

# Partition of symmetric powers of $G$ -sets into orbits: application to the enumeration of force constants

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**Abstract** Using the theory of actions of groups on sets this paper describes an efficient method to obtain the partition of the symmetric powers of a  $G$ -set into orbits, where  $G$  is a finite group. In this method, a generating function is obtained for each representative of the conjugacy classes of subgroups of  $G$ . The coefficients of the generating function corresponding to a representative subgroup  $H \leq G$  give the number of orbits isomorphic to the coset  $G/H$  that are contained in the successive symmetric powers of the  $G$ -set. A direct application of this approach is the attainment of the number and isotropy group of the vibrational force constants associated with a set of internal coordinates for a given molecule. As illustration, the method has been applied to  $XYZ_3$  ( $C_{3v}$ ) molecules.

**Keywords** Enumeration of force constants · Group action · Burnside ring · Table of marks · Symmetric powers of  $G$ -sets

## 1 Introduction

Internal coordinates, such as changes in the bond lengths and in the angles between chemical bonds, provide a physically meaningful set of coordinates for the description of the potential energy of the molecule; in addition, the force constants associated with these coordinates have a direct physical interpretation [1]. For these reasons, a frequent task in vibrational spectroscopy is the enumeration of the force constants associated with a set of internal coordinates,  $X$ , for a given molecule. Two force constants are considered essentially the same if the molecular symmetry group,  $G$ , contains an ele-

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ment that transforms one of them into the other. In consequence, as will be seen later, there exists an isomorphism between the set of force constants of degree  $n$  and the set of orbits of the  $n$ th symmetric power of  $X$ ,  $S^n(X)$ ; hence the enumeration of the force constants of degree  $n$  reduces to the partition of  $S^n(X)$  into orbits. The most used method in vibrational spectroscopy is that of Watson [2]. In this method the number of orbits in  $S^n(X)$  is obtained as the number of times that the unit representation of  $G$  appears in the reduction of the representation  $\Gamma(S^n(X))$  spanned by  $S^n(X)$ . The disadvantages of this method are that it does not give information about the isotropy group of the force constants, the attainment of the characters for  $\Gamma(S^n(X))$  requires the use of a different formula for each value of  $n$ , and the calculation of these characters is very laborious in the case of high values of  $n$  and when the molecule has high symmetry. This method is widely employed by vibrational spectroscopists because of the widespread use of the representation theory in the study of molecular structure. A more efficient but less known method to obtain the number of force constants is provided by polynomial invariant theory [3,4]. In this approach the number of orbits in  $S^n(X)$  is given by the coefficient of  $t^n$  in the Molien series:

$$M(t) = \frac{1}{|G|} \sum_{g \in G} \frac{1}{\det(\Delta(e) - t\Delta(g))} = a_0 + a_1t + a_2t^2 + \dots$$

where  $|G|$  is the order of  $G$ ,  $\Delta$  is the matrix representation of  $G$  spanned by  $X$ , and  $e$  is the unit element of  $G$ . Techniques based on this theory have been developed to obtain algebraically independent invariant polynomials, which are useful in the description of the potential energy of the molecule [5–7].

This paper describes a new procedure for the enumeration of force constants which is based on the theory of actions of finite groups. This approach gives us the number of force constants of a given order associated to a given isotropy group. In contrast to the above methods, it does not require the use of the matrix representation generated by the set of internal coordinates, which is an advantage in the case of high symmetry groups.

## 2 Definitions and mathematical background

In order to fix the notation, we summarize some basic facts about the action of groups on sets. More details and proofs can be found in references [8–11].

Let  $G$  be a finite group acting on a set  $X = \{x, y, z, \dots\}$  with  $|X|$  elements. The action of  $G$  on  $X$  is given by a mapping  $G \times X \rightarrow X$  which sends each  $(g, x) \in G \times X$  to  $gx \in X$ , so that:

- 1)  $ex = x$  for all  $x \in X$
- 2)  $g(hx) = (gh)x$  for all  $g, h \in G$  and  $x \in X$

where  $e$  is the unit element of  $G$ .

