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MARKS OF PERMUTATION GROUPS AND ISOMER ENUMERATION

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Abstract

The concept of the mark of a permutation group is at least eighty years old, but comparatively little use has been made of it until recently. Redfield rediscovered marks in the 1930's, but his work was not published until 1984. He used them to count group reduced distributions according to their symmetry groups. In this paper, the Mark Version of Redfield's Superposition Theorem is used to count isomers. The method is compared with a related method used by Hässelbarth, Mead and Fujita.

1. Introduction

A simple model for a molecule is to regard it as consisting of a skeleton with sites $S_1, S_2, \ldots, S_n$ together with a collection of ligands $L_1, L_2, \ldots, L_n$ with one ligand placed in each site. The correspondence between sites and ligands may be specified by a two-line array

$$\begin{bmatrix} S_{\tau(1)}S_{\tau(2)} \ldots S_{\tau(n)} \\ L_{\sigma(1)}L_{\sigma(2)} \ldots L_{\sigma(n)} \end{bmatrix},$$

where τ and σ are permutations of the set $\{1, 2, \ldots, n\}$ and ligand $L_{\sigma(i)}$ is in site $S_{\tau(i)}$, $i = 1, \ldots, n$. In general, the set of sites has a non-trivial symmetry group and so does the ligand set; furthermore, the order in which the columns of the array are written is unimportant. Thus, two arrays specify equivalent isomers if and only if one can be obtained from the other by a sequence of operations of the following three types:

(1) permuting elements in row 1 by an element of the site group A;

(2) permuting elements in row 2 by an element of the ligand group B;

(3) permuting intact columns of the array by elements of the symmetric group Sym(n) consisting of all permutations of the n columns.

The number of distinct (inequivalent) isomers is the number of equivalence classes (orbits) under the action of the three groups A, B and Sym(n).

It was pointed out by Davidson [1] that this is a special case of the type of problem considered by Redfield in his 1927 paper [2]. Redfield considered $q \times n$

arrays, but in this paper the general case is not needed, so results are stated for the case $q = 2$. In outline, Redfield's method for counting the number of inequivalent arrays (which he called *group reduced distributions*) is as follows.

(1) Form the cycle index polynomials (group reduction functions) Grf$A$ and Grf$B$ associated with A and B.

(2) Compose them together to form a new polynomial, denoted here by Grf$A$ * Grf$B$.

(3) Calculate the sum of the coefficients of Grf$A$ * Grf$B$ – this is the number of inequivalent arrays.

Fuller details, illustrated by chemical examples, may be found in ref. [3]. This procedure for counting group reduced distributions is often called the *Superposition Theorem*.

Each of the group reduced distributions has its own symmetry group Γ (the point group of the isomer for the examples in this paper) and Redfield also attempted to count the number with a specified symmetry group. He showed that Grf$A$ * Grf$B$ is a linear combination of the cycle indices of the possible symmetry groups Γ_i. Specifically, if there are ξ_i structures with symmetry group Γ_i, then

$$\mathrm{Grf}A * \mathrm{Grf}B = \sum_i \xi_i \mathrm{Grf}\Gamma_i . \tag{1}$$

Although Redfield was able to calculate the ξ_i in special cases, he encountered two difficulties in trying to solve the general problem:

(1) non-isomorphic groups can have identical cycle indices;

(2) the polynomials GrfΓ_i are usually linearly dependent, so even if it is known which groups occur, eq. (1) cannot be solved uniquely for the ξ_i.

The tool for finding the ξ_i is not the cycle index but the mark of a permutation group, details of which appear in the second edition of Burnside's book [4]. It appears, however, that Redfield had access to the first edition only, so he had to rediscover the theory of marks for himself (but he did not call them marks). By 1940 he had the complete solution, not only to the problem posed in his 1927 paper but also to a more general problem in which the symmetric group Sym(n) acting on intact columns of the array is replaced by a general group F called the *frame group*; the groups A and B are called *range groups* and must be subgroups of F. Unfortunately, the paper which Redfield wrote in 1940 was not published until 1984 [5].

The purpose of the present paper is to explain the Mark Version of Redfield's Superposition Theorem and to use it to count isomers according to their symmetry groups.

2. Representations of groups

A general problem in group representation theory is to break down a particular type of representation into simpler basic representations. The present paper is concerned

with permutation representations of groups, but since the theory of complex matrix representations is much better-known in mathematical chemistry (see, for example, Schonland [6] or Bishop [7]), this section summarises and contrasts certain results in the two theories. More detailed explanation of some of the terminology is given later.

In the theory of complex matrix representations, group elements are represented by invertible matrices with complex numbers as entries, and the basic representations are *irreducible representations*. A finite group has only finitely many irreducible representations and any representation is equivalent to a direct sum of irreducible representations. The *character* of a representation is the function which maps each group element to the trace of the corresponding matrix. Conjugate elements have the same character and irreducible characters are equinumerous with conjugacy classes of elements. Character functions of irreducible representations are linearly independent and the decomposition problem is equivalent to expressing the character function of a given representation as a linear combination of irreducible characters.

