Generalization of Partial Cycle Indices and Modified Bisected Mark Tables for Combinatorial Enumeration

Shinsaku Fujita

Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585

(Received September 16, 1999)

Generalized partial cycle indices have been proposed as a generalization of partial cycle indices (PCIs) in order to enumerate isomers with a given set of subsymmetries. To evaluate the coefficient of each term appearing in such a generalized PCI, the natures of a mark table and of its inverse have been examined after the proposal of (modified) bisected mark tables and their inverses as well as of (modified) bisected tables of unit subduced cycle indices with chirality fittingness (USCI-CFs). The inverse of a (modified) bisected mark table and the (modified) bisected USCI-CF table have been applied to the enumeration of chiral isomers and achiral isomers.

Pólya's theorem has been widely used to solve various problems of counting isomers.[1—5] It has been also applied to the enumeration of optical isomers.[6—11] More elaborate enumerations of isomers with given formulas and symmetries have been developed, where mark tables have played an important role.[12—18] These methods have been correlated to Pólya's method.[14,19]

We have recently developed four methods for combinatorial enumeration, which are based on the subduction of coset representations: (1) a generating-function method using subduced cycle indices (SCIs) and mark tables,[20] (2) a generating-function method using partial cycle indices (PCIs),[21] (3) a method based on the elemental superposition,[22] and (4) a method based on the partial superposition.[22,21] These methods are collectively called "the unit-subduced-cycle-index (USCI) approach".[20,23] The correlation of USCIs to Pólya's cycle indices has been discussed.[24] They have not been, however, appplied to the counting of optical isomers. Study of such gross enumeration has been considered unnecessary, because the methods of the USCI approach are able to count isomers in itemized manners concerning their symmetries.

More recently, we have developed the characteristic-monomial method for enumerating isomers.[25—29] This method is applied to the enumeration of optical isomers.[30] The procedure for the gross enumeration of optical isomers has required extensive studies on the group-subgroup relationship. The latter have prompted us to examine the applicability of the methods of the USCI approach to such gross enumeration, since we expected to obtain additional information on the nature of mark tables and of USCI tables.

In this paper, we first generalize the PCI method to cover an arbitrary set of subgroups. We then propose bisected or modified bisected tables of marks as well as bisected or modified bisected tables of USCIs with and without chirality fittingness. By virtue of the nature of mark tables and of USCI tables, we apply the methods of the USCI approach to the gross enumeration of optical isomers.

1 Theoretical Formulation

1.1 Generalization of Partial Cycle Indices. Suppose that a set of ligands (or atoms or substituents) selected from

$$\mathbf{X} = \{X_1, X_2, \cdots, X_{|\mathbf{X}|}\} \tag{1}$$

are placed on the positions of a skeleton belonging to the group $\mathbf{G}$, where the positions are governed by a set of coset representations $(\sum_{i=1}^{s} \alpha_i \mathbf{G}(/\mathbf{G}_i))$. Such a set of coset representations corresponds to a set of subgroups represented by

$$\mathrm{SSG}_{\mathbf{G}} = \{\mathbf{G}_1, \mathbf{G}_2, \cdots, \mathbf{G}_s\}, \tag{2}$$

where each $\mathbf{G}_i$ is a representative selected from its conjugate subgroups. The number of isomeric derivatives is calculated by the partial-cycle-index (PCI) method of the unit-subduced-cycle-index (USCI) approach.[23] We have pre-calculated the subduction into each subgroup (up to conjugate), i.e., $\mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}_j$, which are transformed to the corresponding unit subduced cycle index with or without chirality fittingness (USCI-CF or USCI). They are tabulated in the form of a subduction table and a USCI table for the group $\mathbf{G}$, as shown in Appendices C and D of Ref. 23. In the present paper, we will restrict our discussion to USCI-CFs and related matters, but the results obtained hold true for USCIs. The USCI-CFs for every representative group have been collected in the form of UCSI-CF tables in Appendex E of Ref. 23. The USCI-CFs are multiplied according to the subduction,

$$\sum_{i=1}^{s} \alpha_i \mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}_j, \tag{3}$$

to give a subduced cycle index with chirality fittingness (SCI-CF) concerning the subgroup $\mathbf{G}_j$, which is designated by the symbol $\mathrm{ZIC}(\mathbf{G}_j; \$_{d_{jk}})$ (Definition 19.3 (Eq. 19.26) of Ref. 23). For the sake of simplicity, the symbol $\$_{d_{jk}}$ is used to designate a set of ligand inventories, $a_{d_{jk}}$, $b_{d_{jk}}$, and $c_{d_{jk}}$. Thereby, Def. 19.6 (Eq. 16.55) of Ref. 23 gives the partial cyclel index with chirality fittingness (PCI-CF) for $\mathbf{G}_i$ as follows:

$$\mathrm{PCIC}(\mathbf{G}_i; \$_{d_{jk}}) = \sum_{j=1}^{s} \overline{m}_{ji} \mathrm{ZIC}(\mathbf{G}_j; \$_{d_{jk}}) \quad (4)$$

for $i = 1,2,\cdots,s$, where $\overline{m}_{ji}$ is the ji-element of the inverse mark table for $\mathbf{G}$.

Let U be a subset of $\mathrm{SSG}_\mathbf{G}$. Then, we newly define a generalized PIC-CF for the set U as the sum of PCI-CFs:

$$\mathrm{PCIC}(U; \$_{d_{jk}}) = \sum_{G_i \in U} \mathrm{PCIC}(\mathbf{G}_i; \$_{d_{jk}}) = \sum_{G_i \in U} \sum_{j=1}^{s} \overline{m}_{ji} \mathrm{ZIC}(\mathbf{G}_j; \$_{d_{jk}}), \quad (5)$$

where $\mathbf{G}_i$ runs over U. Since $\mathrm{ZIC}(\mathbf{G}_j; \$_{d_{jk}})$ for $G_i \in U$ has the same coefficient if j is tentatively fixed, the order of summations in Eq. 5 can be interchanged to give

$$\mathrm{PCIC}(U; \$_{d_{jk}}) = \sum_{j=1}^{s} \left(\sum_{G_i \in U} \overline{m}_{ji} \right) \mathrm{ZIC}(\mathbf{G}_j; \$_{d_{jk}}). \quad (6)$$

The set U can be selected appropriately for the purpose of enumeration. For example, if U involves all of the chiral groups of $\mathrm{SSG}_\mathbf{G}$, the PCI-CF is used to enumerate all of the chiral isomers based on $\mathbf{G}$. It should be noted that the inner sum of Eq. 6 is concerned with the selected set (U) for each row of the inverse of the mark table.

Let $A_{U\nu}$ be the number of isomers with the weight $W_{[\nu]}$,

$$W_{[\nu]} = \prod_{\ell=1}^{|\mathbf{X}|} X_\ell^{\nu_\ell}, \quad (7)$$

and a given symmetry selected from U ($\subset \mathrm{SSG}_\mathbf{G}$). By starting from Eqs. 5 and 6, we are able to obtain a generating function for giving $A_{U\nu}$, as summarized in a theorem:

Theorem 1. *Let $A_{U\nu}$ be the number of isomers with the weight $W_{[\nu]}$ and a given set (U) of subsymmetries. The generating function for giving $A_{U\nu}$ is represented by*

$$\sum_{[\nu]} A_{U\nu} W_{[\nu]} = \mathrm{PCIC}(U; \$_{d_{jk}}), \quad (8)$$

where the dummy variables \$ in the PCI-CF are replaced by ligand inventories,

$$a_{d_{jk}} = \sum_{\ell=1}^{|\mathbf{X}|} (X_\ell^{(a)})^{d_{jk}} \quad (9)$$

$$b_{d_{jk}} = \sum_{\ell=1}^{|\mathbf{X}|} X_\ell^{d_{jk}} \quad (10)$$

$$c_{d_{jk}} = \sum_{\ell=1}^{|\mathbf{X}|} (X_\ell^{(a)})^{d_{jk}} + 2\sum_{\ell=1}^{|\mathbf{X}|} (X_\ell^{(c)} \overline{X}_\ell^{(c)})^{d_{jk}/2}, \quad (11)$$

where $X_\ell^{(a)}$ is an achiral ligand, while $X_\ell^{(c)}$ represents a chiral ligand.

The right-hand side of Eq. 8 represents a generalized PCI-CF (Eq. 6). Though U may be any subset selected from $\mathrm{SSG}_\mathbf{G}$, it is useful to examine a meaningful subset for the purpose of enhancing our knowledge on chemical combinatorics. Hereafter, we pay special attention to the case in which U consists of all of the chiral subgroups of $\mathrm{SSG}_\mathbf{G}$ as well as the case in which U consists of all of the achiral subgroups of $\mathrm{SSG}_\mathbf{G}$.

As an extreme case, we take all the subgroups (achiral and chiral) into consideration, for the inner sum of Eq. 6 has been calculated in Eq. 16.25 of Ref. 23:

$$N_j = \sum_{i=1}^{s} \overline{m}_{ji} = \begin{cases} \varphi(|\mathbf{G}_j|)/|\mathbf{N}_\mathbf{G}(\mathbf{G}_j)| & \text{if } \mathbf{G}_j \text{ is cyclic} \\ 0 & \text{otherwise} \end{cases}, \quad (12)$$

where the summation ($i = 1$ to s) covers $U = \mathrm{SSG}_\mathbf{G}$; the symbol $\varphi(n)$ represents Euler's function for integer n; and the symbol $\mathbf{N}_\mathbf{G}(\mathbf{G}_j)$ designates the normalizer of the subgroup $\mathbf{G}_j$ within $\mathbf{G}$. When the variable \$ is replaced by s and the set U is selected to be equal to $\mathrm{SSG}_\mathbf{G}$, Eq. 6 can be converted into a cycle index, where the coefficient of each term is given by Eq. 12. The resulting cycle index has been proved to be equivalent to Pólya's cycle index (see Chapter 16 of Ref. 23).

1.2 Bisected and Modified Bisected Tables of Marks. Let $\mathbf{G}$ be a group of finite order and let $\mathbf{G}_i$ and $\mathbf{G}_j$ represent subgroups of $\mathbf{G}$. In the light of Theorem 2 of Ref. 31, a coset representation $\mathbf{G}(/\mathbf{G}_i)$ is subduced into $\mathbf{G}_j$ according to the following relationship:

$$\mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}_j = \sum_{g \in \Gamma} \mathbf{G}_j(/g^{-1}\mathbf{G}_i g \cap \mathbf{G}_j), \quad (13)$$

where Γ represents a transversal of the double coset decomposition concerning $\mathbf{G}_i$ and $\mathbf{G}_j$.

