J Math Chem (2014) 52:703–728
DOI 10.1007/s10910-013-0290-0

ORIGINAL PAPER

Generalization of the Harary–Palmer power group theorem to all irreducible representations of object and color groups- color combinatorial group theory

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Received: 15 October 2013 / Accepted: 4 November 2013 / Published online: 21 November 2013
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Abstract The Harary–Palmer classic power group enumeration theorem applies to a group G acting on a set D of objects such as vertices, edges, faces and simultaneously with a group H acting on another set R of colors such that the power group H^G acts on the set R^D of all functions from D to R. In this paper we show for the first time that the power group enumeration can be generalized to all irreducible representations of the object group G of D and also all irreducible representations of the color group H of R. We have also provided interpretation of various power group generating functions for different irreducible representations in the context of color symmetry group theory. Special cases of the power group enumeration with all irreducible representations of G keeping the color group representation fixed to the totally symmetric representation are shown to have important enumerative combinatorial applications in a number of problems of chemistry, physics and biology that involve color symmetry (color inversions) such as magnetism, neutron imaging, NMR, ESR spectroscopy, catalytic functions of non-rigid disordered proteins, and quantum chromodynamics of strong interactions of fundamental particles.

Keywords Power group enumeration to all irreducible representations · Harary–Palmer · Combinatorial group theory · Color symmetry · NMR · Magnetism · Quantum chromodynamics

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1 Introduction

Color and color symmetry play fundamental roles in both scientific disciplines and arts [1–7]. A number of fascinating problems in mathematics originate from colors, for example, the celebrated four-color problem of combinatorics [8]. Although in a purely mathematical sense, colors facilitate labeling or book-keeping different objects through mappings, aesthetics of different ways of colorings has been intertwined with cultures, traditions and arts. Color symmetry concepts thus naturally arise in many fields of arts and cultures, for example, elegant color patterns called the Rangoli patterns illustrated in Fig. 1 that are native to India. In fact, extensive research has been carried out on cultural, ethnographic, and ecological significances of geometric patterns called Kolams of southern India folklore [9–11].

Color symmetry is fundamental to magnetic spin symmetry of fermions and bosons in that spin flipping can be envisaged as a color inversion operation. That is, for a spin-1/2 fermion this would mean interchanging spin function α with β for all spin-particles. As such a spin-flip operation leads to invariance in the magnitude of the eigenvalues of interactions along the z-component, there is a natural symmetry of signals appearing in NMR and ESR spectroscopies of such systems. For example, $n-2$ multiple-quantum NMR of benzene [12] exhibits symmetric distribution of signals on either side of the central peak- clearly a manifestation of spin-flip or color-inversion symmetry. Likewise

Fig. 1 A Rangoli pattern from India with a hexagonal D_6 symmetry of outer petals (from, http://www.theholidayspot.com/diwali/rangoli.htm). The Power Group Enumeration asks for how many different Rangoli patterns are possible under the action of the D_6 group on petals forming the hexagon with 4 different colors (*white*, *green*, *red*, *yellow*) such that white is fixed and three colors can be interchanged through the action of color group S_3 acting on the three colors (*green*, *red*, and *yellow*). See, Refs [9–11] for ethnographic, ecological and other significances (Color figure online)

for the general boson, the interchange of spin functions for $-I_z$ and $+I_z$ would result in a similar invariance characterized by color symmetry concept of Shubnikov [1]. Consider for instance, bismuth clusters (Bi_n) which are extremely interesting because of both relativistic effects and aromaticity [13,14]. Moreover, ^{209}bismuth exhibits an unusually high nuclear spin quantum number of S=9/2, and consequently, it has been a subject of number of studies in two-dimensional and solid state NMR [15–17]. The spin 9/2 particle would exhibit 10 orientations labeled by −9/2, −7/2, −5/2, −3/2, −1/2, 1/2, 3/2, 5/2,7/2 and 9/2 quantum numbers and thus spin-flips would be characterized by a color group of two operations- one of them involving flips of −9/2 to 9/2, −7/2 to 7/2, −3/2 to 3/2 and −1/2 to 1/2. Thus it is clear that color symmetry combinatorics would find important applications in the enumeration of symmetry-adapted spin functions with S_2 color symmetry that results in all interchange of 2 colors for spins $-I_z$ and $+I_z$.

In the field of quantum chromodynamics of strong interactions, quark states are characterized by three colors (blue, red and green) and thus the SU(3) group and the associated Weyl Tableau play an important role in characterizing the symmetry-adapted functions for the fundamental particles with three quark flavors represented by u, d, and s. The various mixed symmetry states of baryons are then characterized by symmetry adapted linear combinations of three-particle states, where u,d and s designate orthogonal single-particle states in the SU(3) group. In this instance, generating wavefunctions of the baryons involve direct products of three-irreducible representations in the SU(3) group which can be subduced into the S_3 symmetric group to generate the irreducible components. For instance $3 \times 3 \times 3$ direct product in SU(3) subduces into a 27-dimensional reducible representation in the S_3 group resulting in various symmetry-adapted linear combinations of wavefunctions, characterizing different mixed symmetry states of the baryons. Here again one can see the role of the permutation group and color symmetry through Young diagrams and the associated Weyl tableaus.

Combinatorial applications to chemistry in the context of enumeration of isomers, nuclear spin statistics, NMR, ESR spectrocopies and chirality have been the topic of many papers [18–51]. An example of combinatorial application in chemical context that involves color symmetry is association of vectors or directions on various atoms of a molecule. This naturally arises in dealing with molecular vibrational normal modes where each atom is labeled by three orthogonal vectors to designate the three degrees of freedom on each atom. Likewise the p orbitals on each center can be represented by 3 orthogonal vectors on each atom. Hässelbarth [52] has suggested the use of power group enumeration in these instances, except that this application, in fact, does not use the full power group approach in that the group acting on colors is not independent of the group acting on objects. That is, in this particular case, the group acting on the vertices of a graph determines also the action on the colors, and thus we do not have two different groups acting on colors and objects. Thus this amounts to a single group G with different orbits for the vertices and vectors.

Balaban [27,53,54] has employed the power group enumeration theorem and Redfield's [57] cup and cap operations to generate the valence isomers of annulenes. This is a natural application of Harary and Palmer's [60] enumeration of graphs using the power group enumeration. Read [55] and Davidson [56] have independently

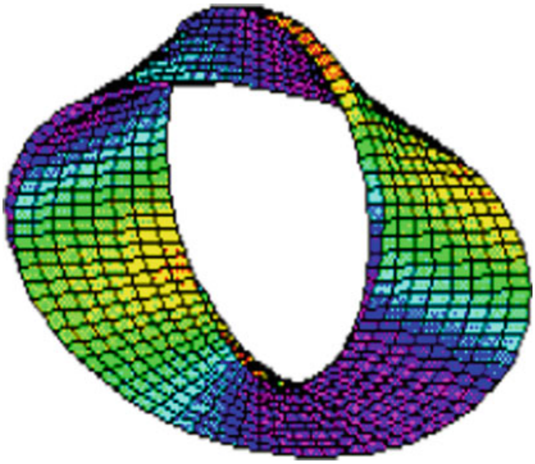

Fig. 2 A Möbius strip provides a suitable representation of the relativistic spinors. The introduction of spin-orbit coupling into the relativistic Hamiltonian causes the periodicity of the symmetry group into double group symmetry, as the rotation by 360° is no longer the identity operation. Generalization of this to other complex phases results in Berry's phase, where a rotation by 360 may yield $\exp(i2\pi/n)$ thus resulting in other kinds of periodicity

considered various applications of Redfield's [57] superposition theorem. Balasubramanian [51] has previously generalized de Bruijn's theorem [58,59] for all irreducible representations. De Bruijn's theorem [59] is a special case of the power group enumeration theorem of Harary and Palmer [60] where the group acting on colors is restricted to the S_2 group, sometimes referred to as inversion of two colors. With the exception of these previous applications, very few studies have considered chemical application of power group enumeration.

Stimulated by the classic work of Longuet–Higgins [61] on the symmetry groups of non-rigid molecules as permutation-inversion groups, Balasubramanian [62] has considered the symmetry groups of non-rigid molecules as generalized wreath products and more recently its extension to relativistic double group spinors of non-rigid molecules [63]. When spin-orbit coupling is introduced into the Hamiltonian, a generalized relativistic representation of the electronic states of molecules emerges, especially for molecules comprised of heavy atoms. Such a treatment requires a Möbius representation as exemplified in Fig. 2. The relativistic double group spinor representations of non-rigid molecules in the double groups of generalized wreath products were considered by Balasubramanian [63] previously. King [64] has exemplified Möbius aromaticity of Rh-centered bismuth clusters such as $RhBi_7$ and it has been shown using combinatorial methods that certain arrangements and electron counts are more favored for such Mobius aromatic clusters.

In this paper, we are presenting for the first time generalization of the power group enumeration theorem to all irreducible representations of not only the object group but also color groups. Thus for the first time a table of $n_G \times n_H$ generating functions is constructed, where n_G is the number of irreducible representations of the group G, while n_H is the number of irreducible representations of the group H. We have also provided a physical interpretation of the newly obtained generating functions for different irreducible representations of the object group G together with the action of the color group H on the set of colors. To the best of author's knowledge, this is the first time such a powerful enumeration is considered for all irreducible representations of the power group and the new table of generating functions thus obtained in the form of a $n_G \times n_H$ table of generating functions consists of a plethora of new results in color combinatorial group theory.