In the case of permutation representations, each group element is represented by a permutation of a set of objects and two objects are in the same *orbit* if there is a group element mapping one to the other. The basic representations are *transitive permutation representations*, that is, representations in which there is only one orbit. Again, a fiinite group has only finitely many transitive permutation representations and any permutation representation is a direct sum of such representations. Now the character of an element is just the number of objects fixed by the element, but the transitive permutation characters are usually linearly dependent, so a knowledge of them is insufficient to solve the decomposition problem.

A transitive permutation representation of G may be obtained by taking any subgroup $H \leq G$ and letting G act on the cosets Hk of H in G by right multiplication, $g: Hk \rightarrow Hkg$. Conjugate subgroups produce equivalent representations and any transitive permutation representation is equivalent to such a representation on cosets of some subgroup H. In fact, if an object ω is chosen from the set, then it is possible to take H as the subgroup of all permutations which fix ω (the group H is then called the stabilizer of ω). Hence, whereas irreducible representations of a group G are equinumerous with conjugacy classes of elements of G, transitive permutation representations are equinumerous with conjugacy classes of subgroups of G. The *mark* of a subgroup $H \leq G$ in a permutation representation (transitive or intransitive) is the number of objects invariant under every $h \in H$. The mark functions of transitive permutation representations are linearly independent, and for permutation representations it is the marks, not the characters, which provide the means to solve the decomposition problem.

In the case of group reduced distributions, the analogue of equation (1) is

$$m(A) \odot m(B) = \sum_i \xi_i m(\Gamma_i),$$

where mark vectors $\boldsymbol{m}$ (see section 3) replace cycle indices. This equation can be solved uniquely to find the number ξ_i of group reduced distributions with symmetry group Γ_i.

3. Permutation representations and their marks

Much of the basic theory of permutation representations, including marks, may be found in Burnside [4], but certain terminology has changed in the intervening eighty years and here more modern terminology is used. Apart from Burnside, few textbooks make any mention of marks, but a recent one which does is Krishnamurthy [8].

Let G be a finite group and let π be a homomorphism from G to a group of permutations of a finite set Ω. This means that each element $g \in G$ is represented by a permutation π_g of Ω. It is customary to say that g *acts on* Ω or that Ω is a *G-set* (or *G-space*) and to write ωg rather than $\pi_g(\omega)$ for the result of applying the permutation π_g to the element $\omega \in \Omega$.

DEFINITIONS

The following sets play important rôles in the theory.

(1) $\mathrm{Orb}(\omega) = \{\psi \in \Omega \mid \psi = \omega g \text{ for some } g \in G\}$, called the *orbit* of $\omega \in \Omega$.

(2) $\mathrm{Sta}(\omega) = \{g \in G \mid \omega = \omega g\}$, called the *stabilizer* of $\omega \in \Omega$; it is a subgroup of G.

(3) $\mathrm{Fix}(g) = \{\omega \in \Omega \mid \omega = \omega g\}$, called the *fixed point set* of $g \in G$.

(4) $\mathrm{Fix}(H) = \{\omega \in \Omega \mid \omega = \omega h, \text{ for all } h \in H\}$, called the *fixed point set* of the subgroup $H \leq G$.

All the above sets are defined with respect to a fixed representation π and when necessary to avoid ambiguity, they may be written $\mathrm{Orb}_\pi(\omega)$, etc.

DEFINITION

Let π be a permutation representation (transitive or intransitive) of a group G on Ω. The *G-mark* $m_{\pi H}$ of the subgroup H in the representation π is defined by $m_{\pi H} = |\mathrm{Fix}_\pi(H)|$, where $|X|$ denotes the number of elements in the set X.

In the case of a cyclic subgroup $C \leq G$, the set $\mathrm{Fix}(C) = \mathrm{Fix}(c)$, where c is any generator of C, and $m_{\pi c} = \chi_\pi(c)$, the permutation character of c.

If two subgroups are conjugate, then they have equal marks in the representation, so to find all transitive representations of G, it suffices to consider a complete set of representative subgroups $H_1, H_2, \ldots, H_t \leq G$, one for each conjugacy class.

The marks of transitive permutation representations are of particular interest.

DEFINITION

The *table of marks*, or *mark matrix*, of a group G is the matrix $M(G)$ with (i, j)-entry m_{ij} equal to the mark of the subgroup H_j in the representation π_i on the cosets of H_i in G. (The mark m_{ij} is also known as the mark of the subgroup H_j in the subgroup H_i.)

It can be shown that $m_{ij} = 0$ unless H_j is conjugate to a subgroup of H_i and that $m_{ii} \geq 1$ for any i. Because of this, if the representative subgroups are numbered in increasing order of size, then the table of marks is lower triangular and since it has no zero entries on the main diagonal, it is an invertible matrix. Redfield, however, adopted a slightly modified ordering in which the cyclic subgroups are numbered before the non-cyclic ones; this still gives a diagonal matrix.

