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The Combinatorics of Symmetry Adaptation

K. Balasubramanian*

Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218, USA

A method is developed for obtaining the generating functions for the equivalence classes of orbitals wherein only orbitals within an equivalence class participate in symmetry adaptation. It is shown that using Williamson's combinatorial theorem the generating functions for the symmetry species contained in each equivalence class can be obtained. The method is illustrated with Porphindianion.

Key words: Combinatorics of symmetry adaptation – Williamson's theorem – Generation of symmetry species of MOs.

1. Introduction

The construction of symmetry-adapted orbitals from atomic orbitals is of considerable importance in quantum chemistry. Such symmetry-adapted orbitals constructed as linear combinations of atomic orbitals are referred to as symmetry adapted linear combinations (SALC) by Cotton [1]. The usual procedure for constructing these orbitals (see Cotton, for example) is to find the characters of the set of atomic orbitals under the action of the molecular point group. Then one applies the projection operator which corresponds to each irreducible representation. However, this method does not explicitly separate the set of atomic orbitals into equivalence classes, wherein only the orbitals within a class mix in any SALC.

Further, when the method developed here is combined with the representation theory of generalized wreath product groups [2] and the group theoretical concepts in NMR spectroscopy [3], the NMR spin species and spin functions can be generated as we will show in a subsequent publication. For reviews on several chemical applications of graph theory see the book of Balaban [4].

* *Present address:* Department of Chemistry, University of California, Berkeley 94720, USA

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The first objective of this paper is to give a method for separating the atomic orbitals into equivalence classes by a special case of the theorem described here. A combinatorial theorem following Williamson [5] is outlined which enables the generation of symmetry species in each equivalence class. The projection operator which corresponds to each symmetry species is applied on the orbitals belonging to that class to generate SALCs. The procedure is illustrated with Porphindianion.

2. Theory

Let G be the molecular point group. Let D be a set of atomic nuclei or atomic orbitals depending upon the context. G acts on D as a group of permutations of D. Let R be a set containing two elements. Let F denote the set of all maps from D to R. If G acts on D it also acts on F in that if $f \in F$ then $g(f(i)) = f(g^{-1}i)$, $i \in D$. Thus the map $f \to gf$ defines the action of G on F. Let V be a $|R|$-dimensional vector space over a field K of characteristic zero [6]. Let $V^d = \bigotimes^d V$ be the d^{th} tensor product of V. Assume D is a discrete set which is usually the case. Let $e_1, e_2, \ldots, e_{|R|}$ be a basis for V with $d = |D|$. To each $f \in F$, we can assign an $e_f = e_{f(1)} \otimes \cdots \otimes e_{f(d)}$; e_f can be seen to be a tensor. The set of tensors $S = \{e_f : f \in F\}$ forms a basis for the tensor product V^d. Define for any $g \in G$, $P(g)e_f = e_{gf}$. Thus $P(g)$ is a permutation operator relative to the basis S since it permutes the tensors in S by way of the action of g on the functions. Consider the map Ω from G to K, $\Omega : G \to K$. In addition let $\Omega \neq 0$ and Ω be an homomorphism (i.e., $\Omega(g_1g_2) = \Omega(g_1)\Omega(g_2)$) [7]. Now let us define an operator which we shall call a symmetry operator as follows.

$$T_G^{\Omega} = \frac{1}{|G|} \sum_{g \in G} \Omega(g)P(g).$$

Consider a map W from F to K, $W : F \to K$ which is also a constant on the orbits resulting from the action of G on F. Alternatively, with each $f \in F$, there is an associated element from the field K. In addition if W satisfies the following property for every f, it is referred to as a weight function.

$$W(f) = \prod_{i=1}^{d} w(f(i))$$

where w is a function, $w : R \to K$; $W(f)$ is also referred to as a weight of a function in combinatorics books [8].

