Unit Subduced Cycle Indices and the Superposition Theorem. Derivation of a New Theorem and Its Application to Enumeration of Compounds Based on a D_{2d}-Skeleton

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(Received May 10, 1990)

A combination of the concept of unit subduced cycle indices (USCIs) and the Redfield-Read superposition theorem affords a new methodology of enumerating geometrical objects such as molecules and polyhedra. This method allows us to enumerate such objects with respect not only to their constitutions but also to their symmetries, in which subduced cycle indices (SCIs) derived from USCIs play an important role. Further derivation of a cycle index from the SCIs and its incorpotation with the superposition theorem are also discussed. The inverse of the mark table and the table of USCIs for $\mathbf{D}_{2d}$ point group are presented for further applications of the USCI approach.

Graph-theoretical approaches have contributed to physical and theoretical chemisty, since chemical structures are represented by a kind of graphs.[1] Thus, various applications of graph theory have been reported in chemical field.[2-5] One of the most important contributions is the systematic enumeration of chemical structures, in which group theory and combinatorics are incorporated.[6,7] Thus, the Pólya-Redfield theorem has been widely utilized to solve most enumeration problems.[8-11] An alternative formulation of the Pólya-Redfield theorem has been reported by Kerber et al.[12] We have recently applied the Pólya-Redfield theorem to the enumeration of organic reactions after slight modification.[13-16]

Ruch et al.[17,18] applied double coset decompositions to counting chemical structures and rearrangement reactions. Davidson[19] pointed out that such problems can be solved by using the Redfield-Read superposition theorem, which was originally established by Redfield,[11] rediscovered independently by Read[20] and later refocussed by several mathematicians.[21,22] Lloyd[23] actually applied this theorem to chemical enumerations. All of these methods are capable of enumerating chemical objects with respect only to their weights (molecular formulas).

On the other hand, more detailed enumerations concerning such weights as well as symmetries have been developed by several authors. For example, Sheehan,[24] and later Hässelbarth[25] presented a method using a table of marks which came from Burnside.[26] Brocas[27] proposed a method combining double cosets and framework groups. Mead[28] reported an alternative formulation by connecting tables of marks and double cosets.

We ourselves[29] reported a new enumeration method based on *unit subduced cycle indices (USCIs)*. The USCIs can be transformed into a cycle index which has an explicitly different form but is essentially equivant to Pólya's cycle index.[30] The USCI approach has been applied to various enumeration problems.[31-33] Although this method is effective to chemical enumerations as well as to the related geometrical or graph-theoretical enumerations, there still remain some apparent disadvantages. The USCI approach requires a table of USCIs for every point group; however, such tables are available at the moment only for a limited number of point groups. The evaluation process of fixed points in this approach is based on the expansion of generating functions; this process should be simplified for some purposes. In a continuation of our work, we will give the table of USCIs for $\mathbf{D}_{2d}$ groups and indicate that a combination of the USCI approach and the Redfield-Read theorem provides a new methodology of solving the latter problem.

The USCI Approach

This section is devoted to giving a minimum set of equations for the present formulation. Let $\mathbf{G}$ be a finite group. Suppose that $\mathbf{G}_i$ is a representative of conjugate subgroups of $\mathbf{G}$. We consider a set of such representatives,

$$\mathrm{SSR}=\{\mathbf{G}_1, \mathbf{G}_2, ..., \mathbf{G}_s\}, \quad (1)$$

where each element is not conjugate to any other element and where $\mathbf{G}_1$ is an identity group and $\mathbf{G}_s=\mathbf{G}$. Each element of the SSR is associated with a coset representation, $\mathbf{G}(/\mathbf{G}_i)$, which comes from the corresponding coset decomposition of $\mathbf{G}$ by $\mathbf{G}_i$. The coset representation (CR) is transitive permutation representations. A set of CRs,

$$\mathrm{SSR}=\{\mathbf{G}(/\mathbf{G}_1), \mathbf{G}(/\mathbf{G}_2), ..., \mathbf{G}(/\mathbf{G}_s)\}, \quad (2)$$

is a complete list of such transitive permutation representations. Any permutation representation ($\mathbf{P}_\mathbf{G}$) acting on a domain (Δ) can be reduced into a sum of CRs in the light of

$$\mathbf{P}_\mathbf{G}=\sum_{i=1}^{s}\alpha_i\mathbf{G}(/\mathbf{G}_i), \quad (3)$$

where $\alpha_i(\leqslant 0)$ is the multiplicity of $\mathbf{G}(/\mathbf{G}_i)$. If we restrict the elements within the subgroup $\mathbf{G}_j$, the resulting subduced representation (SR), $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$, becomes an intransitive representaion of the subgroup $\mathbf{G}_j$. This means that the SR can further be reduced in the sum of CRs of $\mathbf{G}_j$ in terms of

$$\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j=\sum_{k=1}^{s}\beta_k^{(ij)}\mathbf{G}_j(/\mathbf{G}_{jk}), \tag{4}$$

for i=1, 2, ..., s and j=1, 2, ..., s, wherein $\mathbf{G}_{jk}$ is a subgroup $\mathbf{G}_j$ and the multiplicity $(\beta_k^{(ij)})$ is determined to be constant.