The orbit of an element  $x \in X$  is the set  $\mathcal{O}(x) = Gx = \{gx : g \in G\}$ , and the isotropy group or stabilizer of  $x$  is the set  $G_x = \{g \in G : gx = x\}$ . For each  $x \in X$ ,  $G_x$

is a subgroup of  $G$ . The number of elements of the orbit  $\mathcal{O}(x)$  is:

$$|\mathcal{O}(x)| = |G : G_x| = |G|/|G_x|.$$

The set of stabilizers of the elements of  $\mathcal{O}(x)$  are conjugate subgroups. Thus, for each  $x \in X$  and  $g \in G$ ,  $G_{gx} = gG_xg^{-1} = \{ghg^{-1} : \text{for all } h \in G_x\}$ . The set  $X$  can be partitioned into orbits; thus, if we choose a representative  $x_i$  from every orbit, we have:

$$X = \bigcup_i \mathcal{O}(x_i) \quad (\text{disjoint union})$$

then the number of elements of  $X$  satisfies:

$$|X| = \sum_i |\mathcal{O}(x_i)|$$

Let  $H$  be a subgroup of  $G$  and  $g$  be any element of  $G$ . The left coset  $gH$  is defined as  $gH = \{gh : h \in H\}$ . The set of left cosets of  $H$  in  $G$ , denoted by  $G/H$ , is a  $G$ -set via left multiplication; i.e. given two elements  $g_1$  and  $g_2$  of  $G$ , the action of  $g_1$  on  $g_2H$  is defined as  $g_1(g_2H) = (g_1g_2)H$ . Under this  $G$ -action, the stabilizer of the coset  $gH$  is the subgroup  $gHg^{-1} = \{ghg^{-1} : h \in H\}$ , which is conjugate to  $H$ .

Given two subgroups  $H, K \leq G$ , the mark of  $H$  in  $G/K$  is defined as [11]:

$$M_{KH} = |(G/K)^H|$$

where

$$|(G/K)^H| = |\{gK : g \in G, h g K = g K \text{ for all } h \in H\}|$$

is the number of cosets of  $K$  whose stabilizer contains  $H$ . This mark can be also obtained using [12]:

$$M_{KH} = \frac{|N_G(H)|}{|K|} \nu(K, H)$$

where

$$N_G(H) = \{g \in G : gH = Hg\}$$

is the normalizer of  $H$ , and

$$\nu(K, H) = |\{gHg^{-1} : g \in G, gHg^{-1} \leq K\}|$$

is the number of subgroups of  $K$  which are conjugate to  $H$ .

The table of marks of  $G$  is the square matrix whose entries are  $M_{KH}$ , where both  $K$  and  $H$  range over representatives of the conjugacy classes of subgroups of  $G$ .

There exists an isomorphism between the orbit of  $x \in X$  and the set of cosets of  $G_x$ :  $\mathcal{O}(x) \cong G/G_x$ . Thus, the set  $X$  is isomorphic to an element of the Burnside ring of the group  $G$  [10–13]:

$$X \cong \sum_K a(X)_K G/K$$

where  $K$  ranges over representatives of the conjugacy classes of subgroups of  $G$  and  $a(X)_K$  is the number of orbits in  $X$  that are isomorphic to  $G/K$ . The coefficients  $a(X)_K$  can be obtained using:

$$a(X)_K = \sum_H B(G)_{HK} |X^H| \quad (1)$$

where  $|X^H|$  is the number of elements in  $X$  whose stabilizer is the subgroup  $H$  and  $B(G)_{HK}$  is the  $HK$  entry of the Burnside matrix which is the inverse of the table of marks.