2 De Bruijn theorem and the Harary–Palmer power group enumeration theorem

2.1 De Bruijn's theorem and Pólya preliminaries

Let D be a set of objects, which we call the object set and let R be a set of colors, which we call the color set. Moreover let G be a permutation group acting on D *such that* two maps fi and f_2 from D to R are equivalent, if there exists a g ε G such that

$$f_1(d) = f_2(gd)\ for\ all\ d\ \varepsilon\ \mathrm{D}$$

For each r ε GR a weight $w(r)$ can be assigned such that one can define the weight $W(f)$, the weight of a function f: D $\rightarrow$ R as follows:

$$W(f) = \prod_{d\ \varepsilon\ D} w(f(d))$$

Define the ordinary cycle index of a group G acting on a set D as

$$P_G = \frac{1}{|G|}\sum_{g\varepsilon G} s_1^{b_1} s_2^{b_2} \ldots\ldots s_n^{bn} \tag{1}$$

where $s_1^{b_1} s_2^{b_2} \ldots..s_n^{bn}$ in (1) is a cycle representation for $g\ \varepsilon\ G$ if it generates b1 cycles of length 1, b_2 cycles of length 2, etc., upon its action on the elements of the set D. Pólya's theorem [37] yields a generating function for the equivalence classes of maps from f: D $\rightarrow$ R as follows:

$$GF = P_G\left(s_k \rightarrow \sum_{r\varepsilon R} [(w(r)]^k\right) \tag{2}$$

where the arrow symbol in (2) means replace every s_k in P_G by $\sum_{r\varepsilon R} [(w(r)]^k$. This substitution can be called the Pólya substitution in combinatorics, and facilitates computing equivalences classes of all maps R^D, with group G acting on the set D. One can assign say a weight b for blue color, g for green, r for red, v for violet then the Pólya process is tantamount to replacing every $\mathrm{s_k}$ in the cycle index by $b^k + g^k + r^k + v^k \ldots\ldots$ This in turn generates a polynomial in *b, g, r, v..* such that the coefficient of a typical term $w_1^{b_1} w_2^{b_2} \ldots\ldots w_n^{bn}$ generates number of equivalence classes of patterns for $\mathrm{b_1}$

colors of type 1 with weight w_1, b_2 colors of the type 2 with weight w_2.....b_n colors of the type n with weight w_n.

De Bruijn's theorem [59] generalizes Pólya's theorem when the group G acts on the object set D and for a special case where the set R has just two interchangeable colors. Consider a set D of objects and a set R of two different colors (say red and blue).If G is a permutation group acting on D and let H be a permutation group of two elements *{b) (r), ((br)}* of colors. Now consider all maps f : D $\rightarrow$ R. All such maps constitute the set R^D. In De Bruijn's formulation two different Pólya G-equivalence classes (patterns) under the action of G become equivalent under the action of H if there are two representatives in these patterns such that one is transformable into the other by the action of h ε H in the color group . In mathematical terms consider for each $g \varepsilon D$, $f \varepsilon R^D$, the mapping $\gamma_\mathrm{g} : R^D \rightarrow R^D$ defined by

$$\gamma_g (f) = hfg, \tag{3}$$

γ_g permutes R^D for h ε H. The de Bruijn theorem gives the number of distinct patterns (equivalence classes) under the action of both G on D and the permutation h acting on R, the set of colors for the special case that there are only 2 colors and the permutation is imply the switching of the two colors.

In this set up according to de Bruijn [59], the generating function for the equivalence classes of patterns under the action of both G and H is

$$GF = P_G (s_k \rightarrow \mu_k), \tag{4}$$

where

$$\begin{aligned} \mu_k &= \sum_{r\varepsilon R} w(r)w(hr)w(h^2r)w(h^3r)\ldots w(h^{k-1}r), \\ h^k r &= r \end{aligned} \tag{5}$$

Consider coloring vertices of a tetrahedron with 2 colors, say blue and red under the action of the tetrahedral point group T_d acting on the set D and thus R is a set of two colors, red and blue. The group H comprising of two permutations is H = *{(b)(r), (br)}*. The cycle index of the Td group for four vertices is

$$P_{T_d} = \frac{1}{24}[s_1^4 + 6s_1^2 s_2 + 8s_1 s_3 + 3s_2^4 + 6s_4) \tag{6}$$

Let us construct the needed μ_1, μ_2, etc., since h = (br) there is no h such that $hz = z$ for z ε R. Thus = $\mu_1 = 0$, and more over since $h^2 = (br)(br) = (b)(r)$ both red and blue colors in R are left invariant under the action of h^2. Thus

$$\begin{aligned} \mu_2 &= \sum_{g,b} w(r)w(hr) = 2br, \\ \mu_3 &= \sum_{g,b} w(r)w(hr)w(h^2r) = 0 \\ \mu_4 &= \sum_{g,b} w(r)w(hr)w(h^2r)w(h^3r) = r^2b^2 + r^2b^2 = 2r^2b^2 \end{aligned} \tag{7}$$

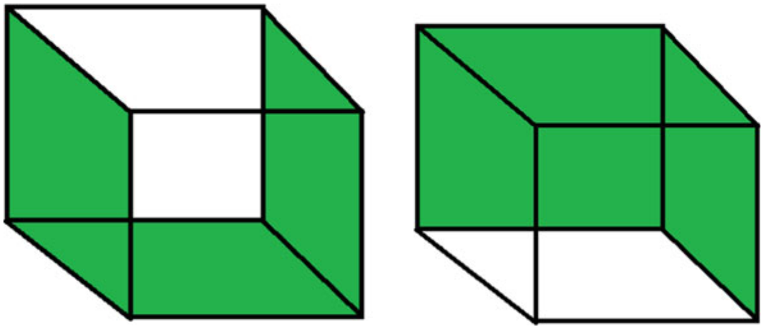

Fig. 3 Number of equivalence classes of patterns for the face colorings of cube under the action of both cubic group on the faces and the S_2 color group acting on *white* and *green colors*, switching the *white* and *green colors*. The patterns invariant to both actions of G and H are shown in this figure and correspond to the coefficient of w^3g^3 in the de Bruijn's enumeration scheme (Color figure online)

If we continue this process we can show that

$$\mu_k = \begin{cases} 2(rb)^{k/2} & if \quad 2|k \\ 0 & otherwise \end{cases} \tag{8}$$

Thus, the equivalence classes under the action of both G and H is given by

$$\begin{aligned} GF &= P_{T_d}(s_k \to \mu_k) \\ &= \frac{1}{24}[0^4 + 6.0^2.2rb + 8.0.0 + 6(2r^2b^2) + 3(2rb)^2] \\ &= r^2b^2 \end{aligned} \tag{9}$$

Thus the only pattern that is invariant under the action of both G on the set of vertices of a tetrahedrons and the color inversion group S_2 acting on R, the set of two colors is the pattern that contains 2 blue colors and 2 red colors.

When de Bruijn's theorem is applied to coloring the faces of a cube again with 2 colors, white or green, we obtain the de Bruijn generating function as $2w^3g^3$ since $\mu_1 = \mu_3 = 0$, $\mu_2 = 2wg$ and $\mu_4 = 2w^2g^2$ the 2 patterns are shown in Fig. 3.

2.2 The Harary–Palmer power group enumeration

The power group theorem is formulated starting with the diagram shown in Fig. 4. As can be seen from this figure, we have two sets D and R, and the corresponding groups G and H acting on these two sets respectively. The most generalized version of power group theorem that yields generating functions in the form of variables x, y, z and so on can be obtained by defining the set R with colors white, blue, green, red, purple and so on such that white is fixed with weight w(white) = 0, and not interchanged with any colors; the group H says permutes colors of one set such that weights of all colors in the set are same, that is, w(all colors in the first set) = 1. In the generating function the

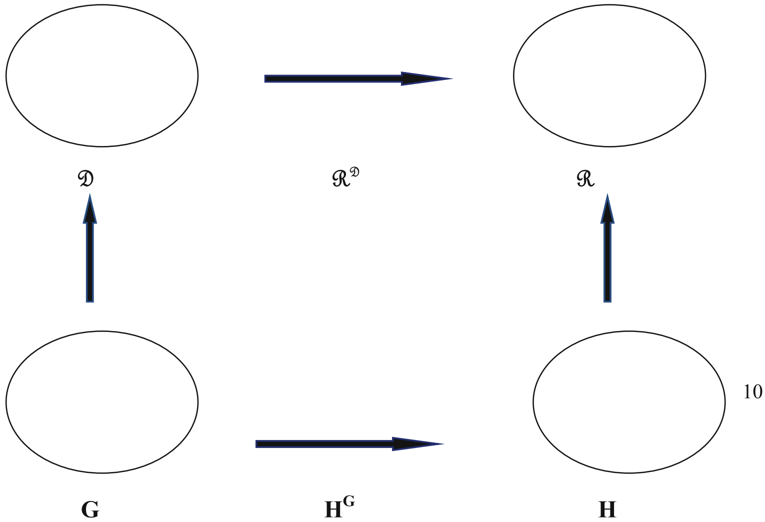

Fig. 4 $\mathbf{H^G}$ is the power group that acts on $\mathscr{R}^{\mathscr{D}}$, the set of all functions from the set $\mathscr{D}$ tof objects to the set $\mathscr{R}$ of colors. We call the group G the group of objects acting on the set $\mathscr{D}$ of objects which could be vertices, edges, faces or segments and H the color group acting on the set the set $\mathscr{R}$ of colors. The power group enumeration seeks generating functions for the equivalence classes or orbits of the set $\mathscr{R}^{\mathscr{D}}$ of all functions from $\mathscr{D}$ to $\mathscr{R}$ that are equivalent under the action of both G on $\mathscr{D}$ and H on $\mathscr{R}$

colors with weights 1 are thus designated with the label x. Likewise, interchangeable colors of the second set such that weights of all colors in that set w(all colors in the second set) = 2, are thus designated with the label y in the generating function and so on. In the most general case then the power group enumeration theorem can be expressed as follows:

The Harary–Palmer Power Group Enumeration theorem in multi-variable power series form: The configuration counting series C(x,y,z..) that enumerates all equivalence classes of functions under the action of power group H^G on the set $\mathscr{R}^{\mathscr{D}}$ of all functions from D to R is given by

$$C(H^G; x, y, z, \ldots) = \frac{1}{|H|}\sum_{h\varepsilon H} Z(G; c_1(h, x, y, z), c_2(h, x, y, z), \ldots\ldots..c_m(h, x, y, z)) \tag{10}$$

where

$$C_k(h, x, y, z, \ldots) = \sum_i \sum_j \sum_l \left(\sum_{s|k} \left(sj_s(h_i, h_j, h_l)\right)\right) x^{ki} y^{kj} z^{kl}, \tag{11}$$

where we use the standard mathematical notation s | k for all s that divide k, and thus the sum is over all integers s that divide k. This sum is obtained using the Mobius inversion formula, however, it is best illustrated using the cycle type of the permutation h in the group H which is further subdivided into various color sets within the set R that are equivalent because of the action of H. That is, all equivalent colors in the ith set of R with the same weight (labeled by x) would be contained within the h_i component of the permutation h, all equivalent colors in the jth set with the same weight (labeled by y) would be contained within the h_j component of the permutation h, and so on.We also note that $Z(G; s_1, s_2, \ldots s_m)$ is the standard Pólya cycle index polynomial of the group G as determined by its action on the set D shown in Eq. (1).