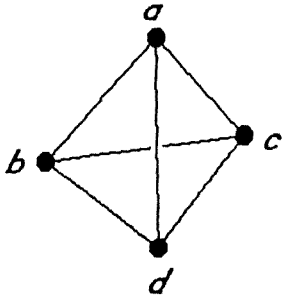

Fig. 1. Tetrahedron.

Example 1

The symmetric group Sym(4) of all permutations of four objects may be thought of as the tetrahedral group T_d acting on the four vertices a, b, c, d of a tetrahedron (see fig. 1). It has eleven conjugacy classes of subgroups and representative subgroups may be chosen and ordered as follows (see Foulkes [9]):

$$
\begin{aligned}
H_1 = E &= \{e\},\\
H_2 = C_s &= \{e, (ab)\},\\
H_3 = C_2 &= \{e, (ab)(cd)\},\\
H_4 = C_3 &= \{e, (abc), (acb\},\\
H_5 = S_4 &= \{e, (abcd), (ac)(bd), (adcb)\},\\
H_6 = D_2 &= \{e, (ab)(cd), (ac)(bd), (ad)(bc)\},\\
H_7 = C_{2v} &= \{e, (ab), (cd), (ab)(cd)\},\\
H_8 = C_{3v} &= \mathrm{Sta}(a) \cong \mathrm{Sym}(3),
\end{aligned}
$$

$H_9 = D_{2d} = \{e, (ac), (bd), (ac)(bd), (abcd), (adcb), (ad)(bc), (ab)(cd)\}$,

$H_{10} = T = \mathrm{Alt}(4)$,

$H_{11} = T_d = \mathrm{Sym}(4)$,

where Alt(n) is the *alternating group* of all even permutations of n objects.

The corresponding table $M(T_d)$ of marks of T_d, omitting zeros above the main diagonal is

$$\begin{bmatrix}
24 & & & & & & & & & & \\
12 & 2 & & & & & & & & & \\
12 & 0 & 4 & & & & & & & & \\
8 & 0 & 0 & 2 & & & & & & & \\
6 & 0 & 2 & 0 & 2 & & & & & & \\
6 & 0 & 6 & 0 & 0 & 6 & & & & & \\
6 & 2 & 2 & 0 & 0 & 0 & 2 & & & & \\
4 & 2 & 0 & 1 & 0 & 0 & 0 & 1 & & & \\
3 & 1 & 3 & 0 & 1 & 3 & 1 & 0 & 1 & & \\
2 & 0 & 2 & 2 & 0 & 2 & 0 & 0 & 0 & 2 & \\
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1
\end{bmatrix}.$$

Clearly, the rows of a mark matrix $M(G)$ are linearly independent. Each entry in column 1 gives the number of cosets in the corresponding representation, and the last row consists entirely of ones since there is only one coset for the subgroup $H_t = G$. Some authors (including Krishnamurthy [8] and Mead [10]) arrange the subgroups in decreasing order of size and this has the effect of transposing the mark table about the top-right/bottom-left diagonal. With such an ordering, the first column consists entirely of ones and the order of the matrices in the products below must be reversed.

DEFINITION

Row i of the table of marks $M(G)$ is called the *mark vector* $\boldsymbol{m}(\pi_i)$ of the representation π_i. More generally, if π is any representation of G (not necessarily transitive), then the *mark vector* (or, as Fujita [11] calls it, the *fixed point vector*)

$$\boldsymbol{m}(\pi) = (m_{\pi 1}, m_{\pi 2}, \ldots, m_{\pi t}),$$

where $m_{\pi i}$ is the mark of H_i in π.

When geometrical or chemical permutation representations occur, they do not usually present themselves immediately in terms of permutations of cosets of subgroups. In some cases, however, it is easy to construct an equivalent representation on cosets.

Example 2

For T_d acting as in example 1, the stabilizer $H = \mathrm{Sta}(a)$ of vertex a is a C_{3v} and the coset decomposition may be written

$$T_d = H \cup H(ab) \cup H(ac) \cup H(ad).$$

Provided one reads products of cycles from left to right, the cosets are:

$$H = \{e,(bcd),\ (bdc),\ (cd),\ (bd),\ (bc)\},$$

$$H(ab) = \{(ab),\ (acdb),\ (adcb),\ (ab)\,(cd),\ (adb),\ (acb)\},$$

$$H(ac) = \{(ac),\ (adbc),\ (abdc),\ (adc),\ (ac)\,(bd),\ (abc)\},$$

$$H(ad) = \{(ad),\ (abcd),\ (acbd),\ (acd),\ (abd),\ (ad)\,(bc)\}.$$

Adopting the convention that $(\ldots xy\ldots)$ or $(y\ldots x)$ in a cycle means that vertex x moves to where vertex y used to be, then

(1) coset H consists of all elements fixing a;

(2) for $x = b, c, d$, coset $H(ax)$ consists of all elements moving vertex a to the old position of vertex x.