Suppose that the coset representation $\mathbf{G}(/\mathbf{G}_i)$ is enantiospheric. The term "enantiospheric" means that the group $\mathbf{G}$ is an achiral group, while the subgroup $\mathbf{G}_i$ is a chiral group.[32] If the group $\mathbf{G}_j$ is achiral, the group $g^{-1}\mathbf{G}_i g \cap \mathbf{G}_j$ in Eq. 13 is chiral, because the group $g^{-1}\mathbf{G}_i g$ is chiral. It follows that all of the coset representations $\mathbf{G}_j(/g^{-1}\mathbf{G}_i g \cap \mathbf{G}_j)$ are enantiospheric, where $|\mathbf{G}_j|/|g^{-1}\mathbf{G}_i g \cap \mathbf{G}_j|$ is an even integer equal to or larger than 2. Hence, we arrive at a theorem:

Theorem 2. *An enantiospheric coset representation is subduced into an achiral subgroup to give a set of enentiospheric coset representations.*

In other words, each of the coset representations $\mathbf{G}_j(g^{-1}\mathbf{G}_i g \cap \mathbf{G}_j)$ is different from $\mathbf{G}_j(/\mathbf{G}_j)$. Since each $\mathbf{G}_j(/\mathbf{G}_j)$ corresponds to a one-membered orbit ($|\mathbf{G}_j|/|\mathbf{G}_j| = 1$) associated with a fixed point, the right-hand side of Eq. 13 indicates that the mark (i.e. the number of fixed points) corresponding to $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$ is equal to zero. Hence we arrive at a corollary as follows.

Corollary 1.1. *Suppose that $\mathbf{G}(/\mathbf{G}_i)$ be an enantiospheric coset representation, where $\mathbf{G}_i$ is a chiral subgroup of an achiral group $\mathbf{G}$. Let $\mathbf{G}_j$ be an achiral subgroup of $\mathbf{G}$. Then, the mark corresponding to the subduction $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$ is equal to zero.*

In the light of Corollary 1.1, a mark table of an achiral group can be modified into an alternative lower triangular matrix in which the rows for enantiospheric coset representations and the columns for chiral subgroups appear in the upper-left part. This operation gathers the marks corresponding to chiral groups, so as to form a "chiral section". The resulting lower triangular matrix is called "a bisected table of marks" or "a bisected mark table (BM table)". The marks of zero value evaluated by Corollary 1.1 are assembled in the upper-right part of the resulting bisected mark table. The lower triangular nature for the upper-left part (the chiral section) or the lower-right part is assured by the comparison of the order of subgroups for the bisected mark table with the one for the original mark table.

Moreover, Theorem 7 of Ref. 33 allows us to gather the marks for cyclic chiral subgroups into the upper-left part as well as to place the marks for cyclic achiral subgroups just after the chiral section. The resulting matrix is called "a modified bisected table of marks" or "a modified bisected mark table (MBM table)". More precisely speaking, let $\mathbf{G}^{(m)}$ be the maximum chiral subgroup of $\mathbf{G}$. Then, the resulting MBM table has the order of columns:

$$\mathbf{G}_{c1}^{(m)}, \mathbf{G}_{c2}^{(m)}, \cdots; \mathbf{G}_{1}^{(m)}, \mathbf{G}_{2}^{(m)}, \cdots, \mathbf{G}^{(m)}; \mathbf{G}_{c1}, \mathbf{G}_{c2}, \cdots; \mathbf{G}_1, \mathbf{G}_2, \cdots, \mathbf{G}$$

and the order of rows:

$$\mathbf{G}(/\mathbf{G}_{c1}^{(m)}), \mathbf{G}(/\mathbf{G}_{c2}^{(m)}), \cdots; \mathbf{G}(/\mathbf{G}_{1}^{(m)}), \mathbf{G}(/\mathbf{G}_{2}^{(m)}), \cdots, \mathbf{G}(/\mathbf{G}^{(m)});$$
$$\mathbf{G}(/\mathbf{G}_{c1}), \mathbf{G}(/\mathbf{G}_{c2}), \cdots; \mathbf{G}(/\mathbf{G}_1), \mathbf{G}(/\mathbf{G}_2), \cdots, \mathbf{G}(/\mathbf{G}),$$

where the subscripts $c1$, $c2$, $\cdots$ represent that they are concerned with cyclic subgroups; and we have

$$|\mathbf{G}_{c1}^{(m)}| \leq |\mathbf{G}_{c2}^{(m)}| \leq \cdots; \quad |\mathbf{G}_{1}^{(m)}| \leq |\mathbf{G}_{2}^{(m)}| \leq \cdots \leq |\mathbf{G}^{(m)}|;$$
$$|\mathbf{G}_{c1}| \leq |\mathbf{G}_{c2}| \leq \cdots; \quad |\mathbf{G}_1| \leq |\mathbf{G}_2| \leq \cdots \leq |\mathbf{G}|.$$

The superscript (m) represents the subjection concerning $\mathbf{G}_{(m)}$. For the sake of simplicity, the subgroups and the coset representations are renumbered according to the orders obtained above. Let $U^{(c)}$ be the subset of all the chiral subgroups (up to conjugate) of $\mathbf{G}$ and let $U^{(a)}$ the subset of all the achiral subgroups (up to conjugate) of $\mathbf{G}$. Then, the renumbered subgroups are categorized as follows:

$$U^{(c)} = \{\mathbf{G}_1, \mathbf{G}_2, \cdots, \mathbf{G}_t\} \text{ for the chiral subgroups} \quad (14)$$

$$U^{(a)} = \{\mathbf{G}_{t+1}, \mathbf{G}_{t+2}, \cdots, \mathbf{G}_s\} \text{ for the achiral subgroups} \quad (15)$$

$$\mathrm{SSG}_{\mathbf{G}} = U^{(c)} + U^{(a)} \text{ for all the subgroups.} \quad (16)$$

In terms of this numbering, we can obtain the MBM table for $\mathbf{G}$ which can be represented by a matrix:

$$M = \left(\begin{array}{cccc|cccc} m_{11} & & & & & & & \\ m_{21} & m_{22} & & & & & & \\ \vdots & \vdots & \ddots & & & & & \\ m_{t1} & m_{t2} & \cdots & m_{tt} & & & & \\ \hline m_{t+1,1} & m_{t+1,2} & \cdots & m_{t+1,t} & m_{t+1,t+1} & & & \\ m_{t+2,1} & m_{t+2,2} & \cdots & m_{t+2,t} & m_{t+2,t+1} & m_{t+2,t+2} & & \\ \vdots & \vdots & & \vdots & \vdots & \vdots & \ddots & \\ m_{s1} & m_{s2} & \cdots & m_{st} & m_{s,t+1} & m_{s,t+2} & \cdots & m_{s,s} \end{array}\right) \quad (17)$$

where the upper-left part (a $t \times t$ matrix) is its chiral section. Obviously, the inverse of the MBM table (M^{-1}) is also a lower triangular matrix.

For the point group $\mathbf{T}_d$, the bisected mark table (BM table) and the modified bisected mark table (MBM table) are identical, as shown in Table 1. The inverse of the MBM table is shown in Table 2. Note that the point groups, $\mathbf{C}_1$, $\mathbf{C}_2$, and $\mathbf{C}_3$, are chiral cyclic subgroups, while the point groups, $\mathbf{C}_s$ and $\mathbf{S}_4$, are achiral cyclic subgroups.

The BM table and the MBM table are also identical with each other for the point group $\mathbf{D}_{2d}$, as shown in Table 3. The inverse of the MBM table is shown in Table 4. The point groups, $\mathbf{C}_1$, $\mathbf{C}_2$, and $\mathbf{C}_2'$, are chiral cyclic subgroups, while the point groups, $\mathbf{C}_s$ and $\mathbf{S}_4$, are achiral cyclic subgroups.

1.3 Modified Bisected USCI-CF Tables. In concord with the procedure for constructing MBM tables, we are able to transform USCI-CF tables[23] into modified bisected USCI-CF tables. For example, Table 5 shows the modified bisected

Table 1. (Modified) Bisected Mark Table for $\mathbf{T}_d$

	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_3$	$\mathbf{D}_2$	$\mathbf{T}$	$\mathbf{C}_s$	$\mathbf{S}_4$	$\mathbf{C}_{2v}$	$\mathbf{C}_{3v}$	$\mathbf{D}_{2d}$	$\mathbf{T}_d$
$\mathbf{T}_d(/\mathbf{C}_1)$	24	0	0	0	0	0	0	0	0	0	0
$\mathbf{T}_d(/\mathbf{C}_2)$	12	4	0	0	0	0	0	0	0	0	0
$\mathbf{T}_d(/\mathbf{C}_3)$	8	0	2	0	0	0	0	0	0	0	0
$\mathbf{T}_d(/\mathbf{D}_2)$	6	6	0	6	0	0	0	0	0	0	0
$\mathbf{T}_d(/\mathbf{T})$	2	2	2	2	2	0	0	0	0	0	0
$\mathbf{T}_d(/\mathbf{C}_s)$	12	0	0	0	0	2	0	0	0	0	0
$\mathbf{T}_d(/\mathbf{S}_4)$	6	2	0	0	0	0	2	0	0	0	0
$\mathbf{T}_d(/\mathbf{C}_{2v})$	6	2	0	0	0	2	0	2	0	0	0
$\mathbf{T}_d(/\mathbf{C}_{3v})$	4	0	1	0	0	2	0	0	1	0	0
$\mathbf{T}_d(/\mathbf{D}_{2d})$	3	3	0	3	0	1	1	1	0	1	0
$\mathbf{T}_d(/\mathbf{T}_d)$	1	1	1	1	1	1	1	1	1	1	1

Table 2. Inverse of (Modified) Bisected Mark Table for $\mathbf{T}_d$

	$(/\mathbf{C}_1)$	$(/\mathbf{C}_2)$	$(/\mathbf{C}_3)$	$(/\mathbf{D}_2)$	$(/\mathbf{T})$	$(/\mathbf{C}_s)$	$(/\mathbf{S}_4)$	$(/\mathbf{C}_{2v})$	$(/\mathbf{C}_{3v})$	$(/\mathbf{D}_{2d})$	$(/\mathbf{T}_d)$	Sum
$\mathbf{C}_1$	$\frac{1}{24}$	0	0	0	0	0	0	0	0	0	0	$\frac{1}{24}$
$\mathbf{C}_2$	$-\frac{1}{8}$	$\frac{1}{4}$	0	0	0	0	0	0	0	0	0	$\frac{1}{8}$
$\mathbf{C}_3$	$-\frac{1}{6}$	0	$\frac{1}{2}$	0	0	0	0	0	0	0	0	$\frac{1}{3}$
$\mathbf{D}_2$	$\frac{1}{12}$	$-\frac{1}{4}$	0	$\frac{1}{6}$	0	0	0	0	0	0	0	0
$\mathbf{T}$	$\frac{1}{6}$	0	$-\frac{1}{2}$	$-\frac{1}{6}$	$\frac{1}{2}$	0	0	0	0	0	0	0
$\mathbf{C}_s$	$-\frac{1}{4}$	0	0	0	0	$\frac{1}{2}$	0	0	0	0	0	$\frac{1}{4}$
$\mathbf{S}_4$	0	$-\frac{1}{4}$	0	0	0	0	$\frac{1}{2}$	0	0	0	0	$\frac{1}{4}$
$\mathbf{C}_{2v}$	$\frac{1}{4}$	$-\frac{1}{4}$	0	0	0	$-\frac{1}{2}$	0	$\frac{1}{2}$	0	0	0	0
$\mathbf{C}_{3v}$	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0	-1	0	0	1	0	0	0
$\mathbf{D}_{2d}$	0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0	$-\frac{1}{2}$	$-\frac{1}{2}$	0	1	0	0
$\mathbf{T}_d$	$-\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	1	0	0	-1	-1	1	0