In the light of Eqs. 3 and 4, we define a *unit subduced cycle index (USCI)*, a *subduced cycle index (SCI)*, and a *cycle index (CI)*.

Definition 1 (USCI, SCI, and CI).

1) A unit subduced cycle index (USCI) corresponding to Eq. 4 is defined as

$$\mathrm{Z}(\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j;\, d_{d_{jk}})=\prod_{k=1}^{v_j}(s_{d_{jk}})^{\beta_k^{(ij)}}, \tag{5}$$

for i=1, 2, ..., s and j=1, 2, ..., s, wherein

$$d_{jk}=|\mathbf{G}_j|/|\mathbf{G}_{jk}|. \tag{6}$$

for i=1, 2, ..., s and j=1, 2, ..., s,

2) A subduced cycle index (SCI) is defined as

$$ZI(\mathbf{G}_{jk};\, s_{d_{jk}})=\prod_{\substack{\alpha=1\\(\alpha_i\neq 0)}}^{\alpha_i}\mathrm{Z}(\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j;\, s_{d_{jk}}) \tag{7}$$

$$=\prod_{k=1}^{v_j}(s_{d_{jk}})^{\sum_{i=1}^{s}\alpha_i\beta_k^{(ij)}} \tag{8}$$

$$\equiv\sum_{(\mu)}b_\mu s_1^{\mu_1}s_2^{\mu_2}\cdots s_q^{\mu_q}, \tag{9}$$

for j=1, 2, ..., s, where the cycle structure (μ) is represented by

$$1\mu_1+2\mu_2+\ldots+q\mu_q=|\Delta|. \tag{10}$$

This cycle structure is dependent upon j; however, this dependence is not denoted for simplicity.

3) A cycle index (CI) is defined as

$$\mathrm{CI}(\mathbf{G};\, s_{d_{jk}})=\sum_{j=1}^{s}\Big(\sum_{i=1}^{s}\overline{m}_{ji}\Big)\mathrm{ZI}(\mathbf{G}_j;\, s_{d_{jk}}), \tag{11}$$

where $\overline{m}_{ji}$ is the ji element of the inverse of the mark table of $\mathbf{G}$.

In this paper, we work out $\mathbf{D}_{2d}$ point group as an example. This group has an SSG:

$$\mathrm{SSR}_{\mathbf{D}_{2d}}=\{\mathbf{G}_1,\, \mathbf{C}_2,\, \mathbf{C}_2',\, \mathbf{C}_s,\, \mathbf{S}_4,\, \mathbf{C}_{2v},\, \mathbf{D}_2,\, \mathbf{D}_{2d}\}, \tag{12}$$

Table 1 shows the inverse of the mark table of $\mathbf{D}_{2d}$ point group. The rightmost column collects the summ of each row, which has been used in the innermost parentheses of Eq. 11.

In accord with the first of Def. 1-(1), Table 2 indicates USCIs for $\mathbf{D}_{2d}$.

Suppose that θ_1 of X_1, θ_2, of X_2, ..., and $\theta_{|\mathbf{X}|}$ of $\mathrm{X}_{|\mathbf{X}|}$ are selected from a codomain, $\mathbf{X}=\{X_1, X_2, \ldots, X_{|\mathbf{X}|}\}$,