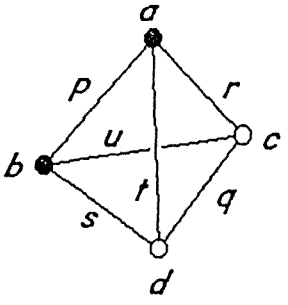

Fig. 2. Tetrahedron with two black and two white vertices.

Example 3

Let T_d act on a tetrahedron with two black vertices a, b and two white vertices c, d (see fig. 2). In this case, $H = \mathrm{Sta}(a)$ is a C_{2v}. The coset decomposition is

$$T_d = H \cup H(ac)\,(bd) \cup H(bc) \cup H(ad) \cup H(bd) \cup H(ac),$$

but it is more illuminating to express the elements as permutations of the edges p, q, r, s, t, u of the tetrahedron. The decomposition becomes

$$T_d = H \cup H(qp)\,(ut) \cup H(rp)\,(sq) \cup H(sp)\,(rq) \cup H(tp)\,(uq) \cup H(up)\,(tq).$$

Here,

(1) each element in coset H fixes edge p;

(2) each element in $H(qp)(ut)$ moves edge q to the old position of p;

(3) for $x = r, s, t, u$, each element in $H(xp)(yq)$ moves edge x to the old position of p (and, necessarily, the edge y opposite to x to the old position of edge q).

4. The Mark Version of Redfield's Superposition Theorem

In section 1, the group A acts on elements in the first row of the array. Let $\boldsymbol{m}(A)$ be the F-mark vector corresponding to the action of F on the cosets of A in F. Similarly, B acts on elements of the second row of the array and has F-mark vector $\boldsymbol{m}(B)$ corresponding to the action of F on the cosets of B. Now if $H_j \leq F$ fixes m_{Aj} cosets Af and m_{Bj} cosets Bg, then it fixes $m_{Aj}m_{Bj}$ pairs (Af, Bg) of cosets. Hence, the mark vector for the action of F on ordered pairs of cosets is the coordinate-by-coordinate product denoted here by $\boldsymbol{m}(A) \odot \boldsymbol{m}(B)$ and defined by

$$\boldsymbol{m}(A) \odot \boldsymbol{m}(B) = (m_{A1}m_{B1}, m_{A2}m_{B2}, \ldots, m_{At}m_{Bt}).$$

Redfield's technique [5] for counting group reduced distributions according to their symmetry groups may be summarised as follows.

SUPERPOSITION THEOREM (MARK VERSION)

Let $M(F)$ be the table of marks of a frame group F, the rows and columns of which correspond to representative subgroups $H_1, H_2, \ldots, H_t$ and let $A, B \leq F$ be range groups. The number ξ_i of group reduced distributions which have a symmetry group conjugate to H_i may be obtained by the following algorithm:

(1) Calculate the F-mark vectors $\boldsymbol{m}(A)$ and $\boldsymbol{m}(B)$ of A and B, respectively.

(2) Multiply them together coordinate by coordinate to obtain the vector $\boldsymbol{m}(A) \odot \boldsymbol{m}(B)$.

(3) Find the vector $\boldsymbol{\xi} = (\xi_1, \xi_2, \ldots, \xi_t)$ such that

$$\boldsymbol{m}(A) \odot \boldsymbol{m}(B) = \boldsymbol{\xi} M(F). \tag{2}$$

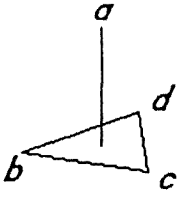

Fig. 3. Trigonal pyramidal skeleton.

Example 4

Let A be the full symmetry group (including reflexions) of the set of sites a, b, c, d on a trigonal pyramidal skeleton (see fig. 3) and let the ligand collection be $XXYZ$. The site group A is a C_{3v} and the ligand group B is a symmetric group Sym(2) generated by the permutation that interchanges the two identical ligands. From rows 2 and 8 of the table $M(T_d)$ of marks,

$$\boldsymbol{m}(B) = [12\ 2\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0]$$

and

$$\boldsymbol{m}(A) = [4\ 2\ 0\ 1\ 0\ 0\ 0\ 1\ 0\ 0\ 0],$$

so

$$\boldsymbol{m}(A) \odot \boldsymbol{m}(B) = [48\ 4\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0].$$

Expressed as a linear combination of rows of $M(T_d)$,

$$\boldsymbol{m}(A) \odot \boldsymbol{m}(B) = [24\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0] + 2[12\ 2\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0],$$

so

$$\boldsymbol{m}(A) \odot \boldsymbol{m}(B) = \boldsymbol{m}(E) + 2\boldsymbol{m}(C_s).$$

The interpretation is that placing the ligands X^2YZ on a skeleton with C_{3v} symmetry leads to three distinct isomers, one with E as point group and the other two with C_s. For such a simple example, this is easy to check and the three isomers are shown in fig. 4.