Table 3. (Modified) Bisected Mark Table for $\mathbf{D}_{2d}$

	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}'_2$	$\mathbf{D}_2$	$\mathbf{C}_s$	$\mathbf{S}_4$	$\mathbf{C}_{2v}$	$\mathbf{D}_{2d}$
$\mathbf{D}_{2d}(/\mathbf{C}_1)$	8	0	0	0	0	0	0	0
$\mathbf{D}_{2d}(/\mathbf{C}_2)$	4	4	0	0	0	0	0	0
$\mathbf{D}_{2d}(/\mathbf{C}'_2)$	4	0	2	0	0	0	0	0
$\mathbf{D}_{2d}(/\mathbf{D}_2)$	2	2	2	2	0	0	0	0
$\mathbf{D}_{2d}(/\mathbf{C}_s)$	4	0	0	0	2	0	0	0
$\mathbf{D}_{2d}(/\mathbf{S}_4)$	2	2	0	0	0	2	0	0
$\mathbf{D}_{2d}(/\mathbf{C}_{2v})$	2	2	0	0	2	0	2	0
$\mathbf{D}_{2d}(/\mathbf{D}_{2d})$	1	1	1	1	1	1	1	1

Table 4. Inverse of (Modified) Bisected Mark Table for $\mathbf{D}_{2d}$

	$(/\mathbf{C}_1)$	$(/\mathbf{C}_2)$	$(/\mathbf{C}'_2)$	$(/\mathbf{D}_2)$	$(/\mathbf{C}_s)$	$(/\mathbf{S}_4)$	$(/\mathbf{C}_{2v})$	$(/\mathbf{D}_{2d})$	Sum
$\mathbf{C}_1$	$\frac{1}{8}$	0	0	0	0	0	0	0	$\frac{1}{8}$
$\mathbf{C}_2$	$-\frac{1}{8}$	$\frac{1}{4}$	0	0	0	0	0	0	$\frac{1}{8}$
$\mathbf{C}'_2$	$-\frac{1}{4}$	0	$\frac{1}{2}$	0	0	0	0	0	$\frac{1}{4}$
$\mathbf{D}_2$	$\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{1}{2}$	$\frac{1}{2}$	0	0	0	0	0
$\mathbf{C}_s$	$-\frac{1}{4}$	0	0	0	$\frac{1}{2}$	0	0	0	$\frac{1}{4}$
$\mathbf{S}_4$	0	$-\frac{1}{4}$	0	0	0	$\frac{1}{2}$	0	0	$\frac{1}{4}$
$\mathbf{C}_{2v}$	$\frac{1}{4}$	$-\frac{1}{4}$	0	0	$-\frac{1}{2}$	0	$\frac{1}{2}$	0	0
$\mathbf{D}_{2d}$	0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	1	0

USCI-CF table for $\mathbf{T}_d$, which is derived from the corrsponding USCI-CF table reported in Appendix E of Ref. 23.[34]

As a matter of course, the columns corresponding to chiral groups contain monomials that consist of dummy variables (b_d) for hemispheric coset representations. This proposition is exemplified by the upper-left and the lower-left parts of Table 5.

The upper-right part of each modified bisected USCI-CF table involves monomials that consist of dummy variables (c_d) for enantiospheric coset representations. This proposition is in agreement with Theorem 2. Table 5 exemplifies such enantiospheric dummy variables, as shown in the upper-right part.

Table 6 shows the modified bisected USCI-CF table for $\mathbf{D}_{2d}$, in which the columns corresponding to chiral groups contain monomials that consist of dummy variables (b_d) for hemispheric coset representations. The upper-right part of Table 6 involves monomials that consist of dummy variables (c_d) for enantiospheric coset representations. These variables are in agreement with Theorem 2.

Table 6. (Modified) Bisected USCI-CF Table for $\mathbf{D}_{2d}$

	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}'_2$	$\mathbf{D}_2$	$\mathbf{C}_s$	$\mathbf{S}_4$	$\mathbf{C}_{2v}$	$\mathbf{D}_{2d}$
$\mathbf{D}_{2d}(/\mathbf{C}_1)$	b_1^8	b_2^4	b_2^4	b_4^2	c_2^4	c_4^2	c_4^2	c_8
$\mathbf{D}_{2d}(/\mathbf{C}_2)$	b_1^4	b_1^4	b_2^2	b_2^2	c_2^2	c_2^2	c_2^2	c_4
$\mathbf{D}_{2d}(/\mathbf{C}'_2)$	b_1^4	b_2^2	$b_1^2b_2$	b_2^2	c_2^2	c_4	c_4	c_4
$\mathbf{D}_{2d}(/\mathbf{D}_2)$	b_1^2	b_1^2	b_1^2	b_1^2	c_2	c_2	c_2	c_2
$\mathbf{D}_{2d}(/\mathbf{C}_s)$	b_1^4	b_2^2	b_2^2	b_4	$a_1^2c_2$	c_4	a_2^2	a_4
$\mathbf{D}_{2d}(/\mathbf{S}_4)$	b_1^2	b_1^2	b_2	b_2	c_2	a_1^2	c_2	a_2
$\mathbf{D}_{2d}(/\mathbf{C}_{2v})$	b_1^2	b_1^2	b_2	b_2	a_1^2	c_2	a_1^2	a_2
$\mathbf{D}_{2d}(/\mathbf{D}_{2d})$	b_1	b_1	b_1	b_1	a_1	a_1	a_1	a_1

1.4 Chiral Sections. Let us consider the chiral section of an MBM table represented by Eq. 17. The corresponding section of the inverse of the MBM table is picked up to give an element, $\overline{m}_{\ell k}$. Then the multiplication of the chiral part and its inverse gives an identity matrix, i.e.,

$$\sum_{\ell=1}^{t} m_{i\ell}\overline{m}_{\ell k} = \delta_{ik} \tag{18}$$

for $i = 1, 2, \cdots, t$ and $k = 1, 2, \cdots, t$, where the symbol δ_{ik} represents Kronecker's delta.

We first focus our attention on the $\mathbf{G}(/\mathbf{G}^{(m)})$-row (i.e. the t-th row) of the MBM table. Since the coset representation $\mathbf{G}(/\mathbf{G}^{(m)})$ is enantiospheric and $|\mathbf{G}|/|\mathbf{G}^{(m)}|$ is equal to 2, its subduction into each subgroup $\mathbf{G}_i^{(m)}$ of $\mathbf{G}^{(m)}$ satisfies the following equation:

$$\mathbf{G}(/\mathbf{G}^{(m)}) \downarrow \mathbf{G}_i^{(m)} = 2\mathbf{G}_i^{(m)}(/\mathbf{G}_i^{(m)}). \tag{19}$$

The resulting coset representation $\mathbf{G}_i^{(m)}(/\mathbf{G}_i^{(m)})$ governs a one-membered orbit associated with a fixed point. It follows that the mark corresponding to each subduction $\mathbf{G}(/\mathbf{G}^{(m)})\downarrow\mathbf{G}_i^{(m)}$ is equal to 2. This proposition is exemplified by the elements appearing in the $\mathbf{T}_d(/\mathbf{T})$-row of Table 1 as well as the $\mathbf{D}_{2d}(/\mathbf{D}_2)$-row of Table 3. Equation 19 is translated into the nature of the element in the t-th row of M, i.e.,

$$m_{t\ell} = 2 \tag{20}$$

where ℓ runs from 1 to t. This equation is introduced into Eq. 18 to give

Table 5. Modified Bisected USCI-CF Table for $\mathbf{T}_d$

	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_3$	$\mathbf{D}_2$	$\mathbf{T}$	$\mathbf{C}_s$	$\mathbf{S}_4$	$\mathbf{C}_{2v}$	$\mathbf{C}_{3v}$	$\mathbf{D}_{2d}$	$\mathbf{T}_d$
$\mathbf{T}_d(/\mathbf{C}_1)$	b_1^{24}	b_2^{12}	b_3^8	b_4^6	b_{12}^2	c_2^{12}	c_4^6	c_4^6	c_6^4	c_8^3	c_{24}
$\mathbf{T}_d(/\mathbf{C}_2)$	b_1^{12}	$b_1^4b_2^4$	b_3^4	b_2^6	b_6^2	c_2^6	$c_2^2c_4^2$	$c_2^2c_4^2$	c_6^2	c_4^3	c_{12}
$\mathbf{T}_d(/\mathbf{C}_3)$	b_1^8	b_2^4	$b_1^2b_3^2$	b_4^2	b_4^2	c_2^4	c_4^2	c_4^2	c_2c_6	c_8	c_8
$\mathbf{T}_d(/\mathbf{D}_2)$	b_1^6	b_1^6	b_3^2	b_1^6	b_3^2	c_2^3	c_2^3	c_2^3	c_6	c_2^3	c_6
$\mathbf{T}_d(/\mathbf{T})$	b_1^2	b_1^2	b_1^2	b_1^2	b_1^2	c_2	c_2	c_2	c_2	c_2	c_2
$\mathbf{T}_d(/\mathbf{C}_s)$	b_1^{12}	b_2^6	b_3^4	b_4^3	b_{12}	$a_1^2c_2^5$	c_4^3	$a_2^2c_4^2$	$a_3^2c_6$	a_4c_8	a_{12}
$\mathbf{T}_d(/\mathbf{S}_4)$	b_1^6	$b_1^2b_2^2$	b_3^2	b_2^3	b_6	c_2^3	$a_1^2c_4$	c_2c_4	c_6	a_2c_4	c_6
$\mathbf{T}_d(/\mathbf{C}_{2v})$	b_1^6	$b_1^2b_2^2$	b_3^2	b_2^3	b_6	$a_1^2c_2^2$	c_2c_4	$a_1^2c_4$	a_3^2	a_2c_4	c_6
$\mathbf{T}_d(/\mathbf{C}_{3v})$	b_1^4	b_2^2	b_1b_3	b_4	b_4	$a_1^2c_2$	c_4	a_2^2	a_1a_3	a_4	a_4
$\mathbf{T}_d(/\mathbf{D}_{2d})$	b_1^3	b_1^3	b_3	b_1^3	b_3	a_1c_2	a_1c_2	a_1c_2	a_3	a_1c_2	a_3
$\mathbf{T}_d(/\mathbf{T}_d)$	b_1	b_1	b_1	b_1	b_1	a_1	a_1	a_1	a_1	a_1	a_1

$$\sum_{\ell=1}^{t} \overline{m}_{\ell k} = \frac{1}{2}\delta_{tk} \tag{21}$$

for $k = 1,2,\cdots t$. The relationship (Eq. 21) clarified that the sum of every column in the chiral section of the inverse MBM table of **G** is equal to zero except that the sum of the t-th column in the chiral section is equal to 1/2. This is exemplified by each column of the chiral section of Table 2 or Table 4. For example, the (/$\mathbf{C}_1$)-column of Table 2 indicates

$$\frac{1}{24} - \frac{1}{8} - \frac{1}{6} + \frac{1}{12} + \frac{1}{6} = 0. \tag{22}$$