Table 1. The Inverse of the Mark Table for $\mathbf{D}_{2d}$ Point Group

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

a) $\mathrm{Sum}=\sum_{i=1}^{s}\overline{m}_{ji}$

Table 2. Unit Subduced Cycle Indices for $\mathbf{D}_{2d}$ Point Group

	$\downarrow\mathbf{C}_1$	$\downarrow\mathbf{C}_2$	$\downarrow\mathbf{C}_2'$	$\downarrow\mathbf{C}_s$	$\downarrow\mathbf{S}_4$	$\downarrow\mathbf{C}_{2v}$	$\downarrow\mathbf{D}_2$	$\downarrow\mathbf{D}_{2d}$
$\mathbf{D}_{2d}(/\mathbf{C}_1)$	s_1^8	s_2^4	s_2^4	s_2^4	s_4^2	s_4^2	s_4^2	s_8
$\mathbf{D}_{2d}(/\mathbf{C}_2)$	s_1^4	s_1^4	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_4
$\mathbf{D}_{2d}(/\mathbf{C}_2')$	s_1^4	s_2^2	$s_1^2s_2$	s_2^2	s_4	s_4	s_2^2	s_4
$\mathbf{D}_{2d}(/\mathbf{C}_s)$	s_1^4	s_2^2	s_2^2	$s_1^2s_2$	s_4	s_2^2	s_4	s_4
$\mathbf{D}_{2d}(/\mathbf{S}_4)$	s_1^2	s_1^2	s_2	s_2	s_1^2	s_2	s_2	s_2
$\mathbf{D}_{2d}(/\mathbf{C}_{2v})$	s_1^2	s_1^2	s_2	s_1^2	s_2	s_1^2	s_2	s_2
$\mathbf{D}_{2d}(/\mathbf{D}_2)$	s_1^2	s_1^2	s_1^2	s_2	s_2	s_2	s_1^2	s_2
$\mathbf{D}_{2d}(/\mathbf{D}_{2d})$	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1
$\sum_{i=1}^{s}\overline{m}_{ji}$	1/8	1/8	1/4	1/4	1/4	0	0	0

wherein

$$[\theta]:\theta_1+\theta_2+\ldots+\theta_{|\mathbf{X}|}=|\Delta|. \tag{13}$$

The corresponding configuration, $f:\Delta\rightarrow\mathbf{X}$, has a weight (molecular formula) of

$$W_\theta=X_1^{\theta_1}X_2^{\theta_2}\cdots X_{|\mathbf{X}|}^{\theta|\mathbf{X}|}. \tag{14}$$

The number $(\rho_{\theta j})$ of fixed configurations having W_θ and $\mathbf{G}_j$ is evaluated by the following lemma.

Lemma 1 (Evaluation of $\rho_{\theta j}$).

A set of such numbers ($\rho_{\theta j}$'s) for the $\mathbf{G}_j$ subsymmetry is given as the coefficients of a generating function,

$$\sum_{[\theta]}\rho_{\theta j}W_\theta=\mathrm{ZI}(\mathbf{G}_j;\, s_{d_{jk}}), \tag{15}$$

where the SCI of the right-hand side is replaced by a figure-inventory,

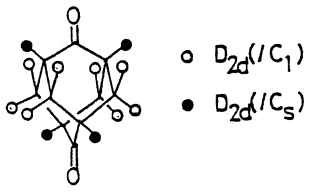
$$s_{d_{jk}}=\sum_{r=1}^{|\mathbf{X}|}X_r^{d_{jk}}. \tag{16}$$

Let the symmbol $A_{\theta i}$ be the number of configurations with W_θ and $\mathbf{G}_i$. If we consider a set containing all of configurations with W_θ, the $A_{\theta i}$ is the number of orbits within this set of configurations. Hence, this is obtained in terms of

Theorem 1.

$$A_{\theta i}=\sum_{j=1}^{s}\rho_{\theta j}\overline{m}_{ji} \tag{17}$$

for i=1, 2, ..., s. The following example illustrates



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enumeration procedures based on the USCI approach. This approach can be applied to any combinatorial enumerations, although we select this example from a chemical field.

Example 1 (Derivatives of an adamantanedione **1**).

Let us enumerate molecules derived from an adamantanedione (**1**). This parent molecule has $\mathbf{D}_{2d}$ symmetry. The twelve hydrogens of this molecule are considered to be substitution positions which are replaced by X, Y, or Z. These twelve positions are divided into two orbits which are denoted by solid circles (4 bridgehead positions) and open circles (8 bridge positions). The assignment of CRs to these orbits can be accomplished by examining a fixed-point vector (FPV). In this case, we can obtain FPV=(12 0 0 2 0 0 0 0) by inspection of **1**. This FPV is multiplied by the inverse of the mark table (1) to give (1 0 0 1 0 0 0 0), which indicates

$$\mathbf{P}_1=\mathbf{D}_{2d}(/\mathbf{C}_1)+\mathbf{D}_{2d}(/\mathbf{C}_s). \tag{18}$$