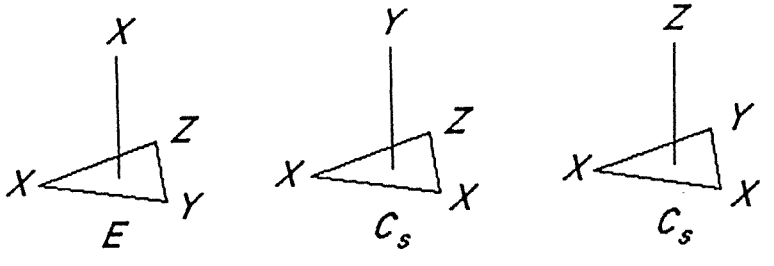

Fig. 4. Isomers with trigonal pyramidal skeleton and ligands $XXYZ$.

A similar procedure is possible for any collection of ligands and, by replacing some of the vectors by matrices, all cases may be treated simultaneously. The possible ligand collections are $WXYZ$, $XXYZ$, $XXYY$, $XXXY$, $XXXX$. The corresponding ligand groups are E, Sym(2), Sym(2) × Sym(2), Sym(3), Sym(4), respectively. Their T_d-mark vectors form the rows of the matrix $N(L)$ below.

$$N(L) = \begin{bmatrix} 24 & & & & & & & & & & & \\ 12 & 2 & & & & & & & & & & \\ 6 & 2 & 2 & 0 & 0 & 0 & 2 & & & & & \\ 4 & 2 & 0 & 1 & 0 & 0 & 0 & 1 & & & & \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix}.$$

The product $\boldsymbol{m}(A) \odot \boldsymbol{m}(B)$ can be written as a matrix product provided one of the vectors is replaced by a diagonal matrix. Here, a fixed skeleton is under consideration, so it is preferable to write $\boldsymbol{m}(A) \odot \boldsymbol{m}(B) = \boldsymbol{m}(B)$ diag $\boldsymbol{m}(A)$, but it would also be possible to consider a fixed ligand collection and all the symmetry types of skeletons to which the ligands could be attached. Equation (2) becomes

$$\boldsymbol{m}(B) \text{ diag } \boldsymbol{m}(A) = \xi M(F).$$

Working with $N(L)$ rather than with $\boldsymbol{m}(B)$ gives the matrix Λ, where

$$N(L) \text{ diag } \boldsymbol{m}(A) = \Lambda = \Xi M(F), \tag{3}$$

and the entry ξ_{ij} in the *isomer counting matrix* Ξ is the number of isomers with symmetry group H_j which may be formed using the ith ligand collection.

Since $M = M(F)$ is invertible, it follows from (3) that

$$\Xi = \Lambda M^{-1},$$

and from (2) that

$$\xi = (\boldsymbol{m}(A) \odot \boldsymbol{m}(B))M^{-1}.$$

In practice, however, it is not necessary to calculate M^{-1}. One needs to express $\boldsymbol{m}(A) \odot \boldsymbol{m}(B)$ as a linear combination of the rows of M. Because M is triangular, working from the bottom row to the top row in M very quickly produces the coordinates of ξ in the reverse order $\xi_t, \ldots, \xi_2, \xi_1$. A similar calculation can be done separately for each row of Λ in order to obtain Ξ.

In the present example, the matrices in eq. (3) are:

$$\begin{bmatrix} 24 & & & & & & & & & & & \\ 12 & 2 & & & & & & & & & & \\ 6 & 2 & 2 & 0 & 0 & 0 & 2 & & & & & \\ 4 & 2 & 0 & 1 & 0 & 0 & 0 & 1 & & & & \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} 4 & & & & & & & & & & & \\ 0 & 2 & & & & & & & & & & \\ 0 & 0 & 0 & & & & & & & & & \\ 0 & 0 & 0 & 1 & & & & & & & & \\ 0 & 0 & 0 & 0 & 0 & & & & & & & \\ 0 & 0 & 0 & 0 & 0 & 0 & & & & & & \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & & & & & \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & & & & \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & & & \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & & \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$= \begin{bmatrix} 96 & & & & & & & & & & \\ 48 & 4 & & & & & & & & & \\ 24 & 4 & 0 & 0 & 0 & 0 & 0 & & & & \\ 16 & 4 & 0 & 1 & 0 & 0 & 0 & 1 & & & \\ 4 & 2 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}$$

$$= \begin{bmatrix} 4 & & & & & & & & & & \\ 1 & 2 & & & & & & & & & \\ 0 & 2 & 0 & 0 & 0 & 0 & 0 & & & & \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & & & \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 24 & & & & & & & & & & \\ 12 & 2 & & & & & & & & & \\ 12 & 0 & 4 & & & & & & & & \\ 8 & 0 & 0 & 2 & & & & & & & \\ 6 & 0 & 2 & 0 & 2 & & & & & & \\ 6 & 0 & 6 & 0 & 0 & 6 & & & & & \\ 6 & 2 & 2 & 0 & 0 & 0 & 2 & & & & \\ 4 & 2 & 0 & 1 & 0 & 0 & 0 & 1 & & & \\ 3 & 1 & 3 & 0 & 1 & 3 & 1 & 0 & 1 & & \\ 2 & 0 & 2 & 2 & 0 & 2 & 0 & 0 & 0 & 2 & \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix}.$$