As for the full summation concerning each column of the MBM table, Eq. 16.26 of Ref. 23 holds true to indicate

$$\sum_{\ell=1}^{s} \overline{m}_{\ell k} = \delta_{sk} \tag{23}$$

for $k = 1,2,\cdots, s$. Hence, the remaining elements in each column of the MBM table (the lower-left part) can be evaluated by using Eq. 21 (the summation from 1 to t) and Eq. 23 (the summation from 1 to s). Thus, the difference between Eq. 23 and Eq. 21 gives

$$\sum_{\ell=t+1}^{s} \overline{m}_{\ell k} = -\frac{1}{2}\delta_{tk} \tag{24}$$

for $k = 1,2,\cdots t$, where the summation is concerned with the achiral subgroups of **G**. Equation 24 means that the sum of every column in the lower-left section of the inverse MBM table of **G** is equal to zero except that the corresponding sum of the t-th column is equal to $-1/2$. This proposition is exemplified by the lower-left part of Table 2 or Table 4. For example, the remaining elements in the (/$\mathbf{C}_1$)-column of Table 2 indicate

$$-\frac{1}{4} + 0 + \frac{1}{4} + \frac{1}{2} + 0 - \frac{1}{2} = 0. \tag{25}$$

Under the condition that i is tentatively fixed, Eq. 18 is summed up from $k = 1$ to t to give

$$\sum_{\ell=1}^{t} m_{i\ell}\Big(\sum_{k=1}^{t} \overline{m}_{\ell k}\Big) = \sum_{k=1}^{t} \delta_{ik} = 1, \tag{26}$$

since Kronecker's delta is equal to 1 only if k is equal to i. Equation 26 holds true for $i = t$ (the t-th row of M). Hence, Eq. 20 is introduced into Eq. 26 to give

$$\sum_{\ell=1}^{t}\Big(\sum_{k=1}^{t} \overline{m}_{\ell k}\Big) = \frac{1}{2}. \tag{27}$$

The upper-right part of zero value in M^{-1} can be added to the inner summation of Eq. 27 without changing the value of the equation. It follows that the covering region from 1 to t is changed into the region from 1 to s so as to give

$$\sum_{\ell=1}^{t}\Big(\sum_{k=1}^{s} \overline{m}_{\ell k}\Big) = \frac{1}{2}. \tag{28}$$

Note that the inner summation $\sum_{k=1}^{s} \overline{m}_{\ell k}$ is equal to N_ℓ, as shown in Eq. 12. Moreover, Eq. 16.26 of Ref. 23 gives

$$\sum_{\ell=1}^{s}\Big(\sum_{k=1}^{s} \overline{m}_{\ell k}\Big) = 1. \tag{29}$$

The comparison between Eqs. 28 and 29 gives

$$\sum_{\ell=t+1}^{s}\Big(\sum_{k=1}^{s} \overline{m}_{\ell k}\Big) = \frac{1}{2}. \tag{30}$$

Equation 30 is concerned with all (up to conjugate) of the achiral subgroups of **G**, while Eq. 28 is concerned with all (up to conjugate) of the chiral subgroups of **G**. These relationships are exemplified the rightmost column (sum) of Table 2 for $\mathbf{T}_d$, i.e., 1/2+1/8+1/4 = 1/2 and 1/4+1/4 = 1/2.

1.5 Maximum Chiral Subgroups. In order to obtain more information on the chiral section of the MBM table for **G** and on its inverse, let us now consider the modified mark table of $\mathbf{G}^{(m)}$ and its inverse. For example, those for the point group **T**, which is the maximum chiral subgroup of $\mathbf{T}_d$, are shown in Tables 7 and 8. These are cited from Appendix A and B of Ref. 23. The target of this section is to obtain the relationship between the chiral section for **G** and the mark table of its maximum chiral group $\mathbf{G}^{(m)}$.

Let $M^{(m)}$ (= $(m_{\ell k}^{(m)})$) be the modified mark table of $\mathbf{G}^{(m)}$ and let $(M^{(m)})^{-1}$ (= $(\overline{m}_{\ell k}^{(m)})$) be its inverse. Then, their multiplication gives an identity matrix, i.e.,

$$\sum_{\ell=1}^{t'} m_{i\ell}^{(m)} \overline{m}_{\ell k}^{(m)} = \delta_{ik} \tag{31}$$

for $i = 1,2,\cdots t'$ and $k = 1,2,\cdots t'$, where δ_{ik} represents Kronecker's delta. Note that t and t' are equal or different according to fusion behavior of the conjugate subgroups in **G** and $\mathbf{G}^{(m)}$. Thus, the target is restated to be the examination of the relationship between Eq. 18 and Eq. 31.

Suppose that the coset representation $\mathbf{G}(/\mathbf{G}_i)$ is enantiospheric. In the light of Lemma 10.1 of Ref. 23, the subduction into $\mathbf{G}^{(m)}$ gives two cases as follows:

$$\mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}^{(m)} = \begin{cases} 2\mathbf{G}^{(m)}(/\mathbf{G}_i) \\ \mathbf{G}^{(m)}(/\mathbf{G}_i) + \mathbf{G}^{(m)}(/\mathbf{G}'_i) \end{cases} \tag{32}$$

where $\mathbf{G}_i$ and $\mathbf{G}'_i$ are conjugate within **G** but not within $\mathbf{G}^{(m)}$. Let $\mathbf{G}_j^{(m)}$ be the maximum chiral subgroup of an achiral subgroup $\mathbf{G}_j$. Further subduction gives

Table 7. (Modified) Mark Table for **T**

	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_3$	$\mathbf{D}_2$	$\mathbf{T}$
$\mathbf{T}(/\mathbf{C}_1)$	12	0	0	0	0
$\mathbf{T}(/\mathbf{C}_2)$	6	2	0	0	0
$\mathbf{T}(/\mathbf{C}_3)$	4	0	1	0	0
$\mathbf{T}(/\mathbf{D}_2)$	3	3	0	3	0
$\mathbf{T}(/\mathbf{T})$	1	1	1	1	1

Table 8. Inverse of (Modified) Mark Table for **T**

	(/$\mathbf{C}_1$)	(/$\mathbf{C}_2$)	(/$\mathbf{C}_3$)	(/$\mathbf{D}_2$)	(/$\mathbf{T}$)	Sum
$\mathbf{C}_1$	$\frac{1}{12}$	0	0	0	0	$\frac{1}{12}$
$\mathbf{C}_2$	$-\frac{1}{4}$	$\frac{1}{2}$	0	0	0	$\frac{1}{4}$
$\mathbf{C}_3$	$-\frac{1}{3}$	0	1	0	0	$\frac{2}{3}$
$\mathbf{D}_2$	$\frac{1}{6}$	$-\frac{1}{2}$	0	$\frac{1}{3}$	0	0
$\mathbf{T}$	$\frac{1}{3}$	0	-1	$-\frac{1}{3}$	1	0

$$\mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}_j^{(m)} = [\mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}^{(m)}] \downarrow \mathbf{G}_j^{(m)} = \begin{cases} 2\mathbf{G}^{(m)}(/\mathbf{G}_i) \downarrow \mathbf{G}_j^{(m)} \\ \mathbf{G}^{(m)}(/\mathbf{G}_i) \downarrow \mathbf{G}_j^{(m)} + \mathbf{G}^{(m)}(/\mathbf{G}'_i) \downarrow \mathbf{G}_j^{(m)} \end{cases} \quad (33)$$

The first case of Eq. 33 indicates that the mark corresponding to $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j^{(m)}$ is twice the mark corresponding to $\mathbf{G}^{(m)}(/\mathbf{G}_i)\downarrow\mathbf{G}_j^{(m)}$. Hence, if i is tentatively fixed, we have

$$m_{i\ell} = 2m_{i\ell}^{(m)} \quad (34)$$

for $\ell = 1,2,\cdots,t$. This relationship is exemplified by the comparison between Table 1 and Table 7.

On the other hand, the second case of Eq. 33 indicates that the mark corresponding to $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j^{(m)}$ is equal to the mark corresponding to $\mathbf{G}^{(m)}(/\mathbf{G}_i)\downarrow\mathbf{G}_j^{(m)}$ plus that corresponding to $\mathbf{G}^{(m)}(/\mathbf{G}'_i)\downarrow\mathbf{G}_j^{(m)}$. This relationship is exemplified by the $\mathbf{D}_{2d}(/\mathbf{C}'_2)$-row of Table 3, which is compared with the $\mathbf{D}_2(/\mathbf{C}'_2)$- and the $\mathbf{D}_2(/\mathbf{C}''_2)$-rows of Table 9. See also Table 10.

In order to examine the second case of Eq. 33 in detail, we place $\mathbf{G}_j^{(m)} = \mathbf{G}_i$ so as to have

$$\mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}_i = \mathbf{G}^{(m)}(/\mathbf{G}_i) \downarrow \mathbf{G}_i + \mathbf{G}^{(m)}(/\mathbf{G}'_i) \downarrow \mathbf{G}_i. \quad (35)$$

To evaluate the mark, the second coset representation in the right-hand side of Eq. 35 is converted into

$$\mathbf{G}^{(m)}(/\mathbf{G}'_i) \downarrow \mathbf{G}_i = \sum_g \mathbf{G}_i(/g^{-1}\mathbf{G}'g \cap \mathbf{G}_i). \quad (36)$$

Since $\mathbf{G}$ is presumed not to be conjugate to $g^{-1}\mathbf{G}'g$ within $\mathbf{G}_{(m)}$, the group $g^{-1}\mathbf{G}'g \cap \mathbf{G}_i$ is a true subset of $\mathbf{G}_i$. This means that any one of the coset representations appearing in the right-hand side of Eq. 36 is not identical with $\mathbf{G}_i(/\mathbf{G}_i)$. It follows that the mark corresponding to Eq. 36 is determined to be zero.

On the other hand, the mark corresponding to $\mathbf{G}^{(m)}(/\mathbf{G}_i)\downarrow\mathbf{G}_i$ in Eq. 35 is calculated to be

$$m_{ii}^{(m)} = |\mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_i)|/|\mathbf{G}_i| = |\mathbf{G}^{(m)}|/|\mathbf{G}_i| \quad (37)$$

in the light of Eq. 24 of Ref. 33. Note that $\mathbf{G}_i$ has no conjugate groups within $\mathbf{G}^{(m)}$ (i.e. $\mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_i) = \mathbf{G}^{(m)}$). Hence, the mark corresponding to Eq. 35 is represented by Eq. 37.