A special case of the Harary–Palmer power group theorem [60] in single-variable x, which is commonly illustrated in the graphical enumeration of Harary and Palmer, is given by

The Harary–Palmer Power Group Enumeration theorem in single-variable power series form: The configuration counting series C(x) that enumerates all equivalence classes of functions under the action of power group H^G on the set $\mathscr{R}^{\mathscr{D}}$ of all functions from D to R is given by

$$C(H^G; x) = \frac{1}{|H|} \sum_{h \varepsilon H} Z(G; c_1(h, x), c_2(h, x), \ldots\ldots.c_m(h, x)) \tag{12}$$

where

$$C_k(h, x) = \sum_i \left(\sum_{s|k} (s j_s(h_i)) \right) x^{ki}, \tag{13}$$

where once again we use the standard mathematical notation s|k for all s that divide k, and thus the sum is over all integers s that divide k.

The power group enumeration theorem is best illustrated with a necklace of four beads with three colors, white, blue and red such that white (pearl) is fixed while the blue and red beads are completely interchangeable. Thus our set D is a set of four vertices arranged in a square and R is the set of white, blue and red colors. Therefore, the group G acting on the set is the dihedral group D_4 acting on the vertices of a square while the color group H acting on colors is simply the permutation group S_2 = *{(w)(b)(r), (w)(br)}*, as white is always fixed allowing only interchange of blue and red colors. If we assign the weights w(white) = 0, w(blue) = w(red) = 1 then the generating function $C(S_2^{D4}; x)$ obtained from the power group theorem enumerates the number of unique necklaces with k colors (blue or red) and 4-k white colors for a necklace of 4 beads.

As a first step, we construct the relevant cycle types, cycle index polynomials, etc., which is similar to the Pólya process of constructing the standard cycle index polynomials from the respective groups. Let us consider the S_2 group of colors with the permutations *{(w)(b)(r), (w)(br)},* the cycle types of the two permutations are shown below: Thus we have

Cycle type permutation	j_1 (number of 1-cycles)	j_2 (number of 2-cycles)	j_3 (number of 3-cycles)	j_4 (number of 4-cycles)
(w)(b)(r)	3	0	0	0
(w)(br)	1	1	0	0

$$\text{For h} = (w)\,(b)\,(r)\; c_1\,(h, x) = 1 + 2x,\; c_2\,(h, x) = 1 + 2x^2, \ldots .c_k\,(h, x) = 1 + 2x^k, \tag{14}$$

For h $= (w)(br)$ $c_1(h, x) = 1$, $c_2\,(h, x) = 1 + 2x^2, \ldots .c_k(h, x) = 1$ if k is odd or $1 + 2x^k$ if k is even.

Consequently, we obtain

$$C\left(S_2^{D_4}, x\right) = \frac{1}{2}\left\{Z(D_4; 1 + 2x, 1 + 2x^2, 1 + 2x^3, 1 + 2x^4) + Z(D_4; 1, 1 + 2x^2, 1, 1 + 2x^4)\right\} \tag{15}$$

$Z(D_4; s_1, s_2, s_3, s_4)$ is the standard cycle index of the group D_4 acting on the vertices of a square and it is given by

$$Z(D_4; s_1, s_2, s_3, s_4) = \frac{1}{8}\left\{Z(s_1^4 + 2s_4 + 3s_2^2 + 2s_1^2 s_2\right\} \tag{16}$$

Replacing every s_1, s_2, s_3 and s_4 by the corresponding c_1, c_2, c_3 and c_4 functions respectively, thus obtained above for each permutation h in H, we obtain the power group enumeration generating function,

$$C\left(S_2^{D_4}, x\right) = 1 + x + 4x^2 + 3x^3 + 4x^4, \tag{17}$$

Thus there is one necklace with 4-beads all white(pearls), one with three whites and one of color, and four necklaces with 2 whites and two of colors and 3 necklaces with one white and three of color and four necklaces with only blue and red colors (Fig. 5).

Consider coloring the interior segments (slices of a hexagonal pie) of a hexagon with four colors, namely, white(fixed) and colors green, blue, and red are completely interchangeable. The power group theorem in the power series form enumerates equivalences classes of colorings for such a case. We formulate the problem with D being the six interior segments of a hexagon with the R set being {white, blue, green, red}. Given that white is fixed, and colors b, g, r can be completely interchanged, we have the group $H = S_1 \times S_3 = S_3$, where S_1 is simply the group acting on white by itself and S_3 is the group of 6 permutations of colors b, g, and r. Thus the permutations of the group H are *{(w)(b)(g)(r), 2(w)(bgr), 3(w)(bg)(r)}*, where we group all permutations with identical cycle structures together or all permutations in the same conjugacy class are coupled together for simplicity. The group G is the D_6 dihedral group acting on the segments of a regular hexagon. We also assign the weights

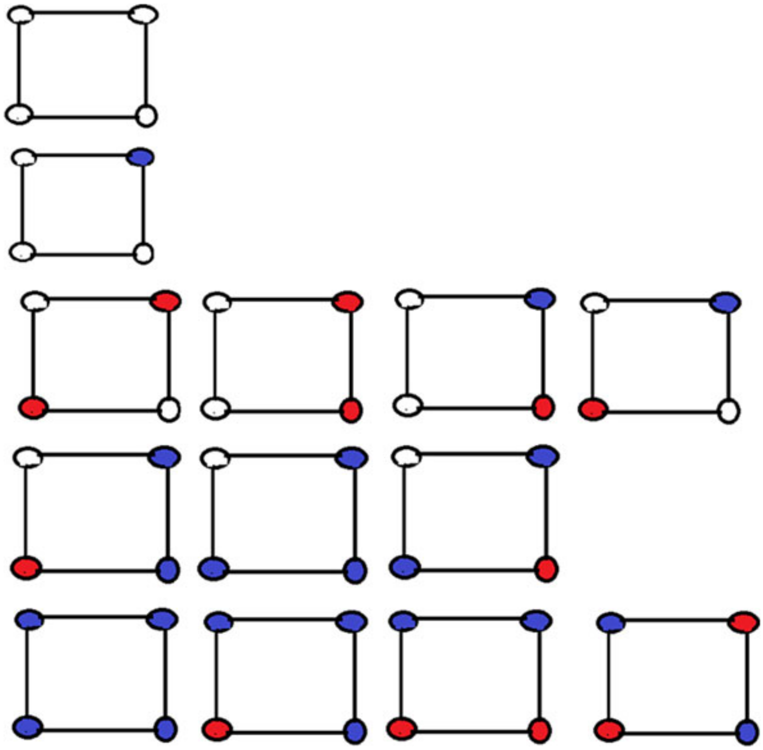

Fig. 5 All distinct necklaces with pearls (*white*) and two colored beads (*red* and *blue*) such that *blue* and *red colors* are interchangeable. All of these patterns are enumerated by the power group theorem with coefficients of x^k yielding k colored beads (*red* or *blue*) and n-k pearls (*white*) in $C(S_2^{D_4}, x)$ (Color figure online)

w(white) = 0, w(blue) = w(green) = w(red) = 1. Given this set up, the power group enumeration generating function is constructed as follows:

For the permutation *(w)(b)(g)(r)* in $S_3 j_1(h_1) = 1, j_1(h_2) = 3$ and all other $j_k(h_i) = 0$, for all $k > 1$. Thus we obtain

$$\begin{aligned} &C_1((w)(b)(g)(r); x) = 1 + 3x; C_2((w)(b)(g)(r); x) \\ &\quad = 1 + 3x^2; \ldots\ldots C_k((w)(b)(g)(r); x) = 1 + 3x^k; \end{aligned} \tag{18}$$

For the permutation type $(w)(bg)(r)$ in $S_3 j_1(h_1) = 1, j_1(h_2) = 1, j_2(h_2) = 1$, and all other $j_k(h_2) = 0$, for all $k > 2$, and and all other $j_k(h_1) = 0$, for all $k > 1$. Thus we obtain

$$C_1((w)(bg)(r); x) = 1 + (1j_1(h_2))\, x = 1 + x; \tag{19}$$

$$C_2((w)(bg)(r); x) = 1 + (1j_1(h_2) + 2j_2(h_2))\, x^2 = 1 + 3x^2; \tag{20}$$

$$C_3((w)(bg)(r); x) = 1 + (1j_1(h_2) + 3j_3(h_2))\, x^3 = 1 + x^3; \tag{21}$$

$$\ldots\ldots C_k((w)(bg)(r);\ x) = 1 + x^k \text{ if k is odd and} 1 + 3x^k \text{ if k is even.} \tag{22}$$