Obviously, a set of the 8 bridge positions is subject to $\mathbf{D}_{2d}(/\mathbf{C}_1)$ and that of the 4 bridgehead positions is governed by $\mathbf{D}_{2d}(/\mathbf{C}_s)$. Hence we adopt USCIs appearing at the $\mathbf{D}_{2d}(/\mathbf{C}_1)$ and $\mathbf{D}_{2d}(/\mathbf{C}_s)$ rows of Table 2. In accord with Eq. 7, we construct an SCI for every subgroup of the SSG:

$$\text{for } \mathbf{C}_1: (s_1^8)(s_1^4)=(x+y+z)^{12} \tag{19}$$

$$\text{for } \mathbf{C}_2: (s_2^4)(s_2^2)=(x^2+y^2+z^2)^6 \tag{20}$$

$$\text{for } \mathbf{C}_2': (s_2^4)(s_2^2)=(x^2+y^2+z^2)^6 \tag{21}$$

$$\text{for } \mathbf{C}_s: (s_2^4)(s_1^2s_2)=(x+y+z)^2(x^2+y^2+z^2)^5 \tag{22}$$

$$\text{for } \mathbf{S}_4: (s_4^2)(s_4)=(x^4+y^4+z^4)^3 \tag{23}$$

$$\text{for } \mathbf{C}_{2v}: (s_4^2)(s_4^2)=(x^2+y^2+z^2)^2(x^4+y^4+z^4)^2 \tag{24}$$

$$\text{for } \mathbf{D}_2: (s_4^2)(s_4)=(x^4+y^4+z^4)^3 \tag{25}$$

and

$$\text{for } \mathbf{D}_{2d}: (s_8)(s_4)=(x^4+y^4+z^4)(x^8+y^8+z^8). \tag{26}$$

The left-hand side of each equation denotes an SCI for each subgroup, in which the first set of parentheses contains the USCI of the $\mathbf{D}_{2d}(/\mathbf{C}_1)$ row and the second contains the USCI of $\mathbf{D}_{2d}(/\mathbf{C}_s)$. The righ-hand side of each equation is obtained by introducing a figure inventory for this case, $s_d=x^d+y^d+z^d$ in the light of Lemma 1.

The expansion of the right-hand sides of the equations affords generating functions, in which the $\rho_{\theta j}$ value with a partition $[\theta]=[\theta_1,\theta_2,\theta_3]$ ($\theta_1+\theta_2+\theta_3=12$) and with the $\mathbf{G}_j$ symmetry is given as the coefficient of the $x^{\theta_1}y^{\theta_2}z^{\theta_3}$ term. Obviously, the coefficients for $[\theta_1,\theta_2,\theta_3]$, $[\theta_2,\theta_3,\theta_1]$, $[\theta_3,\theta_1,\theta_2]$, $[\theta_1,\theta_3,\theta_2]$, $[\theta_2,\theta_1,\theta_3]$, and $[\theta_3,\theta_2,\theta_1]$ are equal to each other.

For illustrating a procedure for obtaining the numbers of isomers, we work out the case of x^8y^4, which is alternatively represented by a ligand partition, [8,4,0]. We collect the coefficients of the x^8y^4 term after the expansion of the above generating functions. We thereby obtain the FPV for the x^8y^4 term, i.e., FPV=(495 15 15 15 3 3 3 1). This FPV is multi-

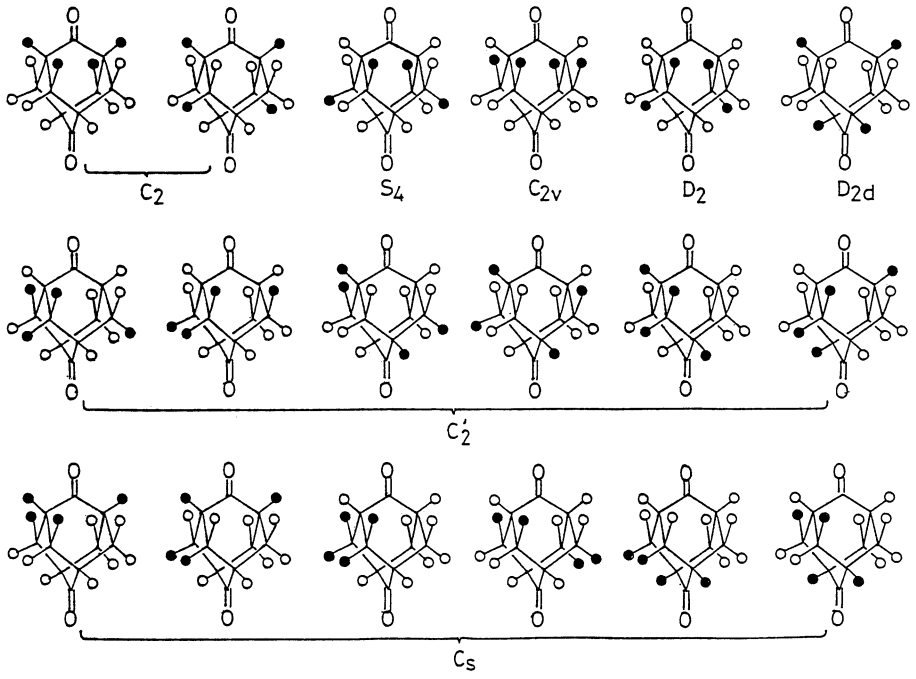

Fig. 1. [8,4,0]-Molecules derived from adamantane-2,6-dione.