Similarly, the mark corresponding to $\mathbf{G}^{(m)}(/\mathbf{G}'_i)\downarrow\mathbf{G}'_i$ is calculated to be

$$m_{i'i'}^{(m)} = |\mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}'_i)|/|\mathbf{G}'_i| = |\mathbf{G}^{(m)}|/|\mathbf{G}'_i|, \quad (38)$$

which is equal to $m_{ii}^{(m)}$ shown in Eq. 37. Thus, we have evaluated the marks for the $\mathbf{G}^{(m)}(/\mathbf{G}'_i)$-row.

Equations 33, 37, and 38 indicate that the $\mathbf{G}^{(m)}(/\mathbf{G}_i)$-row and the $\mathbf{G}^{(m)}(/\mathbf{G}'_i)$-row of the modified mark table of $\mathbf{G}^{(m)}$ are summed up so as to generate the $\mathbf{G}(/\mathbf{G}_i)$-row of the MBM table of $\mathbf{G}$. Hence, the second case of Eq. 33 indicates

$$m_{i\ell} = m_{i\ell}^{(m)} + m_{i'\ell}^{(m)} \quad (39)$$

for $i = 1,2,\cdots t$, where the chiral subgrop $\mathbf{G}_i$ of $\mathbf{G}$ is presumed to correspond to the subgroups $\mathbf{G}_i$ and $\mathbf{G}'_i$ of $\mathbf{G}^{(m)}$.

Suppose that the coset representation $\mathbf{G}(/\mathbf{G}_i)$ is homospheric, i.e. the group $\mathbf{G}$ and $\mathbf{G}_i$ are achiral groups. Let $\mathbf{G}^{(m)}$ be the maximum chiral subgroup of $\mathbf{G}$. And let $\mathbf{G}_i^{(m)}$ be the maximum chiral subgroup of $\mathbf{G}_i$. Then, we have

$$\mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}^{(m)} = \mathbf{G}^{(m)}(/\mathbf{G}_i^{(m)}). \quad (40)$$

When $\mathbf{G}_j^{(m)}$ is chiral, it is a subgroup of $\mathbf{G}^{(m)}$. Hence, Eq. 40 gives the following subduction:

$$\mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}_j^{(m)} = [\mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}^{(m)}] \downarrow \mathbf{G}_j^{(m)} = \mathbf{G}^{(m)}(/\mathbf{G}_i^{(m)}) \downarrow \mathbf{G}_j^{(m)} \quad (41)$$

This relationship is concerned with the lower-left part of the MBM table of $\mathbf{G}$, as discussed in detail in the next subsection.

1.6 PCI-CFs for Achiral and Chiral Groups. Whether a set of equivalent positions (an orbit) is placed in the action of $\mathbf{G}$ (achiral) or in the action of $\mathbf{G}^{(m)}$ (chiral), the restriction of the orbit into a *chiral* subgroup gives the same result of subductions, which has been clarified by Eq. 33 for an enantiospheric orbit and by Eq. 41 for a homospheric orbit. Note that the two halves of such an enantiospheric orbit are divided into two hemispheric orbits, each of which is further restricted in terms of Eq. 33.

More informatively speaking, Eq. 33 describes the relationship between $\mathbf{G}(/\mathbf{G}_i)$ and $\mathbf{G}^{(m)}(/\mathbf{G}_i^{(m)})$, when $\mathbf{G}(/\mathbf{G}_i)$ is enantiospheric. To illustrate this situation, Table 11 shows USCI-CFs for $\mathbf{T}$. The comparison between the upper-left part of Table 5 and Table 11 exemplifies Case 1 of Eq. 33 in the form of USCI-CFs. For example, an orbit governed by $\mathbf{T}_d(/\mathbf{C}_1)$ is regarded as two orbits governed by $\mathbf{T}(/\mathbf{C}_1)$ under the action of $\mathbf{T}$, as found in their USCI-CFs (b_1^{24} vs. b_1^{12} etc.). Thus, the USCI-CF b_1^{24} for $\downarrow\mathbf{C}_1$ under $\mathbf{T}_d$ is the same

Table 9. (Modified) Mark Table for $\mathbf{D}_2$

	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}'_2$	$\mathbf{C}''_2$	$\mathbf{D}_2$
$\mathbf{D}_2(/\mathbf{C}_1)$	4	0	0	0	0
$\mathbf{D}_2(/\mathbf{C}_2)$	2	2	0	0	0
$\mathbf{D}_2(/\mathbf{C}'_2)$	2	0	2	0	0
$\mathbf{D}_2(/\mathbf{C}''_2)$	2	0	0	2	0
$\mathbf{D}_2(/\mathbf{D}_2)$	1	1	1	1	1

Table 10. Inverse of (Modified) Mark Table for $\mathbf{D}_2$

	$(/\mathbf{C}_1)$	$(/\mathbf{C}_2)$	$(/\mathbf{C}'_2)$	$(/\mathbf{C}''_2)$	$(/\mathbf{D}_2)$	Sum
$\mathbf{C}_1$	$\frac{1}{4}$	0	0	0	0	$\frac{1}{4}$
$\mathbf{C}_2$	$-\frac{1}{4}$	$\frac{1}{2}$	0	0	0	$\frac{1}{4}$
$\mathbf{C}'_2$	$-\frac{1}{4}$	0	$\frac{1}{2}$	0	0	$\frac{1}{4}$
$\mathbf{C}''_2$	$-\frac{1}{4}$	0	0	$\frac{1}{2}$	0	$\frac{1}{4}$
$\mathbf{D}_2$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	1	0

Table 11. Modified USCI-CF Table for $\mathbf{T}$

	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_3$	$\mathbf{D}_2$	$\mathbf{T}$
$\mathbf{T}(/\mathbf{C}_1)$	b_1^{12}	b_2^6	b_3^4	b_4^3	b_{12}
$\mathbf{T}(/\mathbf{C}_2)$	b_1^6	$b_1^2b_2^2$	b_3^2	b_2^3	b_6
$\mathbf{T}(/\mathbf{C}_3)$	b_1^4	b_2^2	b_1b_3	b_4	b_4
$\mathbf{T}(/\mathbf{D}_2)$	b_1^3	b_1^3	b_3	b_1^3	b_3
$\mathbf{T}(/\mathbf{T})$	b_1	b_1	b_1	b_1	b_1

result as $(b_1^{12})^2$ for $\downarrow \mathbf{C}_1$ under $\mathbf{T}$. Compare also the remaining pairs: between $\mathbf{T}_d(/\mathbf{C}_2)$ and $\mathbf{T}(/\mathbf{C}_2)$ (b_1^{12} vs. b_1^6 etc.); between $\mathbf{T}_d(/\mathbf{C}_3)$ and $\mathbf{T}(/\mathbf{C}_3)$ (b_1^8 vs. b_1^4 etc.); between $\mathbf{T}_d(/\mathbf{D}_2)$ and $\mathbf{T}(/\mathbf{D}_2)$ (b_1^6 vs. b_1^3 etc.); and between $\mathbf{T}_d(/\mathbf{T})$ and $\mathbf{T}(/\mathbf{T})$ (b_1^2 vs. b_1^1 etc.).

Equation 41 described the relationship between $\mathbf{G}(/\mathbf{G}_i)$ and $\mathbf{G}^{(m)}(/\mathbf{G}_i^{(m)})$ when $\mathbf{G}(/\mathbf{G}_i)$ is homospheric. For example, the $\mathbf{T}_d(/\mathbf{C}_s)$-row of Table 5 and the $\mathbf{T}(/\mathbf{C}_1)$-row of Table 11 give the same USCI-CFs. Similarly, the other pairs of rows for Table 5 and Table 11, i.e., $\mathbf{T}_d(/\mathbf{S}_4)$ and $\mathbf{T}(/\mathbf{C}_2)$; $\mathbf{T}_d(/\mathbf{C}_{2v})$ and $\mathbf{T}(/\mathbf{C}_2)$; $\mathbf{T}_d(/\mathbf{C}_{3v})$ and $\mathbf{T}(/\mathbf{C}_3)$; $\mathbf{T}_d(/\mathbf{D}_{2d})$ and $\mathbf{T}(/\mathbf{D}_2)$; and $\mathbf{T}_d(/\mathbf{T}_d)$ and $\mathbf{T}(/\mathbf{T})$, exemplify the relationship represented by Eq. 41.

Table 12 collects the USCI-CFs for $\mathbf{D}_2$ in order to compare with the data of Table 6 for $\mathbf{D}_{2d}$. The enantiospheric $\mathbf{D}_{2d}(/\mathbf{C}_2')$-row of Table 12 is an example of Case 2 described in Eq. 33. The subduction $\mathbf{D}_{2d}(/\mathbf{C}_2')\downarrow\mathbf{D}_2$ is equal to $\mathbf{D}_2(/\mathbf{C}_2')+\mathbf{D}_2(/\mathbf{C}_2'')$, which corresponds to the USCI-CF b_2^2. According to this subduction, the $\mathbf{D}_{2d}(/\mathbf{C}_2')$-row of Table 6 (in the chiral section) is obtained by combining the $\mathbf{D}_2(/\mathbf{C}_2')$-row and the $\mathbf{D}_2(/\mathbf{C}_2'')$-row of Table 12.

The lower-left section of Table 6 is another example of Eq. 41 for homospheric coset repersentations. Compare the pairs of rows for Table 6 and Table 12, i.e., $\mathbf{D}_{2d}(/\mathbf{C}_s)$ and $\mathbf{D}_2(/\mathbf{C}_1)$; $\mathbf{D}_{2d}(/\mathbf{S}_4)$ and $\mathbf{D}_2(/\mathbf{C}_2)$; $\mathbf{D}_{2d}(/\mathbf{C}_{2v})$ and $\mathbf{D}_2(/\mathbf{C}_2)$; and $\mathbf{D}_{2d}(/\mathbf{D}_{2d})$ and $\mathbf{D}_2(/\mathbf{D}_2)$.

The discussions described in the preceding paragraphs indicate that the SCI-CFs obtained by the action of $\mathbf{G}$ are equal to those obtained by the action of $\mathbf{G}^{(m)}$, since the SCI-CFs are derived from the USCI-CFs listed in such USCI-CF tables. This situation for SCI-CFs holds true in the upper-left and the lower-left section of any modified bisected USCI-CF table.