For the permutation type $(w)(bgr)$ in $\mathrm{S_3 j_1}$ $(\mathrm{h_1}) = 1, \mathrm{j_1(h_2)} = 0, \mathrm{j_2}$ $(\mathrm{h_2}) = 0, \mathrm{j_3}$ $(\mathrm{h_2}) = 0$, and all other $\mathrm{j_k(h_2)} = 0$, for all $\mathrm{k} > 3$, and all other $\mathrm{j_k(h_1)} = 0$, for all $\mathrm{k} > 1$. Thus we obtain

$$\mathrm{C_1}((w)\,(bgr)\,;\mathrm{x}) = 1 + \left(1\mathrm{j_1}\,(\mathrm{h_2})\right)\mathrm{x}\ = 1; \tag{23}$$

$$\mathrm{C_2}((w)\,(bgr);\mathrm{x}) = 1 + \left(1\mathrm{j_1}\,(\mathrm{h_2}) + 2\mathrm{j_2}\,(\mathrm{h_2})\right)\mathrm{x}^2 = 1 + 0.\mathrm{x}^2 = 1; \tag{24}$$

$$\begin{aligned} \mathrm{C_3}\,((w)(bgr)\,;\mathrm{x}) &= 1 + \left(1\mathrm{j_1}\,(\mathrm{h_2}) + 3\mathrm{j_3}\,(\mathrm{h_2})\right)\mathrm{x}^3 = 1 + (0+3)\,\mathrm{x}^3 \\ &= 1 + 3\mathrm{x}^3; \end{aligned} \tag{25}$$

$$\begin{aligned} &\ldots..\mathrm{C_k}((w)(bgr);\mathrm{x}) \\ &\quad = 1 \text{ if k if not a multiple of 3 and} 1 + 3\mathrm{x^k} \text{ if k is a multiple of 3} \end{aligned} \tag{26}$$

Thus for the power group $\mathrm{S_3^{D6}}$ we obtain,

$$\begin{aligned} C(S_3^{D_6}, x) = \frac{1}{6}\{&Z(D_6; 1+3x, 1+3x^2, \ldots.., 1+3x^6) \\ &+3Z(D_6; 1+x, 1+3x^2, 1+x^3, 1+3x^4, 1+x^5, 1+3x^6) \\ &+2Z(D_6; 1, 1, , 1+3x^3, 1, 1, , 1+3x^6)\} \end{aligned} \tag{27}$$

Next we evaluate the various $\mathrm{Z(D_6; \ldots)}$ indices needed for substitution in the above expression. These are readily obtained from the cycle index of the $\mathrm{D_6}$ group with each of the conjugacy class expressed as permutation of the segments of the hexagon under consideration. Thus we have

$$Z(D_6; s_1, s_2, s_3, s_4, s_5, s_6)) = \frac{1}{12}\{Z(s_1^6 + 2s_6 + 3s_3^2 + 4s_2^2 + 3s_1^2 s_2^2\} \tag{28}$$

Replacing each $\mathrm{s_k}$ in the above cycle index of the $\mathrm{D_6}$ group with the corresponding functions we obtain the various $\mathrm{Z(D_6 : \ldots.)}$ needed for the power group enumeration as follows:

$$\begin{aligned} &Z(D_6; 1+3x, 1+3x^2, 1+3x^3, 1+3x^4, 1+3x^5, 1+3x^6) \\ &\quad = \frac{1}{12}\{Z((1+3x)^6 + 2(1+3x^6) + 2(1+3x^3)^2 \\ &\qquad +4(1+3x^2)^3 + 3(1+3x)^2(1+3x^3)^2\} \\ &\quad = 1 + 3x + 18x^2 + 55x^3 + 126x^4 + 135x^5 + 92x^6 \end{aligned} \tag{29}$$

$$\begin{aligned} &Z(D_6; 1+x, 1+3x^2, 1+x^3, 1+3x^4, 1+x^5, 1+3x^6) \\ &\quad = \frac{1}{12}\{Z((1+x)^6 + 2(1+3x^6) + 2(1+x^3)^2 \\ &\qquad +4(1+3x^2)^3 + 3(1+x)^2(1+3x^3)^2\} \\ &\quad = 1 + x + 6x^2 + 5x^3 + 14x^4 + 5x^5 + 12x^6 \end{aligned} \tag{30}$$

$$\begin{aligned} &Z(D_6; 1, 1, 1+3x^3, 1, 1, 1+3x^6) \\ &\quad = \frac{1}{12}\{Z(1^6 + 2(1+3x^6) + 2(1+3x^3)^2 \end{aligned}$$

$$+4(1)^3 + 3(1)^2(1)^2\}$$
$$= 1 + x^3 + 2x^6 \tag{31}$$

Consequently, by substituting the three Z(D_6; . . ..) expressions thus obtained into the power group generating function for C(S_3^{D6}; x), we obtain

$$C(S_3^{D_6}, x) = \frac{1}{6}\{1 + 3x + 18x^2 + 55x^3 + 126x^4 + 135x^5 + 92x^6$$
$$+3(1 + x + 6x^2 + 5x^3 + 14x^4 + 5x^5 + 12x^6)$$
$$+2(1 + x^3 + 2x^6)\} = 1 + x + 6x^2 + 12x^3 + 28x^4 + 25x^5 + 22x^6 \tag{32}$$

The power group enumeration series thus obtained suggests that there is one hexagonal pattern with all 6 pie segments with white color, one of them with 5 white and 1 color (any of b,g, or r), six patterns with 4 white and 2 colors (chosen from any of blue, green or red), twelve with three whites and three colors, 28 with 2 whites and 4 colors, 25 with 1 white and 5 colors and 22 patterns with all segments of hexagons carrying colors b, g or r. Figure 6 shows the 22 patterns thus enumerated by the power group enumeration theorem with all six segments carrying colors chosen from blue, green or red.

3 The generalized character cycle indices for all irreducible representations

The present author [33] has formulated the cycle index polynomials for each irreducible representation of the molecular point group or for any group acting on a set of objects. These generalized character cycle index polynomials and the related tensor products [69,70] and Schur functions [65–71] have been shown to have powerful applications. In the context of molecular and NMR spectroscopy Balasubramanian [33] has shown that these polynomials are very useful in generating nuclear spin statistical weights of rovibronic levels patterns, nuclear spin functions, and in NMR and ESR spectroscopies. A generalized character cycle index (GCCI), P_G^χ, for an irreducible representation Γ with character χ of the group G acting on a set D is defined as

$$P_G^\chi = \frac{1}{|G|}\sum_{g\varepsilon G}\chi(g)s_1^{b_1}s_2^{b_2}\ldots\ldots s_n^{bn} \tag{33}$$

where $\sum_{g\varepsilon G} s_1^{b_1}s_2^{b_2}\ldots\ldots s_n^{bn}$ is a sum over all permutational representations of g ε G that generate b_1 cycles of length 1, b_2 cycles of length 2, ...b_n cycles of length n upon its action on the set of nuclei under consideration. Each term in the cycle index depends on the orbits of the permutational operations that are generated upon the action of g.

The GCCI thus introduced has many important applications in spectroscopy, generation of symmetry-adapted functions, and so on. For example, the nuclear spin species $^{209}Bi_8$ cubic clusters can be generated for all irreducible representation sof

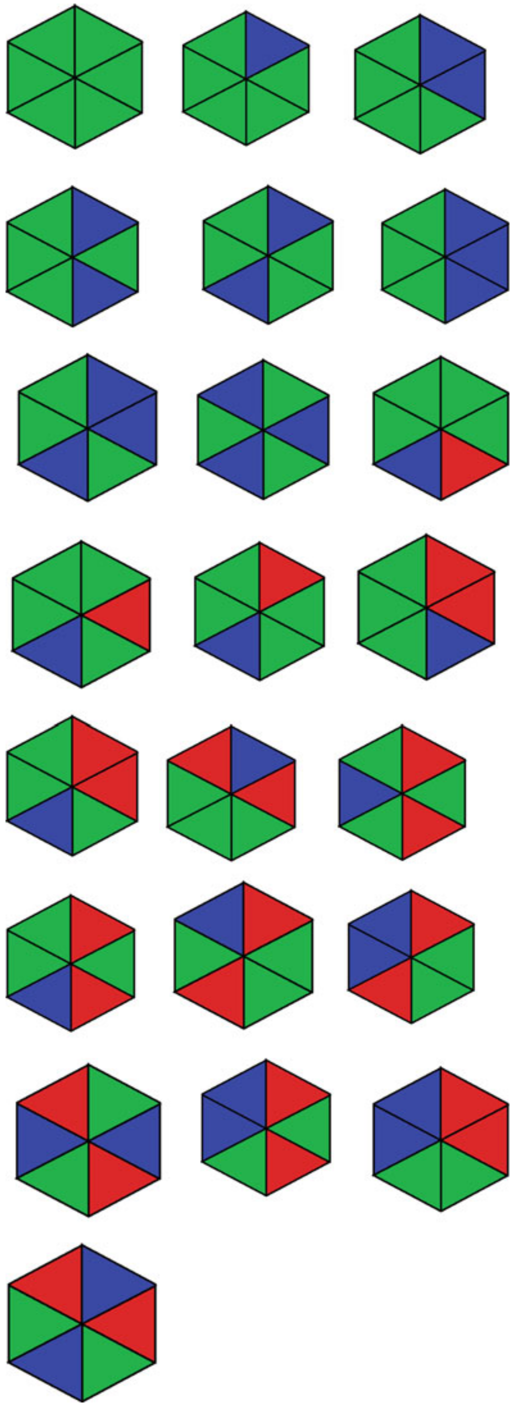

Fig. 6 Twenty-two patterns under power group enumeration for coloring interior segments of a hexagon with colors *blue*, *green* and *red* such that the colors are fully interchangeable. The power group S_3^{D6} is obtained from the D_6 group acting on the six segments of a hexagon and the S_3 group acting on colors. The most general form of configuration counting series is obtained by the four-color problem with white fixed and *blue*, *green*, *red* interchangeable. The expression thus obtained generates various patterns of which coefficient of x^6 generates equivalence classes of patterns with all six segments colored with b, g or r as shown in this figure (Color figure online)

the O_h group. As ^{209}Bi is a spin-9/2 nucleus, there are 10 different spin orientations (m_f) values for each ^{209}Bi nucleus. Let the $10m_s$ spin functions of ^{209}Bi be labeled by $\alpha_1, \alpha_2, \ldots \alpha_{10}$, where α_1 represents $m_s = -9/2$, α_2 represents $m_s = -7/2$. ... and α_{10} stands for $m_s = 9/2$. Then the GCCI of the A_{2g} representation for the $^{209}Bi_8$ cubic cluster would give the generating function for nuclear spin functions of Bi_9 that would transform as A_{2g} representation in the O_h group. The GCCI for A_{2g} of the O_h group acting on the vertices of a cube is given by

$$\begin{aligned} P_G^{A_{2g}} &= \frac{1}{48}\left[s_1^8 + 3s_2^4 + 3s_2^4 + s_2^4 - 6s_1^4 s_2^2 - 6s_2^4 - 6s_4^2 - 6s_4^2 + 8s_1^2 s_3^2 + 8s_2 s_6\right] \\ &= \frac{1}{48}\left[s_1^8 + s_2^4 - 6s_1^4 s_2^2 - 12s_4^2 + 8s_1^2 s_3^2 + 8s_2 s_6\right] \end{aligned} \tag{34}$$