Table 3. Number of Compounds Derived from the Skeleton (**1**)

Ligand partition	Number of isomers with								Total
	C_1	C_2	C_2'	C_s	S_4	C_{2v}	D_2	D_{2d}	
[12,0,0]	0	0	0	0	0	0	0	1	1
[11,1,0]	1	0	0	1	0	0	0	0	2
[10,2,0]	5	1	3	2	0	1	0	0	12
[10,1,1]	16	0	0	1	0	0	0	0	17
[9,3,0]	25	0	0	5	0	0	0	0	30
[9,2,1]	80	0	0	5	0	0	0	0	85
[8,4,0]	54	2	6	6	1	1	1	1	72
[8,3,1]	245	0	0	5	0	0	0	0	250
[8,2,2]	353	7	15	14	0	1	0	0	330
[7,5,0]	94	0	0	10	0	0	0	0	104
[7,4,1]	490	0	0	10	0	0	0	0	500
[7,3,2]	980	0	0	20	0	0	0	0	1000
[6,6,0]	104	4	10	8	0	2	0	0	128
[6,5,1]	688	0	0	10	0	0	0	0	698
[6,4,2]	1696	14	30	28	0	2	0	0	1770
[6,3,3]	2300	0	0	20	0	0	0	0	2320
[5,5,2]	2064	0	0	30	0	0	0	0	2094
[5,4,3]	3450	0	0	30	0	0	0	0	3480
[4,4,4]	4278	18	42	42	3	3	3	0	4389

plied by the inverse (Table 1) to give a row vector, (54 2 6 6 1 1 1 1), which indicates the numbers in the order of the SSG. This means that, as X_8Y_4-isomres, there emerge 54 C_1 (asymmetric) isomers, 2 C_2, 6 C_2', 6 C_s isomers, one S_4, one C_{2v}, one D_2, and one D_{2d} isomer.

This type of calculation is repeated over all partitions $[\theta]$ to give Table 3, in which the intersection between $[\theta_1,\theta_2,\theta_3]$ and a subsymmetry indicates the number of isomers.

For the verification of the values in Table 3, Fig. 1 lists isomers with [8,4,0] and symmetries other than C_1. The present enumeration clarifies both the molecular formula (or the ligand partition) and the symmtery of an isomer. Hence, we can easily draw a concrete structure of the isomer.

Alternative Evaluation of $\rho_{\theta j}$

In the enumeration described in the previous section, the evaluation of the $\rho_{\theta j}$ value is accomplished by expanding a generating function (Eq. 15). This method affords a full list of $\rho_{\theta j}$ over all of the $[\theta]$ partitions. However, there are many cases in which a specific case of $[\theta]$ is to be examined.

Suppose the domain Δ of **G** symmetry, which is originally divided in several orbits (3), is restricted within its subsymmetry $\mathbf{G}_j$. This process results in the subduction of the domain,

$$\mathbf{P}_{G_j}=\sum_{i=1}^{s}\alpha_i\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j \tag{27}$$

which provides the subdivision of the domain represented by the SCI (Eq. 7 or 8). This SCI indicates a pattern of occupation of ligands. Although we consider a direct occupation of ligands on this divided domain in the previous treatment, we here introduce a slightly different formulation.

We consider a ligand partition $[\theta]$ represented by Eq. 13. Let $S^{(\theta r)}$ be the symmetric group of each ligand set associated with θ_r. We define a cycle index for this symmetric group of degree θ_r as being

$$\mathrm{CI}(\$^{(\theta_r)};s)=\frac{1}{\theta_r!}\sum_{(\nu(\theta_r))}n_{(\nu(\theta_r))}s_1^{\nu_1(\theta_r)}s_2^{\nu_2(\theta_r)}\cdots s_{\theta_r}^{\nu_{\theta_r}(\theta_r)}, \tag{28}$$

where the cycle structure $(\nu(\theta_r))$ is represented by

$$(\nu(\theta_r)):1\nu_1(\theta_r)+2\nu_2(\theta_r)+\ldots+\theta_r\nu_{\theta_r}(\theta_r)=\theta_r, \tag{29}$$

and where

$$n_{(\nu(\theta_r))}=\frac{\theta_r!}{1^{\nu_1(\theta_r)}\nu_1(\theta_r)!2^{\nu_2(\theta_r)}\nu_2(\theta_r)!\cdots\theta_r^{\nu_{\theta r}(\theta_r)}\nu_{\theta_r}(\theta_r)!}. \tag{30}$$