If $\mathbf{G}_j$ is chiral, it is a subgroup of $\mathbf{G}$ as well as of $\mathbf{G}^{(m)}$. Hence, Eq. 12 holds true for the group $\mathbf{G}^{(m)}$ to give

$$\sum_{i=1}^{t'} \overline{m}_{ji}^{(m)} = \begin{cases} \varphi(|\mathbf{G}_j|)/|\mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_j)| & \text{if } \mathbf{G}_j \text{ is cyclic} \\ 0 & \text{otherwise} \end{cases} \tag{42}$$

There are two cases: Case 1: Suppose that we have $\sigma^{-1}\mathbf{G}_j\sigma = \mathbf{G}_j$ for $\sigma \in \mathbf{G}-\mathbf{G}^{(m)}$. For $g \in \mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_j)$, we have $\sigma^{-1}g^{-1}\mathbf{G}_j g\sigma = \sigma^{-1}\mathbf{G}_j\sigma = \mathbf{G}_j$. Hence $g\sigma \in \mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_j)\sigma$ is contained in the normalizer $\mathbf{N}_{\mathbf{G}}(\mathbf{G}_j)$. It follows that $\mathbf{N}_{\mathbf{G}}(\mathbf{G}_j) = \mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_j)+\mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_j)\sigma$. Hence, the sizes of the normalizers satisfy $|\mathbf{N}_{\mathbf{G}}(\mathbf{G}_j)| = 2|\mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_j)|$. Case 2: Suppose that we have $\sigma^{-1}\mathbf{G}_j\sigma \neq \mathbf{G}_j$ for all $\sigma \in \mathbf{G}-\mathbf{G}^{(m)}$. Then, $\mathbf{N}_{\mathbf{G}}(\mathbf{G}_j) = \mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_j)$. Hence, the sizes of the normalizers satisfy $|\mathbf{N}_{\mathbf{G}}(\mathbf{G}_j)| = |\mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_j)|$. According to Case 1 and Case 2 of this classification, the comparison between Eq. 12 and Eq. 42 gives the following relationship:

Table 12. (Modified) USCI-CF Table for $\mathbf{D}_2$

	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_2'$	$\mathbf{C}_2''$	$\mathbf{D}_2$
$\mathbf{D}_2(/\mathbf{C}_1)$	b_1^4	b_2^2	b_2^2	b_2^2	b_4
$\mathbf{D}_2(/\mathbf{C}_2)$	b_1^2	b_1^2	b_2	b_2	b_2
$\mathbf{D}_2(/\mathbf{C}_2')$	b_1^2	b_2	b_1^2	b_2	b_2
$\mathbf{D}_2(/\mathbf{C}_2'')$	b_1^2	b_2	b_2	b_1^2	b_2
$\mathbf{D}_2(/\mathbf{D}_2)$	b_1	b_1	b_1	b_1	b_1

$$\sum_{i=1}^{t'} \overline{m}_{ji}^{(m)} = \begin{cases} 2\sum_{i=1}^{t} \overline{m}_{ji} & \text{for Case 1} \\ \sum_{i=1}^{t} \overline{m}_{ji} & \text{for Case 2} \end{cases} \tag{43}$$

for the chiral subgroup $\mathbf{G}_j$. The summation from 1 to s is replaced by the one from 1 to t because of zero values of the upper-right part of the inverse MBM table.

The relationship obtained for Case 2 should be added here. In Case 2, the element $\mathbf{G}_j' = \sigma^{-1}\mathbf{G}_j\sigma$ satisfies

$$\begin{aligned}(\sigma^{-1}g\sigma)^{-1}\mathbf{G}_j'(\sigma^{-1}g\sigma) &= (\sigma^{-1}g^{-1}\sigma)(\sigma^{-1}\mathbf{G}_j\sigma)(\sigma^{-1}g\sigma) \\ &= \sigma^{-1}(g^{-1}\mathbf{G}_j g)\sigma \\ &= \sigma^{-1}\mathbf{G}_j\sigma = \mathbf{G}_j' \end{aligned} \tag{44}$$

for $g \in \mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_j)$. It follows that the normalizer of $\mathbf{G}_j'$ is $\sigma^{-1}\mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_j)\sigma$. Since we have $|\sigma^{-1}\mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_j)\sigma| = |\mathbf{N}_{\mathbf{G}^{(m)}}(\mathbf{G}_j)|$ and $|\mathbf{G}_j'| = |\mathbf{G}_j|$, we obtain

$$\sum_{i=1}^{t'} \overline{m}_{j'i}^{(m)} = \sum_{i=1}^{t'} \overline{m}_{ji}^{(m)} = \sum_{i=1}^{t} \overline{m}_{ji} \tag{45}$$

for the chiral subgroup $\mathbf{G}_j'$ of Case 2.

Let $U^{(c)}$ represent the set of all of the chiral subgroups selected from $\mathrm{SSG}_{\mathbf{G}}$. We here examine a cycle index derived from Eq. 6:

$$\mathrm{PCIC}'(U^{(c)}; \$_{d_{jk}}) = \sum_{j=1}^{t} \left(2\sum_{i=1}^{t} \overline{m}_{ji}\right) \mathrm{ZIC}(\mathbf{G}_j; \$_{d_{jk}}), \tag{46}$$

where the ranges of the outer and the inner summation are restricted to take account of the chiral subgroups.

Example 1. Let us consider an adamantane skeleton having four bridgehead positions and twelve bridge positions as substitution positions. The two sets of positions are governed by the coset representations, $\mathbf{T}_d(/\mathbf{C}_{3v})$ and $\mathbf{T}_d(/\mathbf{C}_s)$. Equation 46 is calculated for this case, giving

$$\begin{aligned}\mathrm{PCIC}'(U^{(c)}; \$_{d_{jk}}) &= 2\times\frac{1}{24}(b_1^{12})(b_1^4) + 2\times\frac{1}{8}(b_2^6)(b_2^2) + 2\times\frac{1}{3}(b_3^4)(b_1b_3) \\ &= \frac{1}{12}b_1^{16} + \frac{1}{4}b_2^8 + \frac{2}{3}b_1b_3^5, \end{aligned} \tag{47}$$

where the coefficients are selected from the rightmost column of Table 2.

On the other hand, the enumeration can be alternatively based on a cycle index for $\mathbf{G}^{(m)}$:

$$\mathrm{CIC}(\mathbf{G}^{(m)}; \$_{d_{jk}}) = \sum_{j=1}^{t'} \left(\sum_{i=1}^{t'} \overline{m}_{ji}^{(m)}\right) \mathrm{ZIC}(\mathbf{G}_j; \$_{d_{jk}}). \tag{48}$$

By virtue of Eqs. 43 and 45, the enumeration based on Eq. 46 gives an equivalent result to that based on Eq. 48. The following example exemplifies the equivalency of the two enumerations.

Example 2. This example is a continuation of Example 1. The orbits $\mathbf{T}_d(/\mathbf{C}_{3v})$ and $\mathbf{T}_d(/\mathbf{C}_s)$ are considered to be governed by $\mathbf{T}(/\mathbf{C}_3)$ and $\mathbf{T}(/\mathbf{C}_1)$. Then, equation Eq. 48 is calculated for this case, giving

$$\mathrm{CIC}(\mathbf{G}^{(m)}; \$_{d_{jk}}) = \frac{1}{12}(b_1^{12})(b_1^4) + \frac{1}{4}(b_2^6)(b_2^2) + \frac{2}{3}(b_3^4)(b_1b_3)$$

$$= \frac{1}{12}b_1^{16} + \frac{1}{4}b_2^8 + \frac{2}{3}b_1b_3^5, \quad (49)$$

where the coefficients are selected from the rightmost column of Table 8. The result (Eq. 49) is identical with the one obtained in Example 1 (Eq. 47).

The enumeration due to Eq. 48 gives a generating function for calculating achiral plus twice chiral isomers. This is designated by the symbol $f_{U^{(a)}}+2f_{U^{(c)}}$, since each enantiomer of an enantiomeric pair is counted once. Thus, Eq. 46 is restated to be

$$f_{U^{(a)}}+2f_{U^{(c)}} = \mathrm{PCIC}'(U^{(c)};\$_{d_{jk}}) = \sum_{j=1}^{t}\left(2\sum_{i=1}^{t}\overline{m}_{ji}\right)\mathrm{ZIC}(\mathbf{G}_j;\$_{d_{jk}}). \quad (50)$$

The generalized PCI-CF (Eq. 6) for calculating $f_{U^{(a)}}+2f_{U^{(c)}}$ is obtained to be

$$\begin{aligned} f_{U^{(a)}}+2f_{U^{(c)}} &= \mathrm{PCIC}(U^{(a)}+2U^{(c)};\$_{d_{jk}}) \\ &= 2\sum_{j=1}^{s}\left(\sum_{i=1}^{t}\overline{m}_{ji}\right)\mathrm{ZIC}(\mathbf{G}_j;\$_{d_{jk}}) \\ &\quad +\sum_{j=1}^{s}\left(\sum_{i=t+1}^{s}\overline{m}_{ji}\right)\mathrm{ZIC}(\mathbf{G}_j;\$_{d_{jk}}) \\ &= \sum_{j=1}^{t}\left(2\sum_{i=1}^{t}\overline{m}_{ji}\right)\mathrm{ZIC}(\mathbf{G}_j;\$_{d_{jk}}) \\ &\quad +2\sum_{j=t+1}^{s}\left(\sum_{i=1}^{t}\overline{m}_{ji}\right)\mathrm{ZIC}(\mathbf{G}_j;\$_{d_{jk}}) \\ &\quad +\sum_{j=t+1}^{s}\left(\sum_{i=t+1}^{s}\overline{m}_{ji}\right)\mathrm{ZIC}(\mathbf{G}_j;\$_{d_{jk}}) \\ &= \sum_{j=1}^{t}\left(2\sum_{i=1}^{t}\overline{m}_{ji}\right)\mathrm{ZIC}(\mathbf{G}_j;\$_{d_{jk}}) \\ &\quad +\sum_{j=t+1}^{s}\left(2\sum_{i=1}^{t}\overline{m}_{ji}+\sum_{i=t+1}^{s}\overline{m}_{ji}\right)\mathrm{ZIC}(\mathbf{G}_j;\$_{d_{jk}}), \end{aligned} \quad (51)$$

where the ranges of the outer and the inner summation are restricted to take account of the chiral subgroups. The comparison between Eq. 50 and Eq. 51 yields

$$\sum_{j=t+1}^{s}\left(2\sum_{i=1}^{t}\overline{m}_{ji} + \sum_{i=t+1}^{s}\overline{m}_{ji}\right)\mathrm{ZIC}(\mathbf{G}_j;\$_{d_{jk}}) = 0. \quad (52)$$

This formula is examined for each $\mathbf{G}_j$ to give

$$2\sum_{i=1}^{t}\overline{m}_{ji} + \sum_{i=t+1}^{s}\overline{m}_{ji} = 0 \quad (53)$$

for $j = t+1, t+2, \cdots, s$ (corrsponding to achiral subgroups). By applying Eq. 12 to Eq. 53 we arrive at a theorem for determining the lower-left and the lower-right part of the inverse MBM table for $\mathbf{G}$.

Theorem 3. *For chiral cyclic groups* $\mathbf{G}_j$, *we have*

$$\sum_{i=1}^{t}\overline{m}_{ji} = -\frac{\varphi(|\mathbf{G}_j|)}{|\mathbf{N}_{\mathbf{G}}(\mathbf{G}_j)|} \quad (54)$$

$$\sum_{i=t+1}^{s}\overline{m}_{ji} = \frac{2\varphi(|\mathbf{G}_j|)}{|\mathbf{N}_{\mathbf{G}}(\mathbf{G}_j)|} \quad (55)$$

for $j = t+1, t+2, \cdots, s$. *Otherwise, for achiral noncyclic groups* $\mathbf{G}_j$, *we have*

$$\sum_{i=1}^{t}\overline{m}_{ji} = \sum_{i=t+1}^{s}\overline{m}_{ji} = 0 \quad (56)$$

for $j = t+1, t+2, \cdots, s$.

