independent particle Hamiltonian operators. The unitary group and symmetric group treatments can be shown to be equivalent by way of generating Gel'fand bases with symmetric group approach which are the

basis sets for unitary group approach.

The present author[78] has developed recently projection operator methods by which the projection operators of NMR groups of very complex polyatomics can be obtained without having to know the character tables of NMR groups. We have shown in that paper that the projection operators of generalized wreath products can be obtained in terms of the projection operators of composing groups. We consider molecules containing as many as 2^{30} NMR spin functions.[78] Using the GCCI's of NMR groups, we obtained the NMR spin multiplets. The spin functions were partitioned into equivalence classes of spin functions using GCCI's and double coset methods. The projection operators are then applied on spin functions in each equivalence class (rather than the entire set of spin functions) and the NMR spin couplings are generated for computations. For details of these techniques the readers are referred to reference 78.

6. APPLICATIONS TO MOLECULAR REARRANGEMENTS AND ISOMERIZATION PROCESSES

Topological and symmetry analysis of isomerization processes is of great interest in recent years.[24,25,28,37] These topological schemes essentially describe interrelationship among a set of isomers of a molecule in its equilibrium geometry (rigid isomers) by non-rigid tunneling processes. These graph theoretical schemes generate diagrams known as isomerization graphs which provide insight not only into pathways and mechanisms that interconvert rigid isomers but also several important applications such as spontaneous generation of optical activity and dynamic NMR spectroscopy. Dynamic NMR enables understanding large amplitude motions as a function of temperature at experimentally feasible conditions. Experimentally, one observes splitting and coalescence of NMR signals as a function of temperature.

Randić[47] and more recently Randić and Klein[63] have studied the symmetry of the rearrangement processes of non-rigid molecules using the associated symmetry groups which are reminescent of non-rigid molecular symmetry groups. The present author[42] developed a topological scheme for this problem in which isomers of the rigid molecule are represented by vertices and the possible interconversions by edges. It was shown by the author[64] that the splitting patterns of these reaction graphs can be obtained by subducing the irreducible representations spanned by the isomers of the non-rigid molecule to the rigid symmetry group. This idea is similar to correlation of rovibronic levels from one symmetry limit to another.

Applications of topological schemes to NMR spectroscopy can be found in the papers of the author.[79] The coalescence and splitting patterns of NMR signals and intensity ratio patterns in dynamic processes can be generated using double coset methods and cycle indices.

The topic of isomers and related problems was recently reviewed by Slanina.[80] The readers are referred to this for more details.

7. APPLICATIONS TO CONFIGURATION INTERACTION CALCULATIONS

Recently the present author[54] showed that the number of symmetry-allowed configurations can be reduced if some of the molecular orbitals (MO's) used in configuration interaction (CI) calculations are degenerated. A CI calculation is essential to introduce correlation to self-consistent field (SCF) description of the electronic states of a molecule. When MO's are degenerate these orbitals can be considered as boxes which can be permuted in our particle-in-box model. Further, each orbital (box) can contain at most 2 electrons and switching the electrons in the boxes generates an equivalent configuration. The symmetry group of configurations can be defined as the permutations of degenerate orbitals and the electrons in the orbitals. This is precisely a generalized wreath product group. Two configurations can be considered equivalent if one is transformable into another by an element in the configuration symmetry group. Thus configurations can be partitioned into equivalence classes using this criterion. In this formalism one needs to evaluate CI matrix elements and formulas between one representative of an equivalence class with all the other elements in another class and matrix elements for each pair of elements in an equivalence class. All the other matrix elements can be constructed using the equivalence of configurations. This cuts down the total number of matrix elements. To illustrate, the configuration symmetry group of hexatriene in the localized orbital representation is the wreath product $S_2[S_2,S_2]$. The number of equivalence classes of space types is 71 while the total number of space types is 141.

8. APPLICATIONS TO CRYSTAL PHYSICS

Wreath product groups are useful in describing symmetry of crystals with structural distortions. The symmetry of crystals determines several interesting phenomena such as X-ray diffraction patterns, selection rules etc. There are several solid state systems such as $NaNO_2$, K_2MoO_4, ionic crystals such as $TaSe_2$ which can not be assigned to a crystallographic space group. These crystals exhibit structural distortions. Their crystallographic properties such as X-ray diffraction patterns cannot be predicted by using simple space groups. Litvin[81] has recently investigated such systems and showed that the space groups of these systems are subgroups of wreath products, in general. We will outline here his formalism as adapted into our notation.

Let R be a 3 x 3 rotation (improper or proper) matrix in eucledian space. Let $\vec{v}$ be a translation column vector. Then an element of the eucledian space

group in 3 dimension $\xi_s(3)$ which consists of all proper and improper rotations and translations in the eucledian space is denoted as $F = (R|\vec{v})$. An element F in $\xi_s(3)$ is a symmetry element of the crystal if

$$F\vec{r} = (R|\vec{v})\vec{r} = R\vec{r} + \vec{v}$$

where both $\vec{r}$ and $F\vec{r}$ are points in the crystal. That is the crystal is invariant under a composition of translation and rotation (proper or improper). The set of all such F's which leave the crystal invariant forms a group $\underline{F}_s$ which simply the symmetry group of the crystal. Let the crystal distortions be determined by a function $\vec{D}(\vec{r})$ which maps the points $\vec{r}$ to vectors $\vec{D}$ of a vector space V^-. The vector $\vec{D}$ is the distortion vector and V^- is the distortion space. Let $\underline{V}^-$ be the group obtained when V^- is considered as an abelian group under vector addition. Then one can see that an operation in the group $\underline{F}$ is in turn induced to the group $\underline{V}^-$. One can define a wreath product of the symmetry group of crystal $\underline{F}$ with that of distortion group, $\underline{V}^-$. It can be denoted as $\underline{F}[\underline{V}^-]$ and it is defined as follows. Let $\vec{v}$ be an element in $\underline{V}^-$ and F be an element in $\underline{F}$. Then the set of elements $(F;\vec{v}(\vec{r}))$ describes the symmetry of a crystal with structural distortions. The product of two elements $(F_1;\vec{v}_1(\vec{r}))$ and $(F_2;\vec{v}_2(\vec{r})$ is defined as in wreath products as

$$(F_1;\vec{v}_1(\vec{r}))(F_2;\vec{v}_2(\vec{r})) = (F_1F_2;\vec{v}_1(\vec{r})\cdot\vec{v}_{2F_1}(\vec{r}))$$

since $\underline{V}^-$ is an abelian group under vector addition the operation '·' in the group is vector addition. Thus

$$\vec{v}_1(\vec{r})\cdot v_{2F_1}(\vec{r}) = \vec{v}_1(r) + \vec{v}_{2F_1}(\vec{r}).$$

Note that as in the definition of wreath products

$$v_{2F_1}(\vec{r}) = \vec{v}_2(F_1^{-1}\,\vec{r}).$$

Inverse of any element $(F;\vec{v}(\vec{r}))$ is thus $(F^{-1};\ -\vec{v}(F\vec{r}))$.

Several applications of the wreath product groups thus defined for crystals with structural distortions such as formulation of a new Bloch's theorem in this group and applications to X-ray diffraction patterns of these crystals can be found in Litvin's paper.

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