We can construct a direct product of such symmetric groups, i.e.,

$$\mathbf{H}=\$^{(\theta_1)}\times\$^{(\theta_2)}\times\ldots\times\$^{(\theta|\mathbf{X}|)}, \tag{31}$$

where $\$^{(\theta_r)}$ is effective only if θ_r is positive.

The cycle index of the direct product (Eq. 31) is the product of the cycle indices of the factors. Hence, Eq. 28 affords

$$\mathrm{CI}(\mathbf{H};s)=\prod_{r=1}^{|\mathbf{X}|}\mathrm{CI}(\$^{(\theta_r)};s) \tag{32}$$

$$\equiv\sum_{(\mu)}a_\mu s_1^{\mu_1}s_2^{\mu_2}\cdots s_q^{\mu_q}, \tag{33}$$

where the cycle structure (μ) is given by Eq. 10.

Now, we consider a superposition of $\mathbf{P}_{G_j}$ (Eq. 27) and **H** (Eq. 31), both of which act on Δ. When we apply an operation (*) introduced by Read,[20] we obtain

$$\mathrm{CI}(\mathbf{H};s)*\mathrm{ZI}(\mathbf{G}_j;s_{d_{jk}})=\sum a_\mu b_\mu(1^{\mu_1}\mu_1!2^{\mu_2}\mu_2!\cdots q^{\mu_q}\mu_q!)s_1^{\mu_1}s_2^{\mu_2}\cdots s_q^{\mu_q}, \tag{34}$$

for $j=1, 2, \ldots, s$. Note that the SCI (Eq. 8) is a monomial. Hence, the corresponding equivalent expression (Eq. 9) indicates that $b_{\mu(\theta)}=1$ for only one specific cycle structure $(\mu_{(\theta)})$ given by the SCI; otherwise $b_{\mu(\theta)}=0$. This superposition affords.

Theorem 2. the $\rho_{\theta j}$ value is evaluated by means of

$$\rho_{\theta j}=a_{\mu(\theta)}b_{\mu(\theta)}(1^{\mu_1(\theta)}\mu_1(\theta)!2^{\mu_2(\theta)}\mu_2(\theta)!\cdots q^{\mu_q(\theta)}\mu_q(\theta)!), \tag{35}$$

for $j=1, 2, \ldots, s$. The cycle structure $(\mu_{(\theta)})$ is equivalent to the $[\theta]$ partition represented by Eq. 13.

Now that we have arrived at such an alternative evaluation of $\rho_{\theta j}$, we introduce this equation to Theorem 1 in order to obtain the numbers $(A_{\theta i})$.

In order to illustrate the present approach, we reexamine Example 1.

Example 2 (Enumeration based on a combinaion of the USCI approach and the superposition theorem).

Let us obtain the number of X_8Y_4-isomers with each subsymmetry which is derived from the parent skeleton (**1**). In this case, we consider

$$\mathbf{P}_{G_j}=\mathbf{D}_{2d}(/\mathbf{G}_1)\downarrow\mathbf{G}_j+\mathbf{D}_{2d}(/\mathbf{C}_s)\downarrow\mathbf{G}_j \tag{36}$$

according to Eq. 18, where $\mathbf{G}_j$ is selected from the $SSR_{\mathbf{D}_{2d}}$. This expression corresponds to each of the SCIs represented by Eqs. 19—26.

In accord with the ligand partition [8,4,0] for this case, we adopt

$$\mathbf{H} = \$^{(8)} \times \$^{(4)}, \tag{37}$$

where $\$^{(8)}$ and $\$^{(4)}$ denote symmetric groups of degree 8 and 4. Their cycle indices are calculated by means of Eq. 28 to be