2 Combinatorial Enumeration

2.1 Enumeration of Enantiomeric Pairs. For the enumeration of chiral isomers, we count enantiomeric pairs corresponding to respective chiral isomers. The elements $\overline{m}_{ji}$ are summed up so as to cover all of the chiral group ($U^{(c)}$ or the range from $i = 1$ to t) to give

$$N_j^{(e)} = \sum_{\mathbf{G}_i \in U^{(c)}} \overline{m}_{ji} = \sum_{i=1}^{t}\overline{m}_{ji} = \begin{cases} \dfrac{\varphi(|\mathbf{G}_j|)}{|\mathbf{N}_{\mathbf{G}}(\mathbf{G}_j)|} & \text{for each chiral cyclic } \mathbf{G}_j \\ -\dfrac{\varphi(|\mathbf{G}_j|)}{|\mathbf{N}_{\mathbf{G}}(\mathbf{G}_j)|} & \text{for each achiral cyclic } \mathbf{G}_j \end{cases} \quad (57)$$

Note that the values $N_j^{(e)}$ for non-cyclic groups vanish to zero. The values for chiral groups $\mathbf{G}_j$ (only cyclic groups) are equal to the sums listed in the rightmost column of the inverse MBM table, while the values for achiral groups $\mathbf{G}_j$ (only cyclic groups) are equal to the minus values of the sums in the same column.

Theorem 1 is modified by the combination of Eq. 6 and Eq. 57 to give a corollary:

Corollary 1.1. *In Theorem 1, the number* ($A_{U^{(c)}\nu}$) *of chiral isomers with the weight* $W_{[\nu]}$ *is calculated by means of Eq. 8, where the PCI-CF is represented by*

$$\mathrm{PCIC}(U^{(c)};\$_{d_{jk}}) = \sum_{j=1}^{s} N_j^{(e)}\mathrm{ZIC}(\mathbf{G}_j;\$_{d_{jk}}). \quad (58)$$

Example 3. This is a continuation of Example 1. An adamantane skeleton has four bridgehead positions ($\mathbf{T}_d(/\mathbf{C}_{3v})$) and twelve bridge positions ($\mathbf{T}_d(/\mathbf{C}_s)$). We use Eq. 58 (Eq. 6) and $N_j^{(e)}$ (Eq. 57). Then, we have

$$\begin{aligned} \mathrm{PCIC}(U^{(c)};\$_{d_{jk}}) &= \frac{1}{24}(b_1^{12})(b_1^4) + \frac{1}{8}(b_2^6)(b_2^2) + \frac{1}{3}(b_3^4)(b_1b_3) \\ &\quad -\frac{1}{4}(a_1^2c_2^5)(a_1^2c_2) - \frac{1}{4}(c_4^3)(c_4) \\ &= \frac{1}{24}b_1^{16} + \frac{1}{8}b_2^8 + \frac{1}{3}b_1b_3^5 - \frac{1}{4}a_1^4c_2^6 - \frac{1}{4}c_4^4, \end{aligned} \quad (59)$$

where the coefficients $N_j^{(e)}$ are selected from the rightmost column of Table 2. When the variables a_d, b_d, and c_d are replaced by s_d, Eq. 59 is identical with Eq. 29 of Example 4 reported in Ref. 30. Hence, the present result involves the previous Example 4 as a special case.

Example 4. Let us consider the eight hydrogens of spiro[2.2]pentane as substitution positions. Since they construct an orbit governed by $\mathbf{D}_{2d}(/\mathbf{C}_1)$, the $\mathbf{D}_{2d}(/\mathbf{C}_1)$-row of Table 6 is adopted for calculating a generalized PCI-CF. By using Eq. 58 (Eq. 6), we have

$$\begin{aligned} \mathrm{PCIC}(U^{(c)};\$_{d_{jk}}) &= \frac{1}{8}b_1^8 + \frac{1}{8}b_2^4 + \frac{1}{4}b_2^4 - \frac{1}{4}c_2^4 - \frac{1}{4}c_4^2 \\ &= \frac{1}{8}b_1^8 + \frac{3}{8}b_2^4 - \frac{1}{4}c_2^4 - \frac{1}{4}c_4^2, \end{aligned} \quad (60)$$

where the coefficients $N_j^{(e)}$ are selected from the rightmost column of Table 4 in agreement with Eq. 57. Suppose that a set of eight atoms is selected from $\mathbf{X} = \{H, X, Y, Z\}$. Then, we have an inventory for this enumeration:

$$s_d = a_d = b_d = c_d = H^d + X^d + Y^d + Z^d. \tag{61}$$

This inventory is introduced into Eq. 60 to give

$$\begin{aligned}\mathrm{PCIC}(U^{(c)};\$_{d_{jk}}) &= \frac{1}{8}(H+X+Y+Z)^8 + \frac{3}{8}(H^2+X^2+Y^2+Z^2)^4 \\ &\quad -\frac{1}{4}(H^2+X^2+Y^2+Z^2)^4 - \frac{1}{4}(H^4+X^4+Y^4+Z^4)^2 \\ &= \frac{1}{8}(H+X+Y+Z)^8 + \frac{1}{8}(H^2+X^2+Y^2+Z^2)^4 \\ &\quad -\frac{1}{4}(H^4+X^4+Y^4+Z^4)^2 = (H^7X+H^7Y+\cdots) \\ &\quad +4(H^6X^2+H^6Y^2+\cdots)+7(H^6XY+H^6XZ+\cdots) \\ &\quad +7(H^5X^3+H^5Y^3+\cdots)+21(H^5X^2Y+H^5X^2Z+\cdots) \\ &\quad +42(H^5XYZ+HX^5YZ+\cdots)+9(H^4X^4+H^4X^4+\cdots) \\ &\quad +35(H^4X^3Y+H^4X^3Z+\cdots) \\ &\quad +54(H^4X^2Y^2+H^4X^2Z^2+\cdots) \\ &\quad +105(H^4X^2YZ+H^2X^4YZ+\cdots) \\ &\quad +70(H^3X^3Y^2+H^3X^3Z^2+\cdots) \\ &\quad +140(H^3X^3YZ+H^3XY^3Z+\cdots) \\ &\quad +140(H^3X^2Y^2Z+H^3X^2YZ^2+\cdots).\end{aligned} \tag{62}$$

The coefficient of each term $H^hX^xY^yZ^z$ in Eq. 62 represents the number of chiral isomers with the formula $H^hX^xY^yZ^z$ (or partition [h,x,y,z]). Since a set of terms in each pair of parentheses can be transformed into one another by the permutation of atoms, they have the same coefficient. For illustrating these results, Fig. 1 depicts four chiral isomers with H^6X^2, where the spiro[2.2]pentane skeleton is projected from the top of one cyclopropane plane to the other cyclopropane plane.

2.2 Enumeration of Achiral Isomers. For the enumeration of achiral isomers, the elements $\overline{m}_{ji}$ are summed up for covering all of the chiral group ($U^{(a)}$ or the range from $i = t+1$ to s). Then, we have

$$N_j^{(a)} = \sum_{\mathbf{G}_i \in U^{(a)}} \overline{m}_{ji} = \sum_{i=t+1}^{s} \overline{m}_{ji} = \begin{cases} 0 & \text{for each chiral cyclic } \mathbf{G}_j \\ \dfrac{2\varphi(|\mathbf{G}_j|)}{|\mathbf{N_G}(\mathbf{G}_j)|} & \text{for each achiral cyclic } \mathbf{G}_j \end{cases} \tag{63}$$

Note again that the values $N_j^{(a)}$ for non-cyclic groups vanish to zero. The values for chiral groups $\mathbf{G}_j$ (only cyclic groups) vanish to zero in the enumeration of achiral isomers. The values for achiral groups $\mathbf{G}_j$ (only cyclic groups) are equal to the minus values of the sums in the rightmost column of the inverse MBM table.

By the combination of Eq. 6 and Eq. 63, Theorem 1 gives the following corollary:

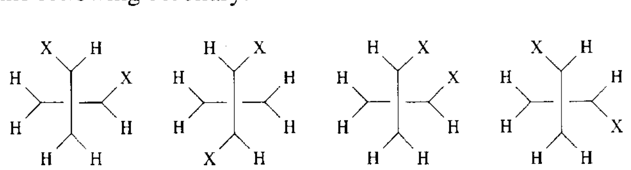

Fig. 1. Chiral isomers with H^6X^2 derived from spiro[2.2]pentane.

Corollary 1.2. *In Theorem 1, the number ($A_{U^{(a)}\nu}$) of achiral isomers with the weight $W_{[\nu]}$ is calculated by means of Eq. 8, where the PCI-CF is represented by*

$$\mathrm{PCIC}(U^{(a)};\$_{d_{jk}}) = \sum_{j=1}^{s} N_j^{(a)} \mathrm{ZIC}(\mathbf{G}_j;\$_{d_{jk}}). \tag{64}$$

Example 5. This is a continuation of Example 3. We also take account of $\mathbf{T}_d(/\mathbf{C}_{3v})$ and $\mathbf{T}_d(/\mathbf{C}_s)$. We use Eq. 64 (Eq. 6) and $N_j^{(a)}$ (Eq. 63). Then, we have

$$\begin{aligned}\mathrm{PCIC}(U^{(a)};\$_{d_{jk}}) &= 2 \times \frac{1}{4}(a_1^2c_2^5)(a_1^2c_2) + 2 \times \frac{1}{4}(c_4^3)(c_4) \\ &= \frac{1}{2}a_1^4c_2^6 + \frac{1}{2}c_4^4,\end{aligned} \tag{65}$$

where the coefficients $N_j^{(e)}$ are selected from the rightmost column of Table 2. When the variables a_d, b_d, and c_d are replaced by s_d, Eq. 65 is identical with Eq. 33 of Example 7 reported in Ref. 30. Hence, the present result contains the Example 7 of Ref. 30 as a special case.

Example 6. This is a continuation of Example 4 concerning spiro[2.2]pentane derivatives. By using Eq. 64 (Eq. 6), we have

$$\begin{aligned}\mathrm{PCIC}(U^{(a)};\$_{d_{jk}}) &= 2 \times \frac{1}{4}c_2^4 + 2 \times \frac{1}{4}c_4^2 \\ &= \frac{1}{2}c_2^4 + \frac{1}{2}c_4^2,\end{aligned} \tag{66}$$

where the coefficients $N_j^{(a)}$ are selected from the rightmost column of Table 4 in agreement with Eq. 63; and the UCSI-CFs are adopted from the $\mathbf{D}_{2d}(/\mathbf{C}_1)$-row of Table 6. The inventory (Eq. 61) is introduced into Eq. 66 to give

$$\begin{aligned}\mathrm{PCIC}(U^{(c)};\$_{d_{jk}}) &= \frac{1}{2}(H^2+X^2+Y^2+Z^2)^4 + \frac{1}{2}(H^4+X^4+Y^4+Z^4)^2 \\ &= (H^8+X^8+\cdots) + 2(H^6X^2+H^6Y^2+\cdots) \\ &\quad + 4(H^4X^4+H^4Y^4+\cdots) \\ &\quad + 6(H^4X^2Y^2+H^4X^2Z^2+\cdots).\end{aligned} \tag{67}$$

For illustrating these results, Fig. 2 depicts two achiral isomers with H^6X^2 derived from the spiro[2.2]pentane skeleton.