Now consider the subspace V_x^d of V^d spanned by all tensors $S_x = \{e_f : W(f) = x \in K\}$. Let the restrictions of the operators T_G and $P(g)$ to the space V_x^d be T_G^x and $P_x(g)$, respectively. Thus one can define a weighted permutation operator and a weighted symmetry operator with the weight W, denoted as $P_W(g)$, T_G^W by the following expressions.

$$P_W(g) = \bigoplus_{x \in K} xP_x(g)$$

$$T_G^W = \bigoplus_{x \in K} xT_G^x$$

where $\bigoplus$ denotes finite direct sum with respect to the associated subspaces V_x^d and x's vary over the elements of R. In a matrix representation of $P_W(g)$,

$$\mathrm{Tr}\, P_W(g) = \sum_f^{(g)} W(f),$$

where the sum is taken over all f for which $gf = f$. In this set up Williamson [5] proved the following theorem

Theorem (Williamson):

$$T_G^W = \frac{1}{|G|} \sum_{g \in G} \Omega(g) P_W(g).$$

Consequently

$$\mathrm{Tr}\, T_G^W = \frac{1}{|G|} \sum_{g \in G} \Omega(g)\, \mathrm{Tr}\,(P_W(g))$$
$$= \frac{1}{|G|} \sum_{g \in G} \Omega(g) \sum_f^{(g)} W(f).$$

Define the cycle index of a group G with character χ of an irreducible representation Γ of G, as

$$P_G^\chi(x_1, x_2, \ldots) = \frac{1}{|G|} \sum \chi(g) x_1^{b_1} x_2^{b_2} \ldots$$

where $x_1^{b_1} x_2^{b_2} \ldots$ is a representation of a typical permutation $g \in G$ having b_1 cycles of length 1, b_2 cycles of length 2, etc. Then by the theorem mentioned above $\mathrm{Tr}\, T_G^W$ which is a generating function for the irreducible representation whose character is χ, is given by

$$\mathrm{Tr}\, T_G^W = P_G^\chi\left(\sum_{r \in R} w(r), \sum_{r \in R} (w(r))^2, \ldots \right).$$

In particular for the identity representation of G

$$\mathrm{Tr}\, T_G^W = P_G\left(\sum_{r \in R} w(r), \sum_{r \in R} (w(r))^2, \ldots \right)$$

which represents the generating function for sets of functions in F containing the identity representation or equivalently G-equivalence classes of F, since each equivalence class contains exactly one identity representation. Thus in this special case Williamson's theorem reduces to the well-known Pólya's theorem [8].

3. Illustration of the Method with Porphindianion

Let us illustrate the use of the above formalism with Porphindianion as an example. Balaban [9] enumerated the isomers of substituted porphyrins using the symmetry of the parent porphindianion (see Fig. 1) whose molecular point group is D_{4h}. The problem we consider here is to construct the SALCs of the p_z-orbitals

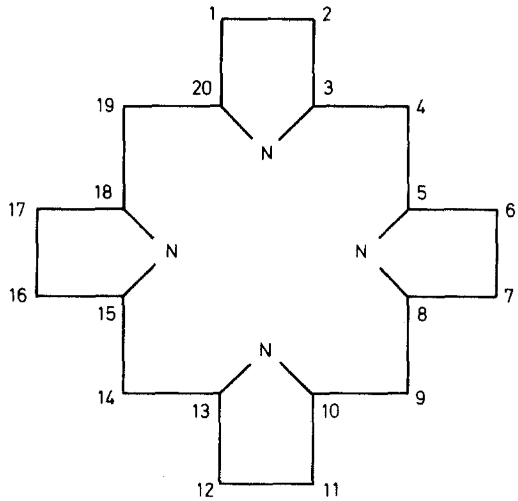

Fig. 1. Porphindianion. The equivalence classes of orbitals and the symmetry species contained in each class which were generated combinatorially are shown in Table 1