$$\begin{aligned}CI(\$^{(8)}; s) = {} & \frac{1}{8}s_8 + \frac{1}{7}s_1s_7 + \frac{1}{12}s_2s_6 + \frac{1}{12}s_1^2s_6 + \frac{1}{15}s_3s_5 + \frac{1}{10}s_1s_2s_5 + \\ & \frac{1}{30}s_1^3s_5 + \frac{1}{32}s_4^2 + \frac{1}{12}s_1s_3s_4 + \frac{1}{32}s_4^2s_4 + \frac{1}{16}s_1^2s_2s_4 + \frac{1}{96}s_1^4s_4 + \\ & \frac{1}{36}s_2s_3^2 + \frac{1}{24}s_1s_2^2s_3 + \frac{1}{36}s_1^2s_3^2 + \frac{1}{36}s_1^3s_2s_3 + \frac{1}{360}s_1^5s_3 + \\ & \frac{1}{384}s_2^4 + \frac{1}{96}s_1^2s_2^3 + \frac{1}{192}s_1^4s_2^2 + \frac{1}{1440}s_1^6s_2 + \frac{1}{40320}s_1^8,\end{aligned} \tag{38}$$

and

$$CI(\$^{(4)}; s) = \frac{1}{4}s_4 + \frac{1}{3}s_1s_3 + \frac{1}{8}s_2^2 + \frac{1}{4}s_1^2s_2 + \frac{1}{24}s_1^4. \tag{39}$$

The multiplication of these cycle indices affords CI($\mathbf{H}$; s) according to Eq. 34. Thus, we obtain

$$\begin{aligned}CI(\mathbf{H}; s) &= CI(\$^{(8)}; s) \times CI(\$^{(4)}; s) \\ &= \ldots + \frac{1}{8}\times\frac{1}{4}s_8s_4 + \ldots + \left(\frac{1}{4}\times\frac{1}{32} + \frac{1}{32}\times\frac{1}{96}\right)s_1^2s_2^2 + \ldots + \\ &\quad \frac{1}{32}\times\frac{1}{4}s_4^3 + \ldots + \left(\frac{1}{384}\times\frac{1}{4} + \frac{1}{96}\times\frac{1}{8}\right)s_1^2s_2^5 + \ldots + \\ &\quad \frac{1}{384}\times\frac{1}{8}s_2^6 + \ldots + \frac{1}{40320}\times\frac{1}{24}s_1^{12} + \ldots,\end{aligned} \tag{40}$$

where other non-effective terms are omitted.

We now consider the superposition of $\mathbf{P}_{\mathbf{G}_j}$(Eq. 36) and $\mathbf{H}$ (Eq. 37). For $\mathbf{C}_1$, the SCI is denoted as $(s_1^4)(s_1^8)=s_1^{12}$, as shown in Eq. 19. The corresponding term of CI($\mathbf{H}$; s) is obtained by $(1/40320)\ s_1^8 \times (1/24)s_1^4$, in which the former comes from Eq. 13 and the latter from Eq. 14. Equation 35 is applied to this case to afford

$$\rho_{\theta C_1} = 1^{12}12! \times \frac{1}{24} \times \frac{1}{40320} = 495. \tag{41}$$

Similarly, other $\rho_{\theta j}$ values are obtained as follows:

$$\rho_{\theta C_2} = 2^6 6! \times \frac{1}{384} \times \frac{1}{8} = 15 \text{ for } \mathbf{C}_2 \text{ of the SCI } (s_2^6), \tag{42}$$

$$\rho_{\theta C_2'} = 2^6 6! \times \frac{1}{384} \times \frac{1}{8} = 15 \text{ for } \mathbf{C}_2' \text{ of the SCI } (s_2^6), \tag{43}$$

$$\begin{aligned}\rho_{\theta C_s} &= 1^2 2! 2^5 5! \times \left(\frac{1}{4}\times\frac{1}{384} + \frac{1}{8}\times\frac{1}{96}\right) \\ &= 15 \text{ for } \mathbf{C}_2 \text{ of the SCI } (s_1^2s_2^5),\end{aligned} \tag{44}$$

$$\rho_{\theta S_4} = 4^3 3! \times \frac{1}{4} \times \frac{1}{32} = 3 \text{ for } \mathbf{S}_4 \text{ of the SCI } (s_4^3), \tag{45}$$

$$\begin{aligned}\rho_{\theta C_{2v}} &= 2^2 2! 4^2 2! \times \left(\frac{1}{4}\times\frac{1}{32} + \frac{1}{32}\times\frac{1}{96}\right) \\ &= 3 \text{ for } \mathbf{C}_{2v} \text{ of the SCI } (s_2^2s_4^2),\end{aligned} \tag{46}$$

$$\rho_{\theta D_2} = 4^3 3! \times \frac{1}{4} \times \frac{1}{32} = 3 \text{ for } \mathbf{D}_2 \text{ of the SCI } (s_4^3), \tag{47}$$

and

$$\rho_{\theta D_{2d}} = 8^1 1! 4^1 1! \times \frac{1}{8} \times \frac{1}{4} = 1 \text{ for } \mathbf{D}_{2d} \text{ of the SCI } (s_4s_4). \tag{48}$$

These are summarized to afford an FPV=(495 15 15 15 3 3 3 1), which is multiplied by the inverse (Table 1). The resulting row vector (54 2 6 6 1 1 1 1) is identical with the [8,4,0] row of Table 3.