### 3 Symmetric powers of $G$ -sets

Let  $\Phi(X, \mathbb{N})$  be the set of functions  $\phi : X \rightarrow \mathbb{N}$ , where  $\mathbb{N}$  is the set of natural numbers,  $\mathbb{N} = \{0, 1, 2, \dots\}$ . The elements of  $\Phi(X, \mathbb{N})$  are the monomial  $x^p y^q z^r \dots$ , where  $x, y, z, \dots \in X$ ;  $p, q, r, \dots \in \mathbb{N}$  and  $\phi(x) = p$ ,  $\phi(y) = q$ ,  $\phi(z) = r, \dots$ . The set  $\Phi(X, \mathbb{N})$  is a graded  $G$ -set that can be decomposed as:

$$\Phi(X, \mathbb{N}) = S^0(X) \cup S^1(X) \cup S^2(X) \cup \dots$$

where  $S^n(X)$  is the  $n$ th symmetric power<sup>1</sup> of  $X$  and contains the monomials of degree  $n$ :

$$S^n(X) = \{x^p y^q z^r \dots | p + q + r + \dots = n\}$$

For example, if  $X = \{x, y, z\}$  we have:

$$\begin{aligned} S^1(X) &= \{x, y, z\} \\ S^2(X) &= \{x^2, xy, xz, y^2, yz, z^2\} \\ S^3(X) &= \{x^3, x^2y, x^2z, xy^2, xyz, xz^2, y^3, y^2z, yz^2, z^3\} \\ &\dots \end{aligned}$$

<sup>1</sup> The  $n$ th symmetric power of  $X$  is also usually defined as the set of unordered  $n$ -tuples of elements of  $X$ .

The number of elements of  $S^n(X)$  is equal to the combinations with repetition of  $|X|$  elements taken from  $n$  in  $n$ :

$$|S^n(X)| = \frac{(|X| + n - 1)!}{(|X| - 1)!n!}$$

Given a subgroup  $H \leq G$ , let us define the power series:

$$f_H(t) = \sum_{n=0}^{\infty} |S^n(X)^H| t^n$$

where  $|S^n(X)^H|$  is the number of elements in  $S^n(X)$  whose stabilizer is  $H$ . It can be shown [14, 15] that:

$$f_H(t) = \frac{1}{(1 - t^{|X_1|})(1 - t^{|X_2|}) \dots} \tag{2}$$

where  $X = X_1 \cup X_2 \cup X_3 \cup \dots$  is the partition of  $X$  into  $H$ -orbits; thus, if  $x \in X_i$ , then  $X_i = \{hx : h \in H\}$ . According to the above,  $|S^n(X)^H|$  is the coefficient of  $t^n$  in the Maclaurin series for:

$$1 / \left( (1 - t^{|X_1|}) (1 - t^{|X_2|}) \dots \right)$$

From Eq. 1, the number of orbits in  $S^n(X)$  that are isomorphic to  $G/H$  is:

$$a(S^n(X))_K = \sum_{H \leq G} B_{HK} |S^n(X)^H|$$

which coincides with the coefficient of  $t^n$  in the power series of the function:

$$\Phi_K(t) = \sum_K B_{HK} f_H(t) \tag{3}$$

### 4 Force constants

Let us consider a molecule belonging to the symmetry group  $G$  whose vibrational motion is described by a symmetrically complete set of internal coordinates  $X = \{r_1, r_2, r_3, \dots\}$ . The force constants are obtained from the derivatives  $(\partial^n V(r_1, r_2, \dots) / \partial^p r_1 \partial^q r_2 \dots)_{\text{eq}}$ , where  $V(r_1, r_2, \dots)$  is the potential energy in terms of internal coordinates. Let us define the set:

$$F(X)^n = \left\{ f_{r_1^p r_2^q \dots} = \left( \frac{\partial^n V(r_1, r_2, \dots)}{\partial^p r_1 \partial^q r_2 \dots} \right)_{\text{eq}} : p + q + \dots = n \right\}$$

