Journal of Mathematical Chemistry 3(1989)227–232

REDUCED CYCLE INDICES AND THEIR APPLICATIONS IN ENUMERATION OF NMR SIGNALS AND EQUIVALENCE CLASSES

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Received 23 May 1988

Abstract

An efficient technique is formulated based on a polynomial structure which we call the reduced cycle index for the enumeration of equivalence classes and NMR signals under group action. The reduced cycle indices are shown to be the cycle index polynomials of a subset of significantly smaller order of the point group of the molecule. Thus, the reduced cycle indices are much simpler and their use leads to a considerable reduction in the computation of the generating functions from the cycle indices and irreducible representations contained in a set.

1. Introduction

The applications of combinatorics and graph theory to problems of chemical interest have been on the increase in the last decade [1–22]. There are numerous chemical applications of Pólya's theorem [23]. These applications range from enumeration of chemical isomers to enumeration of configurations in ab initio CI calculations. The present author [1] has reviewed the applications of Pólya's theory of counting and their ramifications in many areas of spectroscopy, quantum chemistry and stereochemistry.

An important problem in several areas, such as stereochemistry, quantum chemistry, NMR and multiple quantum NMR spectroscopy, is the enumeration of equivalence classes of a set of entities under group action. The set could be the various atoms in the molecule, the possible nuclear spins, or the possible atomic orbitals of a given molecule. The present author [17] showed that Pólya's theorem could be applied to enumerate the equivalence classes. The calculation of the generating functions from the cycle indices could be especially cumbersome if the group contains

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a large number of elements. It is now well known that symmetry groups of non-rigid molecules could have a very large number of nuclear permutations, making it formidably difficult to apply Pólya's theorem to computing generating functions for equivalence classes.

In this investigation, we formulate a polynomial called the reduced cycle index which is actually the cycle index of a much smaller subset of the group. It is shown that significant reduction of computation is achieved by using the reduced cycle index for calculating the generating functions for equivalence classes. Further, extension of these indices to other irreducible characters provides an elegant method of generating the irreducible representations spanned by a set. Section 2 comprises the definitions, reduced cycle indices and a brief description of applications.

2. Reduced cycle indices and their applications

The ordinary cycle index of a group G is defined as

$$P_G = \frac{1}{|G|} \sum_{g \in G} X_1^{b_1} X_2^{b_2} \ldots X_n^{b_n} ,$$

where the sum is over all the elements in the group G, $|G|$ is the number of elements in the group G, $X_1^{b_1} X_2^{b_2} \ldots X_n^{b_n}$ is the cycle representation of $g \in G$ if it generates b_1 cycles of length 1, b_2 cycles of length 2, $\ldots b_n$ cycles of length n upon application of G on the set D of nuclei or atomic orbitals or nuclear spins. The set D is the object of interest which we wish to divide into equivalence classes upon the action of the group G.

To illustrate, the cycle index of the naphthalene molecule (D_{2h} point group), with D being the set of the ten carbon nuclei, is shown below.

$$P = \tfrac{1}{8} [2X_1^{10} + 4X_2^5 + 2X_1^2 X_2^4]$$

$$= \tfrac{1}{4} [X_1^{10} + 2X_2^5 + X_1^2 X_2^4] .$$

Note that the D_2 subgroup and D_{2h} have the same cycle indices since the symmetry planes generate the same nuclear permutations as rotations. Pólya's theorem constructs the generating function for enumeration under group action from the cycle indices. Consider the set of maps from D to R, where R is a set of different types of colors. The present author [17,19] showed that the adaption of Pólya's theorem to a set R of two colors enumerates the equivalence classes. Let the weights of the two colors in the set of R be w_1 and w_2. Then the total generating function for possible ways of coloring the members in D with the colors in R is given by

$$\mathrm{GF} = P_G(X_k \rightarrow w_1^k + w_2^k),$$

where the arrow stands for replacing every cycle of length k by $w_1^k + w_2^k$. It was shown [17] that the coefficient of $w_1^{n-1} w_2$ in the GF gives the number of equivalence classes of D.