Here, the fourth rows of Λ and Ξ correspond to ligands *XXXY*. Since

$$[16\,4\,0\,1\,0\,0\,0\,1\,0\,0\,0] = [12\,2\,0\,0\,0\,0\,0\,0\,0\,0\,0] + [4\,2\,0\,1\,0\,0\,0\,1\,0\,0\,0],$$

or, equivalently,

$$\boldsymbol{m}(C_{3v}) \odot \boldsymbol{m}(C_{3v}) = \boldsymbol{m}(C_s) + \boldsymbol{m}(C_{3v}),$$

it follows that with ligands *XXXY* there are two isomers, one with C_s symmetry and one with C_{3v} (see fig. 5).

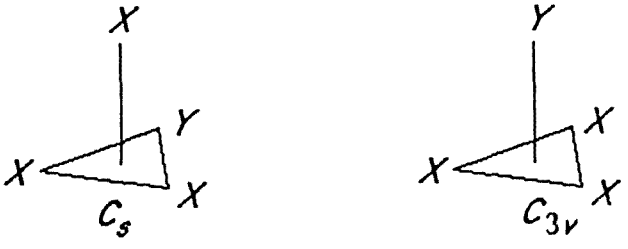

Fig. 5. Isomers with trigonal pyramidal skeleton and ligands *XXXY*.

A great many zeros occur in the above matrices, so it is possible to delete various rows and columns which provide no relevant information. Let:

(1) $N'(L)$, Λ' and Ξ' be the submatrices of $N(L)$, Λ and Ξ obtained by deleting those columns which do not correspond to subgroups of A;

(2) $\boldsymbol{m}'(A)$ be the subvector of $\boldsymbol{m}(A)$ obtained by deleting coordinates which do not correspond to subgroups of A;

(3) $M'(A)$ be the submatrix of $M(F)$ obtained by deleting both rows and columns which do not correspond to subgroups of A.

Then, from eq. (3),

$$N'(L)\ \mathrm{diag}\ \boldsymbol{m}'(A) = \Lambda' = \Xi' M'(A). \tag{4}$$

In example 4, where $F = T_d$ and $A = C_{3v}$, the reduced matrices are

$$\begin{bmatrix} 24 & & & \\ 12 & 2 & & \\ 6 & 2 & 0 & \\ 4 & 2 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} 4 & & & \\ 0 & 2 & & \\ 0 & 0 & 1 & \\ 0 & 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 96 & & & \\ 48 & 4 & & \\ 24 & 4 & 0 & \\ 16 & 4 & 1 & 1 \\ 4 & 2 & 1 & 1 \end{bmatrix} = \begin{bmatrix} 4 & & & \\ 1 & 2 & & \\ 0 & 2 & 0 & \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 24 & & & \\ 12 & 2 & & \\ 8 & 0 & 2 & \\ 4 & 2 & 1 & 1 \end{bmatrix}.$$

5. Alternative calculations using marks

In the examples in section 4, all marks are marks with respect to the group $T_d \cong \mathrm{Sym}(4)$. In general, the groups A and B must be subgroups of F. In the case where the ligands are all different, $B = \mathrm{Sym}(n)$, so it seems to be necessary to take the frame group $F = \mathrm{Sym}(n)$ and, therefore, to work solely with $\mathrm{Sym}(n)$-marks when using the Superposition Theorem to count isomers. However, in their papers, Hässelbarth [12], Mead [10], and Fujita [11] use $\mathrm{Sym}(n)$-marks for the ligand group B only; they use A-marks for the site group A. In some cases (as explained below), the two methods are entirely equivalent, but in other cases, they produce slightly different results.

The diagonal matrix $\mathrm{diag}\ \boldsymbol{m}'(A)$ is invertible, so (4) may be rewritten:

$$N'(L) = \Xi' M'(A)\big(\mathrm{diag}\ \boldsymbol{m}'(A)\big)^{-1}. \tag{5}$$

Let

$$M''(A) = M'(A)\big(\mathrm{diag}\ \boldsymbol{m}'(A)\big)^{-1}.$$

so that

$$N'(L) = \Xi' M''(A). \tag{6}$$

The construction

$$M(\mathrm{Sym}(n)) \rightarrow M'(A) \rightarrow M''(A)$$

consists of deleting redundant rows and colums from $M(\mathrm{Sym}(n))$ to obtain $M'(A)$ and then scaling each column of $M'(A)$ so that the resulting matrix $M''(A)$ has ones in the last row. In example 4,

$$M'(A) = \begin{bmatrix} 24 & & & \\ 12 & 2 & & \\ 8 & 0 & 2 & \\ 4 & 2 & 1 & 1 \end{bmatrix}, \quad M''(A) = \begin{bmatrix} 6 & & & \\ 3 & 1 & & \\ 2 & 0 & 2 & \\ 1 & 1 & 1 & 1 \end{bmatrix}.$$