If one replaces every s_k in the above expression by $\alpha_1^k + \alpha_2^k + \ldots. + \alpha_m^k$ we get the generating function for the nuclear spin functions of Bi_9 cluster that transform as A_{2g}. That is,

$$GF^{\chi} = P_G^{\chi}(s_k \to \sum_i \alpha_i^k) \tag{35}$$

The above function evaluation requires an expansion of a series of decanomials obtained as follows. The decanomial spin generating functions can be formulated by using [n], an ordered partition of n into 10 parts such that

$$n_1 \geq 0, n_2 \geq 0, \ldots.., n_{10} \geq 0, \ \sum_{i=1}^{10} n_i = n \tag{36}$$

Then a multinomial expansion in α's is defined as

$$(\alpha_1 + \alpha_2 + \ldots. + \alpha_{10})^n = \sum_{[n]} \binom{n}{n_1\ n_2\ \ldots\ n_{10}} \alpha_1^{n_1} \underset{2}{\alpha}^{n_2} \ldots \alpha_1^{n_{10}} \tag{37}$$

where $\binom{n}{n_1\ n_2\ \ldots\ n_{10}}$ are multinomial coefficients, and the sum is over all such ordered partitions or compositions of the integer n into p parts. The multinomial coefficients satisfy,

$$\begin{aligned} &\binom{n+q}{n_1\ n_2\ \ldots\ n_{10}} \\ &\quad = \sum_{[k]=n} \binom{n}{k_1\ k_2\ \ldots\ k_{10}} \binom{q}{n_1 - k_1\ n_2 - k_2\ \ldots\ n_{10} - k_{10}} \end{aligned} \tag{38}$$

where [k] stands for all ordered partitions of n such that $k_1 + k_2 + \ldots. + k_{10} = n$, with k_i non-negative integers. Thus for the A_{2g} representation ^{209}Bi nuclear spin generator is given by

$$
\begin{aligned}
GF^{A_{2g}} = \frac{1}{48}\,[&(\alpha_1+\alpha_2+\ldots+\alpha_{10})^8+(\alpha_1^2+\alpha_2^2+\ldots\\
&+\alpha_{10}^2)^4-6(\alpha_1+\alpha_2+\ldots+\alpha_{10})^4(\alpha_1^2+\alpha_2^2+\ldots+\alpha_6^2)^2\\
&-12(\alpha_1^4+\alpha_2^4+\ldots+\alpha_{10}^4)^2-8(\alpha_1+\alpha_2\\
&+\ldots+\alpha_{10})^2(\alpha_1^3+\alpha_2^3+\ldots+\alpha_{10}^3)^2\\
&-8(\alpha_1^2+\alpha_2^2+\ldots+\alpha_{10}^2)(\alpha_1^6+\alpha_2^6+\ldots+\alpha_{10}^6)]
\end{aligned}
\tag{39}
$$

The coefficient of a typical term $\alpha_1^{m_1}\alpha_2^{m2}\ldots\ldots\alpha_{10}^{m_{10}}$ yields the number of ^{209}Bi nuclear spin functions containing m_1 α_1 spins, m_2 α_2 spins .....m_{10} α_{10} spins that transform according to the A_{2g} irreducible representation. These coefficients can then be sorted according to the total m_F quantum numbers to generate all nuclear spin multiplets.

4 Generalization of the Harary–Palmer power group enumeration to all irreducible representations of object group G and color group H

The GCCI formulation and its application to nuclear spin numeration with 10 different colors provide us with a motivation to generalize the Harary–Palmer power group enumeration [60]. In many such spectroscopy and quantum chromodynamics applications we are dealing with an object set D of particles arranged according to some symmetry of the lattice. The set R is the set of colors which may represent different nuclear spin orientations or flavors of the particles. The group G acting on the set D of particles is clearly determined by the arrangement of the particles or the molecular symmetry or the non-rigid permutation-inversion group symmetry depending on the case. The group H acting on the colors is often determined by the nature of the physical problem, for instance, in nuclear spin statistics, it would be the permutation that inverts the spin projections $-m_f$ with $+m_f$. That is, for the case of ^{209}Bi with spin-9/2 the group is S_2 comprised of identity and the permutation that switches $-m_f$ with $+m_f$, that is, (−9/2 9/2)(−7/2 7/2)(−5/2 5/2)(−3/2 3/2)(1/2 1/2) where in each parentheses we have an orbit of 2-elements permuting $-m_f$ with $+m_f$. The color symmetry is here is that of inversion some times, denoted as, the group Rev_i, when it involves reversal or inversion of i spin orientations (i=10), as in the case of ^{209}Bi the color group S_2 can be donated further as Rev_{10}. Given such a color group R acting on colors (spin orientations or flavors of quarks, etc..) and given the group G action of the set D of particles, the power group enumeration theorem can be formulated for all irreducible representations of both groups G and H in H^G power group acting on $R^{\underline{\underline{D}}}$, set of all functions from D to R. For most of the physical applications thus far, it appears the special case where the irreducible representation of the group H is fixed to the totally symmetric representation with all irreducible representations of G provide valuable information. However we formulate the power group enumeration theorem for all irreducible representations of G and H.

Let $\beta \in G$ be an irreducible representation of the group G while $\Gamma \in H$ be an irreducible representation of the group H. Furthermore let us assume that there are two types of colors, a fixed white color and remaining colors are all interchangeable, and that the weights for colors are w(white) =0, and w(colors)=1, for all colors. Then the power group generating function for a single variable x $C^{\beta\in G}_{\Gamma\in H}(H^G; x)$ is given by the following expressions for all irreducible representations in the group G and H.

$$C^{\beta\in G}_{\Gamma\in H}(H^G; x) = \frac{1}{|H|}$$
$$\sum_{h\in H} \chi^{\Gamma}(h) Z^{\beta}(G; c_1(h,x), c_2(h,x), c_3(h,x), \ldots\ldots.., c_k(h,x)) \tag{40}$$

where

$$C_k(h,x) = \sum_i \left(\sum_{s|k} (s j_s(h_i)\right) x^{ki} \tag{41}$$

Note that the above power group generating function for all irreducible representations can also be readily generalized to multi-variables x,y,z etc., when colors are partitioned into multiple sets (more than 2) such that only colors within a set are permuted and are thus equivalent.

The special case of the above generalization for $\Gamma = A_1$ (totally symmetric representation) of the group H gives an important result. That is, for $\Gamma = A_1$ for the H group, the $C^{\beta\in G}_{A_1\in H}(H^G; x)$ function generates the number of symmetry-adapted functions in R^D that transform as the irreducible representation β in G. That is the coefficient x^k in $C^{\beta\in G}_{A_1\in H}(H^G; x)$ generates the number of functions with k colors and n−k white in in R^D that transform according to β in G under the equivalence action of the group H acting on the colors in the set R.

Yet another special case of the power group theorem when both $\Gamma = A_1$ (totally symmetric representation) and $\beta = A_1$ (totally symmetric representation) for both groups G and H, then the generating function obtained for the power group becomes the Harary–Palmer power theorem that has been used extensively in the enumeration of graphs of different kinds and finite automata.

We now illustrate the power group generalization with different examples. Consider the colorings of vertices of a triangle with four different colors {w,b,g,r} such that white is fixed and colors are all permuted. Thus we have the group D_3 acting on the vertices of a triangle and the group S_3 acting on the three colors b, g, r with white fixed. Let us consider the generating functions for which the irreducible representation of the S_3 group of colors is totally symmetric. Then the various GFs for the irreducible representations of the group D_3 are obtained using the power group theorem generalization:

$$\mathrm{C}^{\mathrm{A1}}\left(\mathrm{S}_3^{\mathrm{D3}}, \mathrm{x}\right) = 1 + \mathrm{x} + 2\mathrm{x}^2 + 2\mathrm{x}^3 \tag{42}$$

$$\mathrm{C}^{\mathrm{E}}\left(\mathrm{S}_3^{\mathrm{D3}}, \mathrm{x}\right) = 1/6\left[\mathrm{Z}^{\mathrm{E}}\left(\mathrm{D}_3; 1+3\mathrm{x}, 1+3\mathrm{x}^2, 1+3\mathrm{x}^3\right)\right.$$
$$\left. +3\mathrm{Z}^{\mathrm{E}}\left(\mathrm{D}_3; 1+\mathrm{x}, 1+3\mathrm{x}^2, 1+\mathrm{x}^3\right) + 2\mathrm{Z}\left(\mathrm{D}_3; 1, 1, 1+3\mathrm{x}^3\right)\right],$$
$$\text{where } \mathrm{Z}^{\mathrm{E}}(\mathrm{s}_1, \mathrm{s}_2, \mathrm{s}_3) = 1/6\left[2\mathrm{s}_1^3 - 2\mathrm{s}_3\right], \tag{43}$$

We obtain each of the Z^{E} generating function needed to evaluate the power group generating function for the irreducible representation E as follows:

$$Z^{E}\left(D_3;\, 1+3x,\, 1+3x^2,\, 1+3x^3\right) = 1/6\left[2\,(1+3x)^3 - 2\left(1+3x^3\right)\right]$$
$$= 3x + 9x^2 + 6x^3 \tag{44}$$
$$Z^{E}\left(D_3;\, 1{+}x,\, 1{+}3x^2,\, 1{+}x^3\right) = 1/6\left[2\,(1{+}x)^3 - 2\left(1+x^3\right)\right] = x + x^2 \tag{45}$$
$$Z^{E}\left(D_3;\, 1,\, 1,\, 1+3x^3\right) = 1/6\left[2\,(1)^3 - 2\left(1+3x^3\right)\right] = -x^3, \tag{46}$$