2.3 Enumeration of All Isomers. For the enumeration of all chiral and achiral isomers, the elements $\overline{m}_{ji}$ are summed up so as to cover all of the groups ($U^{(a)}+U^{(c)}$ or the range from $i = 1$ to s). The coefficients for such enumerations are calculated as follows:

$$N_j = \sum_{\mathbf{G}_i \in U^{(a)}+U^{(c)}} \overline{m}_{ji} = \sum_{i=1}^{s} \overline{m}_{ji} = \frac{\varphi(|\mathbf{G}_j|)}{|\mathbf{N_G}(\mathbf{G}_j)|}, \tag{68}$$

for each cyclic $\mathbf{G}_j$. Note again that the values N_j for non-cyclic groups vanish to zero. The values for chiral and achiral groups $\mathbf{G}_j$ (only cyclic groups) are equal to the sums

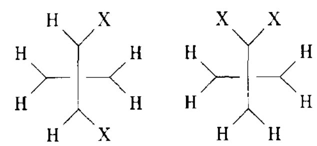

Fig. 2. Achiral isomers with H^6X^2 derived from spiro[2.2]pentane.

collected in the rightmost column of the inverse MBM table. Obviously, we have

$$N_j = N_j^{(e)} + N_j^{(a)}. \qquad (69)$$

By the combination of Eq. 6 and Eq. 68, Theorem 1 gives the following corollary:

Corollary 1.3. *In Theorem 1, the number* $(A_{(U^{(a)}+U^{(c)})\nu})$ *of chiral and achiral isomers with the weight* $W_{[\nu]}$ *is calculated by means of* Eq. 8, *where the PCI-CF is represented by*

$$\mathrm{PCIC}(U^{(a)} + U^{(c)}; \$_{d_{jk}}) = \sum_{j=1}^{s} N_j \mathrm{ZIC}(\mathbf{G}_j; \$_{d_{jk}}). \qquad (70)$$

This collorary can be proved to involve Pólya's theorem as a special case, since the latter is obtained by placing $s_d = a_d = b_d = c_d$.[24]

Example 7. This is a continuation of Example 5, where the four bridgehead positions ($\mathbf{T}_d(/\mathbf{C}_{3v})$) and twelve bridge positions ($\mathbf{T}_d(/\mathbf{C}_s)$) of an adamantane skeleton are considered. We use Eq. 70 (Eq. 6) and N_j (Eq. 68). Thereby, we have

$$\begin{aligned}
&\mathrm{PCIC}(U^{(a)}+U^{(c)};\$_{d_{jk}})\\
&=\frac{1}{24}(b_1^{12})(b_1^4)+\frac{1}{8}(b_2^6)(b_2^2)+\frac{1}{3}(b_3^4)(b_1b_3)+\frac{1}{4}(a_1^2c_2^5)(a_1^2c_2)+\frac{1}{4}(c_4^3)(c_4)\\
&=\frac{1}{24}b_1^{16}+\frac{1}{8}b_2^8+\frac{1}{3}b_1b_3^5+\frac{1}{4}a_1^4c_2^6+\frac{1}{4}c_4^4, \qquad (71)
\end{aligned}$$

where the coefficients N_j are selected from the rightmost column of Table 5. When the variables a_d, b_d, and c_d are replaced by s_d, Eq. 71 is identical with Eq. 18 of Example 4 reported in Ref. 30. Hence, the present result contains the previous Example 4 as a special case.

Example 8. This example is a continuation of Examples 4 and 6 concerning spiro[2.2]pentane. Let us now enumerate all of the isomers by placing a set of eight atoms selected from $\mathbf{X} = [H, X, Y, Z]$ on the eight positions of spiro[2.2]pentane. By using Eq. 70 (Eq. 6), we have a PCI-CF for this case:

$$\begin{aligned}
\mathrm{PCIC}(U^{(c)} + U^{(a)}; \$_{d_{jk}}) &= \frac{1}{8}b_1^8 + \frac{1}{8}b_2^4 + \frac{1}{4}b_2^4 + \frac{1}{4}c_2^4 + \frac{1}{4}c_4^2\\
&= \frac{1}{8}b_1^8 + \frac{3}{8}b_2^4 + \frac{1}{4}c_2^4 + \frac{1}{4}c_4^2, \qquad (72)
\end{aligned}$$

where the coefficients N_j are selected from the rightmost column of Table 4 in agreement with Eq. 68. The inventory represented by Eq. 61 is introduced into Eq. 72 to give

$$\begin{aligned}
&\mathrm{PCIC}(U^{(a)} + U^{(c)}; \$_{d_{jk}})\\
&=\frac{1}{8}(H+X+Y+Z)^8+\frac{3}{8}(H^2+X^2+Y^2+Z^2)^4\\
&\quad+\frac{1}{4}(H^2+X^2+Y^2+Z^2)^4+\frac{1}{4}(H^4+X^4+Y^4+Z^4)^2\\
&=\frac{1}{8}(H+X+Y+Z)^8+\frac{5}{8}(H^2+X^2+Y^2+Z^2)^4+\frac{1}{4}(H^4+X^4+Y^4+Z^4)^2\\
&=(H^8+H^8+\cdots)+(H^7X+H^7Y+\cdots)+6(H^6X^2+H^6Y^2+\cdots)\\
&\quad+7(H^6XY+H^6XZ+\cdots)+7(H^5X^3+H^5Y^3+\cdots)\\
&\quad+21(H^5X^2Y+H^5X^2Z+\cdots)+42(H^5XYZ+HX^5YZ+\cdots)\\
&\quad+13(H^4X^4+H^4X^4+\cdots)+35(H^4X^3Y+H^4X^3Z+\cdots)\\
&\quad+60(H^4X^2Y^2+H^4X^2Z^2+\cdots)+105(H^4X^2YZ+H^2X^4YZ+\cdots)\\
&\quad+70(H^3X^3Y^2+H^3X^3Z^2+\cdots)+140(H^3X^3YZ+H^3XY^3Z+\cdots)\\
&\quad+140(H^3X^2Y^2Z+H^3X^2YZ^2+\cdots) \qquad (73)
\end{aligned}$$

Equation 73 is alternatively obtained by the summing-up of Eq. 62 of Example 4 and Eq. 67 of Example 6. For exmaple, we find 4+2 = 6 for the term H^6X^2 etc., 9+4 = 13 for the term H^4X^4 etc., and 54+6 = 60 for the term $H^4X^2Y^2$ etc. These results are in agreement with Eq. 69.

3 Conclusion

The partial-cycle-index (PCI) method has been generalized in order to apply to the enumeration of isomers having a given set of subsymmetries, where an extended PCI with and without chirality fittingness is defined to describe the enumeration properties of the set. Modified bisected tables of marks and their inverses are proposed to evalulate the coefficients of each term appearing in the extended PCI. Unit subduced cycle indices with chirality fittingness (USCI-CFs) have been rearranged to give modified bisected USCI-CFs tables, which have been applied to the enumeration of chiral isomers and achiral isomers.

References

1 G. Pólya, *Acta Math.*, **68**, 145 (1937).

2 F. Harary and E. M. Palmer, "Graphical Enumeration," Academic Press, New York (1973).

3 A. T. Balaban, "Chemical Applications of Graph Theory," Academic Press, London (1976).

4 K. Balasubramanian, *Chem. Rev.*, **85**, 599 (1985).

5 G. Pólya and R. C. Read, "Combinatorial Enumeration of Groups, Graphs, and Chemical Compounds," Springer-Verlag, New York (1987).

6 W. J. Taylor, *J. Chem. Phys.*, **11**, 532 (1943).

7 T. L. Hill, *J. Chem. Phys.*, **11**, 294 (1943).

8 S. G. Williamson, *J. Combinatorial Theory*, **8**, 163 (1970).

9 S. G. Williamson, *J. Combinatorial Theory*, **11**, 122 (1971).

10 K. Balasubramanian, *Theor. Chim. Acta*, **51**, 37 (1979).

11 R. Merris, *Linear Algebra and Applications*, **29**, 255 (1980).

12 W. Burnside, "Theory of Groups of Finite Order," 2nd ed, Cambridge University Press, Cambridge (1911).

13 J. Sheehan, *Can. J. Math.*, **20**, 1068 (1968).

14 A. Kerber and K.-J. Thürlings, in "Combinatorial Theory," ed by D. Jngnickel and K. Vedder, Springer, Berlin (1982), pp. 191—211.

15 J. H. Redfield, *J. Graph Theory*, **8**, 205 (1984).

16 W. Hässelbarth, *Theor. Chim. Acta*, **67**, 339 (1985).

17 E. K. Lloyd, *J. Math. Chem.*, **11**, 207 (1992).

18 C. A. Mead, *J. Am. Chem. Soc.*, **109**, 2130 (1987).

19 W. Hässelbarth, *Theor. Chim. Acta*, **67**, 427 (1985).

20 S. Fujita, *Theor. Chim. Acta*, **76**, 247 (1989).

21 S. Fujita, *J. Math. Chem.*, **12**, 173 (1993).

22 S. Fujita, *Theor. Chim. Acta*, **82**, 473 (1992).

23 S. Fujita, "Symmetry and Combinatorial Enumeration in Chemistry," Springer-Verlag, Berlin and Heidelberg (1991).

24 S. Fujita, *J. Math. Chem.*, **5**, 99 (1990).

25 S. Fujita, *Theor. Chem. Acc.*, **99**, 224 (1998).

26 S. Fujita, *Bull. Chem. Soc. Jpn.*, **71**, 1587 (1998).

27 S. Fujita, *Bull. Chem. Soc. Jpn.*, **71**, 2071 (1998).

28 S. Fujita, *Bull. Chem. Soc. Jpn.*, **71**, 2309 (1998).

29 S. Fujita, *Theor. Chem. Acc.*, **99**, 404 (1998).
30 S. Fujita, *Bull. Chem. Soc. Jpn.*, **72**, 13 (1999).
31 S. Fujita, *J. Graph Theory*, **18**, 349 (1994).
32 S. Fujita, *J. Am. Chem. Soc.*, **112**, 3390 (1990).
33 S. Fujita, *Theor. Chem. Acta*, **91**, 291 (1995).
34 The USCI-CF table for $\mathbf{T}_d$ reported in Appendix E of Ref. 23 contains a misprint. The USCI-CF for $\mathbf{T}_d(/\mathbf{T})\downarrow\mathbf{S}_4$ should read c_2.