In this example, $M''(A) = M(A)$, the table of marks of A, so (6) can be rewritten:

$$N'(L) = \Xi' M(A). \tag{7}$$

In general, however, $M''(A) \neq M(A)$. For example, two subgroups which are non-conjugate in A may be conjugate in Sym(n) by an element which lies outside A. In such a case, the matrices $M''(A)$ and $M(A)$ are different sizes. Nevertheless, it still seems to be the case that there are corresponding matrices $N''(L)$ and Ξ'' such that:

$$N''(L) = \Xi'' M(A). \tag{8}$$

An equation of this form is used by Hässelbarth [12], Mead [10], and Fujita [11] in some of their calculations on isomer enumeration. The rows of $N''(L)$ are mark vectors of a hybrid nature: their entries are Sym(n)-marks, but the columns correspond not to conjugacy classes of subgroups of Sym(n) but to conjugacy classes of subgroups of A.

Example 5

The group C_{2v} has five conjugacy classes of subgroups, with representatives

$H_1 = E \quad = \{e\},$

$H_2 = C_{sh} = \{e, (ab)\},$

$H_3 = C_{sv} = \{e, (cd)\},$

$H_4 = C_2 \quad = \{e, (ab)(cd)\},$

$H_5 = C_{2v} = \{e, (ab), (cd), (ab)(cd)\},$

Its table of marks is

$$\begin{bmatrix} 4 & & & & \\ 2 & 2 & & & \\ 2 & 0 & 2 & & \\ 2 & 0 & 0 & 2 & \\ 1 & 1 & 1 & 1 & 1 \end{bmatrix}.$$

When C_{2v} is considered as a subgroup of T_d, the subgroups H_2 and H_3 are conjugate under $(ac)(bd)$ since

$$(ac)(bd) \times (cd) \times (ac)(bd) = (ab).$$

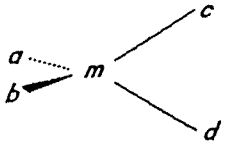

Fig. 6. Skeleton with C_{2v} symmetry.

A geometrical explanation may be given by considering the action of C_{2v} on the sites a, b, c, d in fig. 6. Here, a, b lie in a horizontal plane, c, d lie in a vertical plane, and bond lengths $am = bm \neq cm = dm$. Each of the subgroups H_2 and H_3 is a C_s, but they are sometimes distinguished by calling them C_{sh} and C_{sv}. In the action under C_{2v}, the sets $\{a, b\}$ and $\{c, d\}$ form separate orbits but the action under Sym(4) places all four into a common orbit – the latter action ignores the differences in bond lengths. A calculation using the Superposition Theorem with Sym(4) marks and reduced matrices gives

$$\begin{bmatrix} 24 & & & \\ 12 & 2 & & \\ 6 & 2 & 2 & 2 \\ 4 & 2 & 0 & 0 \\ 1 & 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} 6 & & & \\ 0 & 2 & & \\ 0 & 0 & 2 & \\ 0 & 0 & 0 & 2 \end{bmatrix} = \begin{bmatrix} 144 & & & \\ 72 & 4 & & \\ 36 & 4 & 4 & 4 \\ 24 & 4 & 0 & 0 \\ 6 & 2 & 2 & 2 \end{bmatrix}$$

$$= \begin{bmatrix} 6 & & & \\ 2 & 2 & & \\ 1 & 0 & 0 & 2 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 24 & & & \\ 12 & 2 & & \\ 12 & 0 & 4 & \\ 6 & 2 & 2 & 2 \end{bmatrix}.$$

Using $M''(A)$, the matrices are

$$\begin{bmatrix} 24 & & & \\ 12 & 2 & & \\ 6 & 2 & 2 & 2 \\ 4 & 2 & 0 & 0 \\ 1 & 1 & 1 & 1 \end{bmatrix} = \begin{bmatrix} 6 & & & \\ 2 & 2 & & \\ 1 & 0 & 0 & 2 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 4 & & & \\ 2 & 1 & & \\ 2 & 0 & 2 & \\ 1 & 1 & 1 & 1 \end{bmatrix}.$$

By contrast, the corresponding calculation using eq. (8) and the C_{2v} mark table is

$$\begin{bmatrix} 24 & & & & \\ 12 & 2 & 2 & & \\ 6 & 2 & 2 & 2 & 2 \\ 4 & 2 & 2 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{bmatrix} = \begin{bmatrix} 6 & & & & \\ 2 & 1 & 1 & & \\ 1 & 0 & 0 & 0 & 2 \\ 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 4 & & & & \\ 2 & 2 & & & \\ 2 & 0 & 2 & & \\ 2 & 0 & 0 & 2 & \\ 1 & 1 & 1 & 1 & 1 \end{bmatrix}.$$

The single column in $N'(L)$ corresponding to C_s is replaced in $N''(L)$ by a pair of identical columns, one for C_{sh}, the other for C_{sv}. Consequently, the second column col(2 0 2 0) in Ξ' splits into two separate but identical columns col(1 0 1 0) in Ξ''. So the second calculation counts isomers with C_{sh} symmetry separately from those with C_{sv} symmetry; the first calculation does not. The isomers corresponding to the entries in Ξ'' (apart from those with four different ligands $WXYZ$) are shown in fig. 7.