Finally substituting the expressions for different Z^{E}'s thus obtained we get,

$$C^{E}\left(S_3^{D3}, x\right) = 1/6\left[\left(3x + 9x^2 + 8x^3\right) + 3\left(x + x^2\right) + 2\left(-x^3\right)\right]$$
$$= x\; + 2x^2 + x^3. \tag{47}$$

Thus there is one E function in the set of functions that contain one color and two whites, two E functions in the set that contains one white and 2 colors and one E representation in the set that has all vertices of the triangle colored with g, r, or b such that the colors are all permuted by the group S_3. It can be readily seen that the symmetry-adapted linear combinations for the coloring with all three different colors that transform as E is:

$$E : \begin{cases} \frac{1}{6}(2bgr - rbg - grb) \\ \frac{1}{\sqrt{2}}(rbg - grb) \end{cases} \tag{48}$$

As another non-trivial example that requires some computational labor, let us consider 4^6 functions for the colorings of pie segments of a hexagon with 4 different colors {w,b,g,r} such that white is fixed but b,g, and r are all permuted by the group S_3. In order to apply the power group enumeration for all characters, we need to first obtain the action of the permutation h in the group S_3 as this is the first step toward applying the power group. For the case of set R={w,b,g,r} with the group S_3 permuting the colors b,g,r with w fixed, we have already obtained the various generators for the action of h in H for each of its conjugacy class. These are given by Eqs. (18)–(26) already obtained before for the ordinary power group enumeration for the power group S_3^{D6} for coloring the interior segments of a hexagon. The needed generators for the totally symmetric A_1 representation for the D_6 group for this has already been obtained as

$$Z^{A1}(D_6;\, 1+3x,\, 1+3x^2,\, 1+3x^3,\, 1+3x^4,\, 1+3x^5,\, 1+3x^6)$$
$$= 1 + 3x + 18x^2 + 55x^3 + 126x^4 + 135x^5 + 96x^6$$
$$Z^{A_1}(D_6;\, 1+x,\, 1+3x^2,\, 1+x^3,\, 1+3x^4,\, 1+x^5,\, 1+3x^6)$$
$$= 1 + x + 6x^2 + 5x^3 + 14x^4 + 5x^5 + 12x^6 \tag{49}$$
$$Z^{A_1}(D_6;\, 1,\, 1,\, 1+3x^3,\, 1,\, 1,\, 1+3x^6) = 1 + x^3 + 2x^6 \tag{50}$$

Thus assembling the Z^{A1} polynomials we obtain the generating function for the power group for the A_1 representation which has been obtained before as

$$C_{A_1 \in S_3}^{A_1 \in D_6}(x) = 1 + x + 6x^2 + 12x^3 + 28x^4 + 25x^5 + 22x^6 \tag{51}$$

We illustrate this with the A_2 irreducible representation of the S_3 group and A_1 irreducible representation for the D_6 group. The power group generating function for this case is given by

$$\begin{aligned} C_{A_2 \in S_3}^{A_1 \in D_6}(x) &= \frac{1}{6}\Big\{1 + 3x + 18x^2 + 55x^3 + 126x^4 + 135x^5 + 92x^6 \\ &\quad -3(1 + x + 6x^2 + 5x^3 + 14x^4 + 5x^5 + 12x^6) + 2(1 + x^3 + 2x^6)\Big\} \\ &= 7x^3 + 28x^4 + 20x^5 + 10x^6 \end{aligned} \tag{52}$$

Likewise the generating function for the E representation of the S_3 group and the A_2 representation of the D_6 group is obtained as

$$\begin{aligned} C_{A_2 \in S_3}^{E \in D_6}(x) &= \frac{1}{6}\{2(1 + 3x + 18x^2 + 55x^3 + 126x^4 + 135x^5 + 92x^6) \\ &\quad -2(1 + x^3 + 2x^6)\} \\ &= x + 6x^2 + 18x^3 + 42x^4 + 45x^5 + 30x^6 \end{aligned} \tag{53}$$

In order to compute all generating functions for all representations of the power group it would be easier to construct a table of all $Z^{\beta}(D_6;\, x)$ polynomials for all the irreducible representation of the group D_6 for each of the conjugacy class type of the group S_3. This table is constructed by repetitive application of the various cycle type representations for the permutations in the conjugacy classes of the S_3 group for each irreducible representation of the D_6 group. As there are 3 conjugacy classes in the S_3 group and 6 irreducible representations in the D_6 group, we obtain a 6×3 table of polynomials as shown in Table 1.

We can construct the generating functions for the power group for the various irreducible representations of the group D_6 and the color group S_3 using Table 1. For example, for the case of E_2 representation of the D_6 group and the E representation of the S_3 group the power group generating function is obtained using the polynomials listed in the last row of Table 1. Thus we obtain

$$\begin{aligned} C_{E \in S_3}^{E_2 \in D_6}(x) &= \frac{1}{6}\{2(3x + 24x^2 + 89x^3 + 207x^4 + 243x^5 + 124x^6) \\ &\quad -2(-x^3 - 2x^6)\} \\ &= x + 8x^2 + 30x^3 + 69x^4 + 81x^5 + 42x^6 \end{aligned} \tag{54}$$

The power group generating functions thus obtained for all the irreducible representations of the group D_6 acting on the six segments of the hexagon and for all the irreducible representations of the group S_3 acting on three colors b, g, and r with

Table 1 Various components for the generating functions for the generalized power group enumeration theorem for the irreducible representations of hexagonal D_6 group for the four color problem (*including white*) with the S_3 group acting on colors (*not white*)

Γ	Irred. Rep β		
	$Z^\beta(D_6; 1+3x, 1+3x^2, 1+3x^3, 1+3x^4, 1+3x^5, 1+3x^6)$	$Z^\beta(D_6; 1+x, 1+3x^2, 1+x^3, 1+3x^4, 1+x^5, 1+3x^6)$	$Z^\beta(D_6; 1, 1, 1+3x^3, 1, 1, 1+3x^6)$
A_1	$1+3x+18x^2+55x^3+126x^4+135x^5+92x^6$	$1+x+6x^2+5x^3+14x^4+5x^5+12x^6$	$1+x^3+2x^6$
A_2	$6x^2+37x^3+81x^4+108x^5+46x^6$	$-2x^2-x^3-7x^4-4x^5-4x^6$	x^3+2x^6
B_1	$9x^2+37x^3+90x^4+108x^5+46x^6$	$x^2-x^3+2x^4-4x^5+2x^6$	x^3+x^6
B_2	$3x+12x^2+55x^3+108x^4+135x^5+73x^6$	$x+5x^3+5x^5-2x^6$	x^3+x^6
E_1	$3x+21x^2+89x^3+198x^4+243x^5+116x^6$	$x+x^2+3x^3-2x^4+x^5-4x^6$	$-x^3-x^6$
E_2	$3x+24x^2+89x^3+207x^4+243x^5+124x^6$	$x+4x^2+3x^3+7x^4+x^5+4x^6$	$-x^3-2x^6$

Table 2 Generalized power group enumeration generating functions for the irreducible representations of hexagonal D_6 group acting on faces (or vertices) of a hexagon for the four color problem (including white) with the S_3 group acting on three colors other than white

D_6	S_3		
	A_1	A_2	E
A_1	$1+x+6x^2+12x^3+28x^4+25x^5+22x^6$	$7x^3+14x^4+20x^5+10x^6$	$x+6x^2+18x^3+42x^4+45x^5+30x^6$
A_2	$6x^3+10x^4+16x^5+4x^6$	$2x^2+7x^3+17x^4+20x^5+9x^6$	$2x^2+12x^3+27x^4+36x^5+12x^6$
B_1	$2x^2+6x^3+16x^4+16x^5+6x^6$	$x^2+7x^3+14x^4+20x^5+7x^6$	$3x^2+12x^3+30x^4+36x^5+15x^6$
B_2	$x+2x^2+12x^3+18x^4+25x^5+9x^6$	$2x^2+7x^3+18x^4+20x^5+16x^6$	$x+4x^2+18x^3+36x^4+45x^5+24x^6$
E_1	$x+4x^2+16x^3+32x^4+41x^5+17x^6$	$3x^2+13x^3+34x^4+40x^5+21x^6$	$x+7x^2+30x^3+66x^4+81x^5+39x^6$
E_2	$x+3x^2+16x^3+38x^4+41x^5+22x^6$	$2x^2+13x^3+31x^4+40x^5+18x^6$	$x+8x^2+30x^3+69x^4+81x^5+42x^6$

Coefficient of x^k generates functions with k colors and n-k whites

white fixed are shown in Table 2. The generating functions shown in Table 2 provide exhaustive information for all of 4^6 functions of the set R^D. In particular the first column is of particular geometrical and physical interest as this generates the number of irreducible representations contained in the R^D functions that transform as the irreducible representation of the D_6 group for various distributions of colors. That is the coefficient of x^k is the number of times the irreducible representation occurs in the set R^D for k colors and 6-k white colors. The first diagonal element in Table 2 is the ordinary power group enumerator.