Alternative Formulation of Cycle Indices

The Cycle index (CI) formulated in Eq. 11 can be proven to be identical with Pólya's cycle index, although their explicit forms are quite different.[30] In this section, we illustrate the application of the present type of CI and its combination with the Redfield-Read superposition theorem.

Example 3 (Enumeration based on the novel formulation of cycle indices and the superpoition theorem).

Let us reexamine Example 1. The cycle index (Eq. 11) for this case is obtained to be

$$\begin{aligned}CI(\mathbf{D}_{2d}; s_d) &= \frac{1}{8}(s_1^8)(s_1^4) + \frac{1}{8}(s_2^4)(s_2^2) + \frac{1}{4}(s_2^4)(s_2^2) + \frac{1}{4}(s_2^4)(s_2^2s_2) + \frac{1}{4}(s_4^2)(s_4) \\ &= \frac{1}{8}s_1^{12} + \frac{3}{8}s_2^6 + \frac{1}{4}s_1^2s_2^5 + \frac{1}{4}s_4^3,\end{aligned} \tag{49}$$

where the USCIs of each monomial comes from the $\mathbf{D}_{2d}(/\mathbf{C}_1)$ and $\mathbf{D}_{2d}(/\mathbf{C}_s)$ rows of Table 2 and the coefficient of each monomial is taken up from the bottom of the same Table. When we introduce the figure inventory shown in Example 1, i.e. $s_d = x^d + y^d + z^d$, into the CI (Eq. 50), we obtain

$$\begin{aligned}CI(\mathbf{D}_{2d}; x^d + y^d + z^d) = {} & x^{12} + 2x^{11}y + 2x^{11}z + 12x^{10}y^2 + 17x^{10}yz + 12x^{10}z^2 + 30x^9y^3 \\ & + 85x^9yz^2 + 30x^9z^3 + 72x^8y^4 + 250x^8y^3z + 390x^8y^2z^2 + 250x^8yz^3 \\ & + 72x^8z^4 + 104x^7y^5 + 500x^7y^4z + 1000x^7y^3z^2 + 1000x^7y^2z^3 \\ & + 500x^7yz^4 + 104x^7z^5 + 128x^6y^6 + 698x^6y^5z + \ldots,\end{aligned} \tag{50}$$

after expansion. These coefficients are identical with the values collected at the rightmost column of Table 3 which are obtained by the direct summantion of the respective rows.

The following calculation is a direct application of the superposition theorem;[23] however, the present new formulation of cycle index allows us to apply this theorem more conveniently than before. We now consider the superposition of Eqs. 50 and 40. This

operation affords the total number of isomers with the partition [8,4,0]. The * operation leaves the terms s_1^{12}, s_2^6, $s_1^2 s_2^5$, and s_4^3. Their coefficients are added to be

$$1^{12}12!\frac{1}{40320}\times\frac{1}{24}\times\frac{1}{8}+2^66!\frac{1}{384}\times\frac{1}{8}\times\frac{3}{8}+$$
$$1^22!2^55!\left(\frac{1}{384}\times\frac{1}{4}+\frac{1}{96}\times\frac{1}{8}\right)\times\frac{1}{4}+4^33!\frac{1}{32}\times\frac{1}{4}\times\frac{1}{4}=72. \quad (51)$$

This value is identical to the total of the [8,4,0] row listed in Table 3 and to the coefficient of the x^8y^4 term of Eq. 51.

Concluding Remarks

An combination between our method based on unit subduced cycle indices (USCIs) and the Redfield-Read superposition theorem affords a new versatile methodology for enumerations. Subduced cycle indices (SCIs) derived from the USCIs are superimposed upon a cycle index for a given ligand partition $[\theta]$ in order to evaluate $\rho_{\theta j}$ values, which are in turn used to calculate the number of isomers with the $[\theta]$ partition and the $\mathbf{G}_j$-symmetry. The superposition between a cycle index derived from the SCIs and the cycle index for the ligand partition give the number of isomers with the $[\theta]$ partition. The present enumeration method is exemplified by using a parent $\mathbf{D}_{2d}$ skeleton.

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