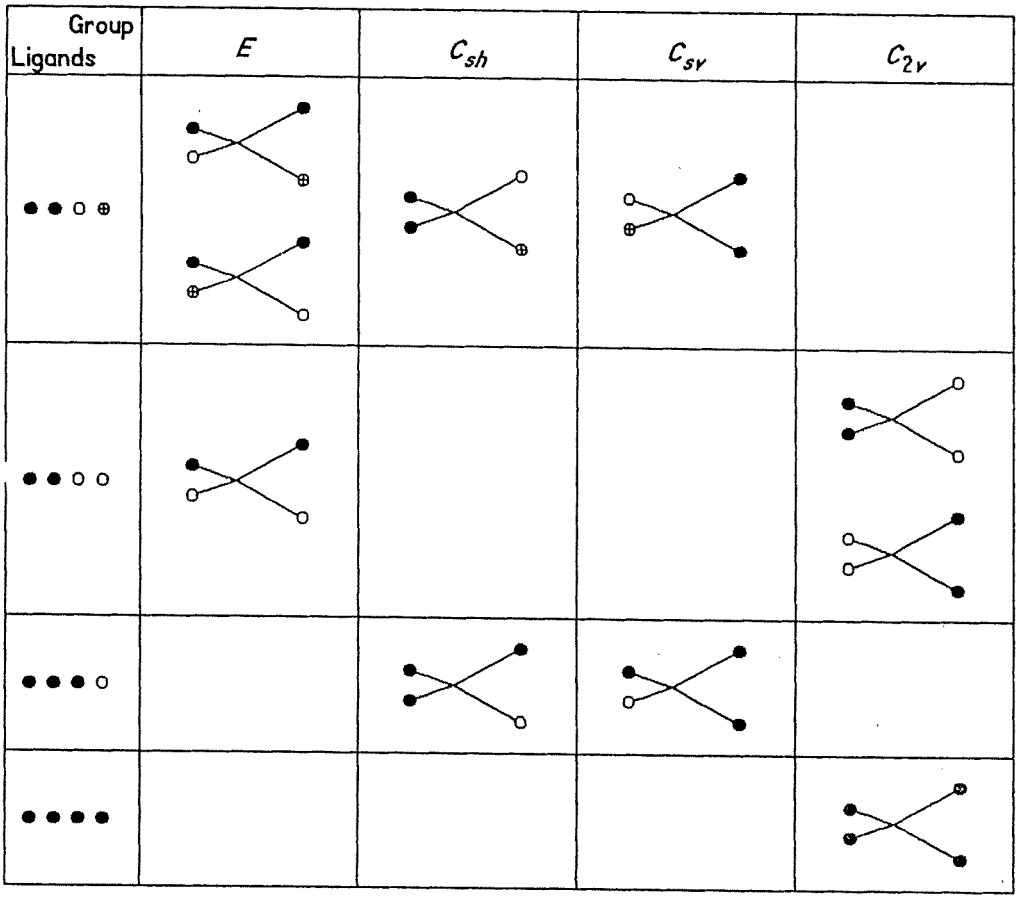

Fig. 7. Isomers with C_{2v} skeleton. There are also six with four different ligands (any two of which may be in sites a and b); all of these have E symmetry. There are no isomers with C_2 symmetry.

6. Concluding remarks

It is often possible to formulate a problem in terms of frame group and range groups in more than one way and different formulations may involve different numbers of range groups. This suggests that there may be a reformulation which enables eq. (8) to be deduced directly from the Superposition Theorem, but it is not immediately clear how this might be done.

In the Pólya theory of enumeration, much use is made of generating functions (see Pólya [13], Read [14], and Lloyd [15]). Both Hässelbarth [12] and Fujita [11] have used generating functions in combination with marks.

Several papers have appeared in the chemistry literature on the use of double cosets in isomer enumeration (see, for example, Brocas [16], and Mead [10]). Both

the original Redfield Superposition Theorem and the Mark Version may be construed in terms of double cosets; further details may be found in Hall, Palmer and Robinson [17].

Redfield's second paper was not published until forty-four years after it was written and in the meantime, some of the results in it were rediscovered independently by other authors. Hall et al. [17] discuss the relationship between Redfield's results and those in more recent articles.

Note added in proof

Burnside first introduced marks in 1901 (see ref. [18]); two recent books [19,20] include mark tables for several groups.

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