As the octahedral group of a cube occurs in many applications and it is the special case of hypercubic group in 3-dimension, representation by the wreath product $S_3[S_2]$, it occurs in a number of applications including the $^{209}Bi_8$ cluster, a number of octahedral molecules and so on. Thus we illustrate the power group enumeration for this case. Consider the case of vertices of a cube with four different colors among which white is fixed and b,g,r are allowed to be permuted. The cycle index of the E_u irreducible representation for the action on the vertices of the cube is given by

$$P_G^{E_u} = \frac{1}{48}\left[2s_1^8 - 8s_1^2s_3^2 - 2s_2^4 + 8s_2s_6\right] \tag{55}$$

We have already obtained the relevant C_k polynomials for the various conjugacy classes of the S_3 group for the four-color problem. Thus we have

$$\begin{aligned} C_{E\in S_3}^{E_u\in O_h}(x) = \frac{1}{6}\{&2Z^{E_u}(O_h; 1+3x, 1+3x^2, 1+3x^3, \ldots\ldots 1+3x^8) \\ &-2Z^{E_u}(O_h; 1, 1, 1+3x^3, \ldots\ldots 1+3x^6, 1, 1)\} \end{aligned} \tag{56}$$

The individual polynomials in the above expression are evaluated as follows:

$$\begin{aligned} &Z^{E_u}(O_h; 1+3x, 1+3x^2, 1+3x^3, \ldots\ldots 1+3x^8) \\ &= \frac{1}{48}[2(1+3x)^8 - 8(1+3x)^2(1+3x^3)^2 \\ &\quad -2(1+3x^2)^4 + 8(11+3x^2)(1+3x^6)] \\ &= 9x^2 + 62x^3 + 228x^4 + 558x^5 + 845x^6 + 720x^7 + 258x^8 \end{aligned} \tag{57}$$

$$\begin{aligned} &Z^{E_u}(O_h; 1, 1, 1+3x^3, 1, 1, 1+3x^6, 1, 1) = \frac{1}{48}[2(1)^8 - 8(1)^2(1+3x^3)^2 \\ &-2(1)^4 + 8(1)(1+3x^6)] \\ &= -x^3 - x^6 \end{aligned} \tag{58}$$

By way of substituting the above two expressions in to the power group generator formula we obtain,

$$\begin{aligned} C_{E\in S_3}^{E_u\in O_h}(x) &= \frac{1}{6}\{2[9x^2 + 62x^3 + 228x^4 + 558x^5 + 845x^6 + 720x^7 + 258x^8] \\ &-2(-x^3 - x^6)\} = 3x^2 + 21x^3 + 76x^4 + 186x^5 + 282x^6 + 240x^7 + 86x^8 \end{aligned} \tag{59}$$

We can obtain the entire set of power group generating functions for all irreducible representations of the O_h group and for all irreducible representations of the S_3 color group through repeated applications of the above process. The power group enumeration method when generalized to all irreducible representations, thus, yields plethora of important combinatorial results.

5 Application to symmetric groups S_n and special unitary groups SU(n)

The connection between the SU(n) group and S_n group provides an avenue for the treatment of multi-particle wavefunctions of fundamental particles in terms of the irreducible representations of the S_n groups and the associated generalized Young Tableau. In chemical context many-electron wavefunctions can be generated by the Schur function algebra of the S_n groups and the associated generalized Young Tableau with filling the cells with spin up (α) or spin down (β). In quantum chromodynamics the wave functions for the fundamental particles can be constructed by associating symbols u, d and s for the three flavors of quarks. Here again the general case involves the Schur functions of the S_n group for the SU(n) algebra. This results in the Weyl tableaus where the cells of the young tableau for the irreducible representations [65–67] of the S_n group are filled with quark flavors u, d, s in a specified lexicographic order (u,d,s). We shall illustrate this with patterns as enumerated by the Schur-functions [65–67] of the symmetric groups S_n. The irreducible representations of S_n are characterized by Young diagrams for the various partitions of an integer n, denoted by [n]. The states of many-particles (including bosons and fermions) that possess multiple spin orientations can be represented by generalized young Tableau. Figure 7 shows all possible generalized Young Tableau of the partitions of 6 occupied by six particles that have three spin orientations (for example, a spin-1 particle such as the bosonic deuterium nucleus) with the possibility that 2 have the first kind of spin orientation, 2 have second kind and last 2 particles have the third kind. We denoted this by $[1^2 2^2 3^2]$ shape as shown below in Fig. 7.

As can be seen from Fig. 7, the GYTs have numbers in any column in strictly ascending order while the numbers in any row must be in non-decreasing order. These tableaus represent the nuclear spin functions that transform according to the particular irreducible representation that the diagram represents. It is interesting to note that for a spin-1 particle such GYTs can have at the most 3 rows and likewise for electrons, which are spin-1/2 particles, the GYTs can have at the most 2 rows. In general for a spin-j particle there can only be at most 2j+1 rows in the GYTs. The same tableaus also become the Weyl tableaus for fundamental particles of strong interactions when 1 is mapped to u, 2 is mapped to d and 3 is mapped to s. The resulting symmetry-adapted wavefunctions represent the various 1/2ixed symmetry states of the Baryons in quantum chromodynamics.

The enumeration of GYTs for the various shapes of spin distributions can be accomplished through polynomials called the Schur functions [65–67] of the symmetric group S_n. The Schur function corresponding to a partition λ of n is denoted by {λ} and it is defined as

$$\{\lambda\} = \frac{1}{n!} \sum_{g \varepsilon G} \chi^{\lambda}(g) s_1^{b_1} s_2^{b_2} \ldots\ldots s_n^{b_n} \tag{60}$$

where$\chi^{\lambda}(g)$ is the character value for g in the group $G=S_n$ corresponding to the irreducible representation [λ] of the group S_n. Indeed S-functions are the GCCIs of the symmetric groups S_n. To illustrate the Schur function corresponding to the partition 4+1+1 of 6 is given by the Schur function, {6;4,1,1,}, shown below:

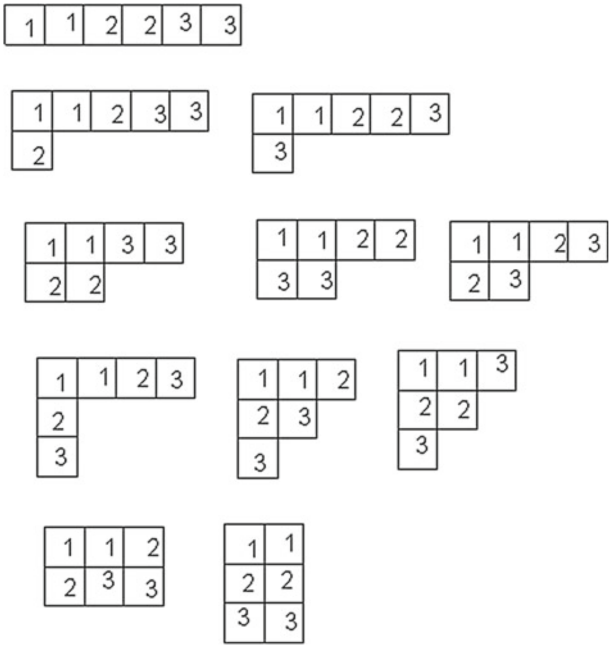

Fig. 7 Generalized Young Tableau (GYT) for the partition of 6 for a spin-1 Boson (e.g., Deuterium) corresponding to the spin distribution 2 particles with the first spin orientation, 2 with the second orientation, 2 with the third or $[1^2 2^2 3^2]$ shape

$$\{6; 4, 1, 1\} = \frac{1}{720}\Big[10s_1^6 + 30s_1^4 s_2 + 40s_1^3 s_3 - 90s_1^2 s_2^2$$
$$-120s_1 s_2 s_3 - 30s_2^3 + 40s_3^2 + 120s_6\Big] \tag{61}$$

The generators for the GYTs can be obtained by replacing every s_k in the Schur function or S-function by $\sum_i \lambda_i^k$. The coefficient of a typical term $\lambda_1^{a_1}\lambda_2^{a_2}\ldots\ldots\lambda_m^{a_m}$ in the generating function thus obtained yields the number of GYTs with the shape $[1^{a_1}2^{a_2}\ldots.m^{a_m}]$. The GYT generators are so powerful that they also enumerate the atomic states when applied to electronic spin functions which are GYTs with only 2 rows. In addition to the symmetric group S_n acting on the particles if there is a group H that acts on the colors of the set R, which is most commonly the reversal group, Rev_i, defined by two operations, identity, and reversal of colors, we have a situation where direct application of the current generalization of the Harary–Palmer power group theorem [60] arises. For nuclear spins of n/2-spin particle, the color group would be $\{(-n/2)\ldots\ldots(-1/2)\ldots\ldots(n/2), (-n/2\ n/2)\ldots..(-i/2\ i/2)\ldots\ldots..(-1/2\ 1/2)\}$.

6 Conclusion

In this paper we have generalized the Harary–Palmer power group enumeration theorem to all the irreducible representations of the group G acting on the set D of objects

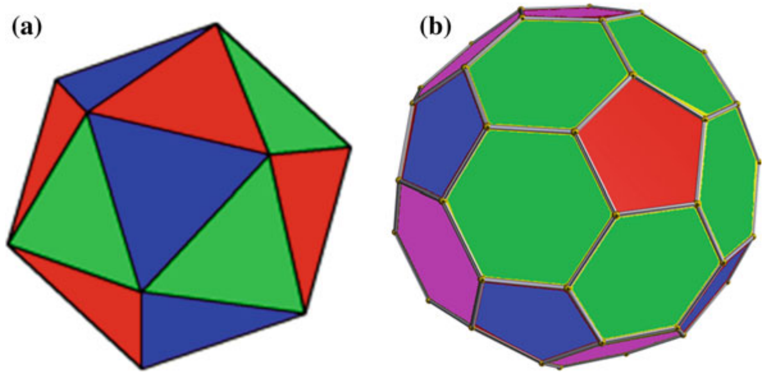

Fig. 8 *Left* **a** Face colorings of an icosahedron with three colors (*blue*, *green* and *red*). There are 3^{20} all possible face coloring mappings in the set R^D, 3^{12} all possible vertex-colorings and 3^{30} all possible edge-colorings for an icosahedron. *Right* **b** one of 4^{32} face coloring maps of Buckminsterfullerene with 4 colors (*blue*, *green*, *red* and *violet*); there are 4^{90} edge coloring maps and 4^{60} vertex coloring maps for the soccer ball buckminsterfullerene, many of which are equivalent under the action of the icosahedral I_h group and color group . There are $6^{54} = 1.7394784 \times 10^{18}$ Avogadro number of possible face coloring maps for a Rubik's cube with the group G acting on the faces of the Rubik's cube, which is the direct product of 2 wreath products: $S_8[C_3] \times S_{12}[C_2]$ comprising of $8! \times 3^8 \times 12! \times 2^{12}$ or 519,024,039,293,878,272,000 permutations (Color figure online)

and the group H acting on the set R of colors. The generalization was shown to yield powerful results in multiple areas of chemistry, physics and mathematics, and it is of general interest in the context of color symmetry. There still remain many problems and applications of this powerful color combinatorial group theory. For example, there are 3^{20} functions that map colors to the faces of an icosahedron with 3 colors and one such coloring is shown in Fig. 8a.