perpendicular to the plane of the molecule. All the 20 carbon p_z-orbitals do not mix in any of the SALCs. The above problem first reduces to finding the equivalence classes of 20 nuclei such that only those p_z-orbitals centered on the nuclei in a class mix to form a SALC. As far as the author is aware it appears that there is no organized technique for enumerating these classes, in general. The solution for this problem is obtained by setting χ to be the character of the identity representation in the theorem outlined in Sect. 2. Let D be the set of 20 carbon nuclei. Let α_1 and α_2 be the elements in K which are the weights of elements in R. Then for this case

$$\mathrm{Tr}\, T^W_{D_{4h}} = \frac{1}{16}[2(\alpha_1+\alpha_2)^{20} + 4(\alpha_1^4+\alpha_2^4)^5 + 6(\alpha_1^2+\alpha_2^2)^{10} + 4(\alpha_1+\alpha_2)^2(\alpha_1^2+\alpha_2^2)^9].$$

The coefficient of $\alpha_1^{19}\alpha_2$ in the above expression gives the number of patterns or the number of identity representations in each pattern. This is equal to

$$\frac{2}{16}\left[\binom{20}{1}+2\binom{2}{1}\right]=3.$$

The classes of nuclei are

$$C_1=\{1, 2, 6, 7, 11, 12, 16, 17\}$$

$$C_2=\{3, 5, 8, 10, 13, 15, 18, 20\}$$

$$C_3=\{4, 9, 14, 19\}.$$

To construct the SALCs now we look at the transformation properties of vectors perpendicular to the plane of the molecule belonging to a class. A generating function for the irreducible representations in the class C_i can be obtained by

Table 1

S. No.	Irreducible representation	Class	GF	Frequency of occurrence
1.	A_{1g}	C_1, C_2	0	0
2	A_{2g}	C_1, C_2	0	0
3.	B_{1g}	C_1, C_2	0	0
4.	B_{2g}	C_1, C_2	0	0
5.	E_g	C_1, C_2	$2\alpha_1^7\alpha_2+6\alpha_1^6\alpha_2^2+14\alpha_1^5\alpha_2^3+16\alpha_1^4\alpha_2^4+14\alpha_1^3\alpha_2^5+6\alpha_1^2\alpha_2^6+2\alpha_1\alpha_2^7$	2
6.	A_{1u}	C_1, C_2	$\alpha_1^7\alpha_2+2\alpha_1^6\alpha_2^2+7\alpha_1^5\alpha_2^3+7\alpha_1^4\alpha_2^4+7\alpha_1^3\alpha_2^5+2\alpha_1^2\alpha_2^6+\alpha_1\alpha_2^7$	1
7.	A_{2u}	C_1, C_2	$\alpha_1^8+\alpha_1^7\alpha_2+6\alpha_1^6\alpha_2^2+7\alpha_1^5\alpha_2^3+13\alpha_1^4\alpha_2^4+7\alpha_1^3\alpha_2^5+6\alpha_1^2\alpha_2^6+\alpha_1\alpha_2^7+\alpha_2^8$	1
8.	B_{1u}	C_1, C_2	$\alpha_1^7\alpha_2+4\alpha_1^6\alpha_2^2+7\alpha_1^5\alpha_2^3+9\alpha_1^4\alpha_2^4+7\alpha_1^3\alpha_2^5+4\alpha_1^2\alpha_2^6+\alpha_1\alpha_2^7$	1
9.	B_{2u}	C_1, C_2	$\alpha_1^7\alpha_2+4\alpha_1^6\alpha_2^2+7\alpha_1^5\alpha_2^3+9\alpha_1^4\alpha_2^4+7\alpha_1^3\alpha_2^5+4\alpha_1^2\alpha_2^6+\alpha_1\alpha_2^7$	1
10.	E_u	C_1, C_2	0	0
11.	A_{1g}	C_3	0	0
12.	A_{2g}	C_3	0	0
13.	B_{1g}	C_3	0	0
14.	B_{2g}	C_3	0	0
15.	E_g	C_3	$\alpha_1^3\alpha_2+\alpha_1^2\alpha_2^2+\alpha_1\alpha_2^3$	1
16.	A_{1u}	C_3	0	0
17.	A_{2u}	C_3	$\alpha_1^4+\alpha_1^3\alpha_2+2\alpha_1^2\alpha_2^2+\alpha_1\alpha_2^3+\alpha_2^4$	1
18.	B_{1u}	C_3	$\alpha_1^3\alpha_2+\alpha_1^2\alpha_2^2+\alpha_1\alpha_2^3$	1
10.	B_{2u}	C_3	$\alpha_1^2\alpha_2^2$	0
20.	E_u	C_3	0	0