We formulate here a structure called the reduced cycle index. The reduced cycle index $P_{G'}$ is defined as

$$P_{G'} = \frac{1}{|G|} \sum_{g' \in G'} X_1^{b_1} X_2^{b_2} \ldots X_n^{b_n},$$

where G' is a subset of all permutations in the point group (rotational subgroup) G of the molecule which leave *at least one* nucleus *invariant*. For example, the permutation (1234) of four nuclei cannot be a member of G' since all the four nuclei are shifted by this permutation. Note that G', in general, is *not* a group. For example, the set G' would consist of the identity and the C_3 operations for a cube if D is the vertices of the cube. It can be easily seen that G' is not a group for cube. The reduced cycle index of naphthalene is shown below.

$$P_{S_2} = \tfrac{1}{4} [X_1^{10} + X_1^2 X_2^4] .$$

Note that the reduced cycle index of naphthalene contains only two terms and the group G is D_2 since the symmetry planes do not generate any new permutations. A generating function for the equivalence classes of the nuclei is obtained by replacing $X_k \rightarrow w_1^k + w_2^k$ and collecting the coefficient of $w_1^9 w_2$ (since there are ten carbon nuclei). The reduced GF for naphthalene is shown below.

$$\begin{aligned}\mathrm{RGF} &= \tfrac{1}{4} [(w_1 + w_2)^{10} + (w_1 + w_2)^2 (w_1^2 + w_2^2)^4] \\ &= \tfrac{1}{4} [2w_1^{10} + 12w_1^9 w_2 + 50w_1^8 w_2^2 + 128w_1^7 w_2^3 + 220w_1^6 w_2^4 + 264w_1^5 w_2^5 \\ &\quad + 220w_1^4 w_2^6 + 128w_1^3 w_2^7 + 50w_1^2 w_2^8 + 12w_1 w_2^9 + 2w_2^{10}] .\end{aligned}$$

In the RGF computed above, only the coefficient of $w_1^9 w_2$ is meaningful since the other coefficients are only partial. The coefficient of $w_1^9 w_2$ in the above expression is seen to be three, implying that there are three equivalence classes in the set of ten ^{13}C nuclei of naphthalene. Note that the reduced cycle index does not generate the total generating function for the various ways of coloring the elements in D. However, the coefficient of $w_1^{n-1} w_2$ in RGF is always an integer and represents the number of equivalence classes of the set D.

Table 1

The full cycle indices and reduced cycle indices for a few systems

Structure	D	$\lvert G\rvert P_G$	$\lvert G\rvert P_{G'}$
Cube	Vertices	$X_1^8 + 6X_4^2 + 9X_2^4 + 8X_1^2X_3^2$	$X_1^8 + 8X_1^2X_3^2$
Cube	Edges	$X_1^{12} + 6X_4^3 + 3X_2^6 + 8X_3^4 + 6X_1^2X_2^5$	$X_1^{12} + 6X_1^2X_2^5$
Anthracene	Carbon vertices	$X_1^{14} + 2X_2^7 + X_1^2X_2^6$	$X_1^{14} + X_1^2X_2^6$
Non-rigid butane	Protons	$X_1^{10} + 4X_1^7X_3 + 4X_1^4X_3^2 + 3X_2^5 + 6X_2^2X_6$	$X_1^{10} + 4X_1^7X_3 + 4X_1^4X_3^2$
Rigid butane	Protons	$X_1^{10} + X_2^5$	X_1^{10}
Triphenylene	Carbons	$X_1^{18} + 2X_3^6 + 3X_2^9$	X_1^{18}
Octahedron	Vertices	$X_1^6 + 6X_1^2X_4 + 3X_1^2X_2^2 + 8X_3^2 + 6X_2^3$	$X_1^6 + 6X_1^2X_4 + 3X_1^2X_2^2$
I (fig. 1)	Carbons	$X_1^{96} + 2X_6^{16} + 2X_3^{32} + 4X_2^{48} + 3X_1^8X_2^{44}$	$X_1^{96} + 3X_1^8X_2^{44}$
II (fig. 1)	Carbons	$X_1^{42} + 2X_6^7 + 2X_3^{14} + 4X_2^{21} + 3X_1^6X_2^{18}$	$X_1^{42} + 3X_1^6X_2^{18}$
III (fig. 1)	Carbons	$X_1^{90} + 2X_6^{15} + 2X_3^{30} + 4X_2^{45} + 3X_1^6X_2^{42}$	$X_1^{90} + 3X_1^6X_2^{42}$
IV (fig. 1)	Carbons	$X_1^{84} + 2X_6^{14} + 2X_3^{28} + 4X_2^{42} + 3X_1^2X_2^{40}$	$X_1^{84} + 3X_1^2X_2^{40}$

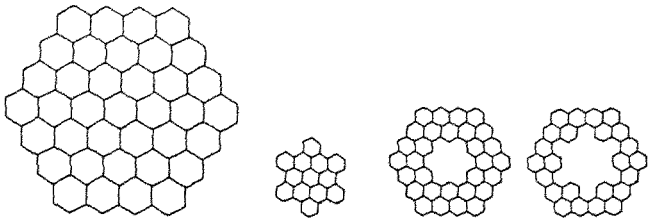

Fig. 1.