The generalization of power group enumeration can yield not only the unique patterns for different colors but also nuclear spin distributions, nuclear spin statistics and interesting information on the chirality of colorings. We foresee many such future applications including to fullerene cages, nanotubes, high symmetry virus particles, non-rigid proteins, and self-assembled monolayers of functionalized mesoporous materials. More detailed applications of these methods to multiple-quantum NMR, ESR spectroscopies and chirality [71] will be the subject of future studies. Another important topic has to do with generalization of the power group enumeration to the hypercubic groups, which are wreath products of $S_n[S_2]$ in n-dimensional space and these groups have applications both in chemistry and quantum chromodynamics. More recently the theory of non-rigid molecular symmetry in terms of wreath products groups is shown to have important applications in our understanding of chirality of biosystems through the functionality of intrinsically disordered proteins [72,73]. It appears that intrinsically disordered non-rigid proteins are more likely to be involved in moonlighting functionality than ordered proteins, and thus understanding the non-rigid group theory, especially group-subgroup chain relations seem to play a critical role in our understanding the catalytic behavior of these proteins. That is, our understanding of the fuzzy lock-and-key mechanism can be enhanced through matching group/subgroup subduction chains between these proteins and binding sites through mirror relations or chirality. Therefore combinatorial group theory of the non-rigid disordered protein structures is important to understand chirality in biosystems [71–73] and moonlight functionality of proteins in nature, and hence the generalization of power group enumeration developed here could result in such novel biological applications.

References

1. A.V. Belov, N.V. Shubnikov, Color Symmetry, first edition. McMillan (Pergamon Press, 1964) 263p
2. W. Opechowski, R. Guccione, in *Magnetism, vol. 2A, Chap. 3*, eds. G.T. Rado, H. Suhl, (Academic Press, New York, 1965)
3. R.L.E. Schwarzenberger, Colour symmetry. Bull. Lond. Math. Soc. **16**, 209–240 (1984)
4. D.B. Litvin, W. Opechowski, Spin groups. Physica **76**, 538–554 (1974)
5. R. Lifshitz, Rev. Mod. Phys. **69**, 1181 (1997)
6. J. Kappraff, *Connections, The Geometric Bridge Between Art and Science, 2nd edn*. The (World Scientific Publishing co, 2001), 470 pp
7. W.M. Gibson, B.R. Pollard: *Symmetry Principles in Elementary Particle Physics*. (Cambridge University Press, Cambridge, 1980), 402p
8. P.G. Tait, Remarks on the colourings of maps. Proc. R. Soc. Edinb. **10**, 729 (1880)
9. V.R. Nagarajan, *Hosting the divine: the Kolam in Tamil Nadu* in *Mud, Mirror, and Thread: Folk Traditions of Rural India* (ed.) N. Fisher, (Museum of New Mexico Press, 1993)
10. V.R. Nagarajan, Drawing down desires: woman, ritual, and art in Tamil Nadu. Forma **22**, 127–128 (2007)
11. K. Balasubramanian, in *Symmetry in Cultural Context: An Interdisciplinary Workshop, vol. 1*, ed. by D. Nagy Arizona State University, Tempe, AZ, 1987, pp. 12–15
12. W.S. Warren, A. Pines, J. Chem. Phys. **74**, 2808 (1981)
13. K. Balasubramanian, Mol. Phys. **107**, 797–807 (2009)
14. K. Balasubramanian, *Relativistic Effects in Chemistry* (Wiley-Interscience, Parts A & B, 1997)
15. S. Simon, L. Baia, A. Radu, J. Raman Spectrosc. **37**, 183 (2006)
16. M.-Y. Liao, G.S. Harbison, J. Chem. Phys. **111**, 3077 (1999)
17. A.P. Reyes, R.H. Heffner, P.C. Canfield, J.D. Thompson, Z. Fisk, Phys. Rev. B **49**, 16321 (1994)
18. K. Balasubramanian, K.S. Pitzer, H.L. Strauss, J. Mol. Spectrosc. **93**, 447 (1982)
19. K. Balasubramanian, Chem. Phys. Lett. **183**, 292 (1991)
20. K. Balasubramanian, Chem. Phys. Lett. **318**, 15 (2004)
21. K. Balasubramanian, J. Math. Chem. **35**, 345 (2004)
22. K. Balasubramanian, Chem. Phys. Lett. **391**, 69 (2004)
23. R.B. King, J. Math. Chem. **7**, 51 (1991)
24. R.B. King, *Applications of Graph Theory and Topology in Inorganic Cluster and Coordination Chemistry*. (CRC Press, Boca Raton, 1993)
25. R.B. King, Mol. Phys. **100**, 1567 (2002)
26. A.T. Balaban, *Chemical Applications of Graph Theory* (Academic Press, New York, 1976)
27. A.T. Balaban, M. Banciu, V. Ciorba, *Annulenes, Benzo-, Hetero-, Homo-Derivatives and Their Valence Isomers, vol. 3, chapter 8* (CRC Press, Boca Raton, Florida, 1986)
28. K. Balasubramanian, Chem. Rev. **85**, 599 (1985)
29. K. Balasubramanian, J. Chem. Phys. **95**, 8273 (1991)
30. K. Balasubramanian, T.R. Dyke, J. Phys. Chem. **88**, 4688 (1984)
31. K. Balasubramanian, J. Comput. Chem. **3**, 69 (1982)
32. K. Balasubramanian, J. Comput. Chem. **3**, 75 (1982)
33. K. Balasubramanian, J. Chem. Phys. **74**, 6824 (1981)
34. K. Balasubramanian, J. Chem. Phys. **75**, 4572 (1981)
35. V. Krishnamurthy, *Combinatorics: Theory and Applications* (Harwood, New York, 1985)
36. S. Fujita, *Symmetry and Combinatorial Enumeration in Chemistry* (Springer, Berlin, 1991)
37. G. Pólya, R.C. Read, *Combinatorial Enumeration of Groups, Graphs and Chemical Compounds* (Springer, New York, 1987)
38. E. Ruch, D.J. Klein, Theor. Claim. Acta **63**, 447 (1963)

39. D.H. Rouvray, Chem. Soc. Rev. **3**, 355 (1974)
40. K. Balasubramanian, Theor. Chim. Acta **51**, 37 (1979)
41. K. Balasubramanian, Theor. Chim. Acta **53**, 129 (1979)
42. K. Balasubramanian, Indian J. Chem. **16B**, 1094 (1978)
43. K. Balasubramanian, J. Magn. Reson. **48**, 165 (1982)
44. K. Balasubramanian, J. Magn. Reson. **91**, 45 (1991)
45. K. Balasubramanian, Int. J. Quantum Chem. **20**, 1255 (1981)
46. K. Balasubramanian, J. Phys. Chem. **86**, 4668 (1982)
47. K. Balasubramanian, J. Chem. Phys. **78**, 6358 (1983)
48. K. Balasubramanian, J. Chem. Phys. **78**, 6369 (1983)
49. K. Balasubramanian, *Group Theory of Non-rigid Molecules and its Applications*. Elsevier Publishing Co. **23**, 149–168 (1983)
50. K. Balasubramanian, Theor. Chim. Acta **78**, 31 (1990)
51. K. Balasubramanian, J. Math. Chem. **14**, 113 (1993)
52. W. Hässelbarth, Theor. Chim. Acta. **61**, 91 (1984)
53. A.T. Balaban, Enumerating isomers, in *Chemical Graph Theory* ed. by D. Bonchev, D.H. Rouvray (Gordon Beach Publishers, 1991)
54. A.T. Balaban, Rev. Roum. Chim. **15**, 463 (1970)
55. R.C. Read, Math. Mag. **60**, 275 (1987)
56. R.A. Davidson, J. Am. Chem. Soc. **103**, 212 (1981)
57. J.H. Redfield, Am. J. Math. **49**, 433 (1927)
58. N.G. de Bruijn, in *Applied Combinatorial Mathematics* ed. E.F. Beckenbach (Wiley, New York, 1964)
59. N.G. de Bruijn, J. Comb. Theory **2**, 418 (1967)
60. F. Harary, E.M. Palmer, *Graphical Enumeration* (Academic Press, New York, 1979)
61. H.C. Longuet-Higgins, Mol. Phys. **6**, 445 (1963)
62. K. Balasubramanian, J. Chem. Phys. **72**, 665 (1980)
63. K. Balasubramanian, J. Chem. Phys. **120**, 5524 (2004)
64. R.B. King, *Dalton Transactions* (2003) p. 395
65. D.E. Littlewood, *The Theory of Group Characters and Matrix Representations of Groups* (Clarendon Press, Oxford, 1950)
66. W. Ledermann, *Introduction to Group Characters*, 2nd edn. (Cambridge University Press, Cambridge, 1987)
67. I.G. MacDonald, *Symmetric Functions and Hall Polynomials* (Clarendon Press, Oxford, 1979)
68. H.O. Foulkes, Cand. J. Math. **18**, 1060 (1966)
69. G. Williamson, J. Comb. Theory **11** (1971) 122; **8** (1970) 163
70. R. Merris, Linear Algebra Appl. **29**, 255 (1980)
71. G.H. Wagniére, *On Chirality and the Universal Asymmetry, Reflections on Image and Mirror Image*. Wiley-VCH, Zürich, Switzerland (2007)
72. R. Wallace, Nat. Proc. **4** (2011), hdl:10101/npre.2011.6413.1: Posted 14 Sep 2011
73. R. Wallace, Mol. BioSyst. **8**, 374 (2012)