finding Tr $T^W_{D_{4h}}$ with W being the weight restricted to C_i, with the following definition of P^χ_G. Let $\boldsymbol{d}_i$ denote a vector centered on the atom d_i perpendicular to the plane of the paper. Then define

$$P^\chi_G\,[C_j]=\frac{1}{|G|}\sum_{g\in G}\varepsilon_g\chi(g)\,x_1^{b_1}\,x_2^{b_2}\ldots$$

where

$$\varepsilon_g=\begin{cases}-1 & \text{if } g\boldsymbol{d}_i=-\boldsymbol{d}_k \text{ for some } k\\ 1 & \text{otherwise.}\end{cases}$$

$\boldsymbol{C}_j$ denotes the set of vectors centered on the nuclei in the class C_j. Now by Williamson's theorem

$$GF^{C_j}(\Gamma_i) = P_G^{\chi}[\boldsymbol{C}_j]\left(x_k \to \sum_l \alpha_l^k\right)$$

where $GF^{C_j}(\Gamma_i)$ denotes the generating function of irreducible representation Γ_i whose character is χ contained in the class C_j. Expressions thus obtained for all irreducible representations of D_{4h} and for each equivalence class are shown in Table 1. The coefficient of $\alpha_1^{m-1}\alpha_2$ in each expression, where $m = |C_j|$ gives the number of times the irreducible representation Γ_i occurs in the set C_j. They are indicated in the last column of Table 1. The complete generating function for all f's in F is shown in Table 1, even though for the present problem only the coefficient of $\alpha_1^{m-1}\alpha_2$ is significant. However, the other coefficients do have combinatorial significance *viz*, a typical coefficient $\alpha_1^{m_1}\alpha_2^{m_2}$ in the generating function which corresponds to the irreducible representation Γ and the class C_j represents the number of colorings of vectors with m_1 colors of the type 1 and m_2 colors of the type 2 that belong to the irreducible representation Γ and the class C_j. We also note the following results which can be proved in general, namely,

$$\sum_{i=1}^{n_G} \dim(\Gamma_i) GF^{C_j}(\Gamma_i) = (\alpha_1 + \alpha_2)^{|C_j|}$$

where $\dim(\Gamma_i)$ is the dimension of the irreducible representation Γ_i; n_G is the number of irreducible representations in G.

Now the projection operator which corresponds to each irreducible representation of p-orbitals is applied on that class. This yields an orthogonal set of symmetry adapted orbitals. The SALCs thus obtained for Porphindianion are shown in Table 2.

The results of Porphindianion are simple but sufficient for the sake of illustration. A nontrivial example would be that of polycyclic fully pericondensed compounds. A few of these served as illustrative examples elsewhere [10] (see Figs. 3 and 4). For these compounds the number of equivalence classes grows as l^2, where l is the number of layers (see Ref. [10]). For a compound containing 8 layers there are 36 equivalence classes as predicted by this method. The irreducible representations in each class can also be generated combinatorially.