The advantage of the reduced cycle index is that it contains fewer terms and thus the computation of the generating function is rapid. The coefficient of $w_1^9 w_2$ is also three in the original generating function obtained from the full cycle index, but this generating function is generally more difficult to evaluate.

Table 1 compares the full cycle indices and reduced cycle indices for a few rigid and non-rigid molecules. As one can see from this table, the reduced cycle index provides an alternative and efficient method for computing the generating functions for equivalence classes.

Table 2 shows the actual coefficients of the terms which enumerate the equivalence classes for the structures listed in table 1 from the reduced generating functions.

Table 2

The number of equivalence classes generated by reduced generating functions

Structure	D	Coefficient of $w_1^{\|D\|-1} w_2$ in RGF
Cube	Vertices	1
Cube	Edges	1
Anthranene	Carbons	4
Non-rigid butane	Protons	3
Rigid butane	Protons	5
Triphenylene	Carbons	3
Octahedron	Vertices	1
I (fig. 1)	Carbons	10
II (fig. 1)	Carbons	5
III (fig. 1)	Carbons	9
IV (fig. 1)	Carbons	8

The enumeration and construction of equivalence classes have numerous applications. If the set D contains ^{13}C nuclei, then the RGF enumerates the number of NMR signals. If the set D contains the various atomic orbitals in the molecule or basis functions in ab initio calculations, then the RGFs enumerate the number of equivalence classes of basis functions. If the set D consists of the atomic orbitals, then the RGF enumerates the equivalence classes of orbitals wherein atomic orbitals in a class only mix in the symmetry-adapted linear combination (SALC) of molecular orbitals. There are many such applications, and thus the reduced cycle indices should provide for a convenient method of enumerating the equivalence classes.

The reduced cycle indices can be extended to various other irreducible representations in the group as shown below.

$$P_{G'}^{\chi} = \frac{1}{|G|} \sum_{g' \in G'} \chi(g') X_1^{b_1} X_2^{b_2} \ldots X_n^{b_n},$$

where $\chi(g')$ is the character which corresponds to the element $g' \in G'$. A reduced generating function can be obtained by replacing every X_k by $w_1^k + w_2^k$. The coefficient of $w_1^{n-1}w_2$ is $P_{G'}^{\chi}$, which enumerates the number of times the irreducible character χ occurs in the set D. Thus, this appears to be a very rapid and efficient method of finding all the irreducible representations panned by the set D; thus, the present procedure is superior to the textbook [24] method of finding the irreducible representations in a set.

References

[1] K. Balasubramanian, Chem. Rev. 85(1985)599.
[2] V. Krishnamurthy, *Combinatorics: Theory and Applications* (Ellis Horwood, Chichester, 1986).
[3] D.H. Rouvray, Chem. Soc. Rev. 3(1972)355.
[4] A.T. Balaban, *Chemical Applications of Graph Theory* (Academic Press, New York, 1976).
[5] A.T. Balaban, E. Palmer and F. Harary, Rev. Roum. Chim. 22(1977)517.
[6] R.B. King, J. Math. Chem. 1(1987)5.
[7] N. Trinajstić, *Chemical Graph Theory* (CRC Press, Boca Raton, Florida, 1983).
[8] M. Randić, D.O. Oakland and D.J. Klein, J. Comput. Chem. 7(1986)35.
[9] D.J. Klein and A.H. Cowley, J. Amer. Chem. Soc. 97(1975)1633.
[10] D.J. Klein and A.H. Cowley, J. Amer. Chem. Soc. 100(1978)2593.
[11] D.J. Klein and E.H. Ruch, Theor. Chim. Acta 63(1983)447.
[12] M. Randić, Chem. Phys. Lett. 42(1976)383.
[13] M. Randić, Int. J. Quant. Chem. 25(1979)663.
[14] M. Randić, Chem. Phys. Lett. 42(1976)383.
[15] S. El-Basil, J. Math. Chem. 2(1987)153.
[16] R.W. Robinson, F. Harary and A.T. Balaban, Tetrahedron 32(1976)355.
[17] K. Balasubramanian, Theor. Chim. Acta 51(1979)37.
[18] K. Balasubramanian, Theor. Chim. Acta 53(1979)129.
[19] K. Balasubramanian, J. Mag. Reson. 48(1982)165.
[20] K. Balasubramanian, Theor. Chim. Acta 59(1981)47.
[21] K. Balasubramanian, Theor. Chim. Acta 59(1981)237.
[22] K. Balasubramanian, Theor. Chim. Acta 74(1988)111.
[23] G. Pólya, Acta Math. 65(1937)145.
[24] F.A. Cotton, *Chemical Applications of Group Theory* (Wiley, New York, 1971).