In this paper we considered the combinatorics of symmetry adaptation. A method for enumerating the equivalence classes of nuclei under the action of molecular point group was expounded as a special case of the theorem presented here. Further, the generating functions for the irreducible representations contained in each class were obtained with a theorem of Williamson. The use of the present procedure for the enumeration of Gel'fand tableaux and the construction of symmetry-adapted spin functions will be the subject of a future paper [11]. The procedure developed here is especially useful in generating symmetry-adapted NMR spin functions. The usual method to obtain the classes and the symmetry species in each class would require the complete character table. However, the

Table 2. SALCs of Porphindianion

S. No.	Class	Irreducible representation	SALC
1.	{1, 2, 6, 7, 11, 12, 16, 17}	A_{2u}	$\frac{1}{\sqrt{8}}(\phi_1+\phi_2+\phi_6+\phi_7+\phi_{11}+\phi_{12}+\phi_{16}+\phi_{17})$
		A_{1u}	$\frac{1}{\sqrt{8}}(\phi_1-\phi_2+\phi_6-\phi_7+\phi_{11}-\phi_{12}+\phi_{16}-\phi_{17})$
		B_{1u}	$\frac{1}{\sqrt{8}}(\phi_1-\phi_2-\phi_6+\phi_7+\phi_{11}-\phi_{12}-\phi_{16}+\phi_{17})$
		B_{2u}	$\frac{1}{\sqrt{8}}(\phi_1+\phi_2-\phi_6-\phi_7+\phi_{11}+\phi_{12}-\phi_{16}-\phi_{17})$
		E_g	$\begin{cases}\frac{1}{2}(\phi_1+\phi_2-\phi_{11}-\phi_{12})\\ \frac{1}{2}(\phi_6+\phi_7-\phi_{16}-\phi_{17})\end{cases}$
		E_g	$\begin{cases}\frac{1}{2}(\phi_1-\phi_2-\phi_{11}+\phi_{12})\\ \frac{1}{2}(\phi_6-\phi_7-\phi_{16}+\phi_{17})\end{cases}$
2.	{3, 5, 8, 10, 13, 15, 18, 20}	A_{2u}	$\frac{1}{\sqrt{8}}(\phi_3+\phi_5+\phi_8+\phi_{10}+\phi_{13}+\phi_{15}+\phi_{18}+\phi_{20})$
		A_{1u}	$\frac{1}{\sqrt{8}}(\phi_3-\phi_5+\phi_8-\phi_{10}-\phi_{13}+\phi_{15}+\phi_{18}-\phi_{20})$
		B_{1u}	$\frac{1}{\sqrt{8}}(\phi_3+\phi_5-\phi_8-\phi_{10}+\phi_{13}+\phi_{15}-\phi_{18}-\phi_{20})$
		B_{2u}	$\frac{1}{\sqrt{8}}(\phi_3-\phi_5-\phi_8+\phi_{10}-\phi_{13}+\phi_{15}-\phi_{18}+\phi_{20})$
		E_g	$\begin{cases}\frac{1}{2}(\phi_3+\phi_5-\phi_{13}-\phi_{15})\\ \frac{1}{2}(\phi_8+\phi_{10}-\phi_{18}-\phi_{20})\end{cases}$
		E_g	$\begin{cases}\frac{1}{2}(\phi_3-\phi_5-\phi_{13}+\phi_{15})\\ \frac{1}{2}(\phi_8-\phi_{10}-\phi_{18}+\phi_{20})\end{cases}$
3.	{4, 9, 14, 19}	A_{2u}	$\frac{1}{2}(\phi_4+\phi_9+\phi_{14}+\phi_{19})$
		B_{1u}	$\frac{1}{2}(\phi_4-\phi_9-\phi_{14}+\phi_{19})$
		E_g	$\begin{cases}\frac{1}{\sqrt{2}}(\phi_4-\phi_{14})\\ \frac{1}{\sqrt{2}}(\phi_9-\phi_{19})\end{cases}$

method developed here can generate the symmetry species and classes without knowing the character tables of NMR groups (wreath products), for these generating functions can be generated combinatorially by knowing just the character tables of the composing groups of wreath products.

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