The action of  $G$  on the elements of  $F(X)^n$  is given by:

$$gf_{r_1^p r_2^q \dots} = \left( \frac{\partial^n (gV)}{\partial^p (gr_1) \partial^q (gr_2) \dots} \right)_{\text{eq}}$$

for any  $g \in G$ . The potential energy remains unchanged under the action of  $G$ , i.e.  $gV = V$ ; then

$$gf_{r_1^p r_2^q \dots} = f_{(gr_1)^p (gr_2)^q \dots}$$

Let us define a mapping  $\psi : F(X)^n \rightarrow S(X)^n$  as  $\psi(f_{r_1^p r_2^q \dots}) = r_1^p r_2^q \dots$ . This mapping is a bijection and satisfies:

$$g\psi \left( d_{r_1^p r_2^q \dots} \right) = g(r_1^p r_2^q \dots) = (gr_1)^p (gr_2)^q \dots = \psi \left( d_{(gr_1)^p (gr_2)^q \dots} \right) = \psi \left( gd_{r_1^p r_2^q \dots} \right)$$

Hence this bijection is an isomorphism between  $G$ -sets:  $F(X)^n \cong S(X)^n$

Due to the molecular symmetry, the values of the derivatives  $f_{r_1^p r_2^q \dots}$  remain unchanged under the action of  $G$ :  $gf_{r_1^p r_2^q \dots} = f_{r_1^p r_2^q \dots}$ ; this means that two derivatives are essentially distinct if they belong to different orbits of  $F(X)^n$ , hence we can associate a force constant to each orbit of  $F(X)^n$  and, due to the isomorphism  $F(X)^n \cong S(X)^n$ , to each orbit of  $S(X)^n$ . In consequence, the attainment of the number of force constants of degree  $n$  reduces to the calculation of the number of orbits in  $S(X)^n$ ; each of these orbits is isomorphic to a coset  $G/H$ , where  $H$  is the isotropy group of the corresponding force constant.

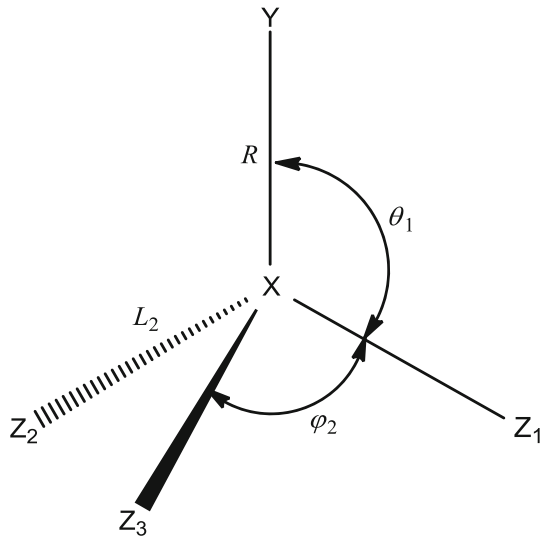
## 5 Application to $XYZ_3(C_{3v})$ molecules

The vibrational motion of a  $XYZ_3(C_{3v})$  molecule can be described by a set of ten internal coordinates [16]  $X = \{R, L_1, L_2, L_3, \vartheta_1, \vartheta_2, \vartheta_3, \varphi_1, \varphi_2, \varphi_3\}$ , where  $R$  and  $L_i$  are the  $X - Y$  and  $X - Z_i$  length bonds respectively,  $\vartheta_i$  is the  $Y - X - Z_i$  angle, and  $\varphi_i$  is the  $Z - X - Z$  angle opposite to the  $X - Z_i$  bond (see Fig. 1).

The  $C_{3v}$  symmetry group consists of the identity element  $e$ , two rotations  $C_3^1$  and  $C_3^2$  around the  $X - Y$  bond, and three reflections  $\sigma_1, \sigma_2$  and  $\sigma_3$  on the planes defined by the atoms  $Y - X - Z_1, Y - X - Z_2$  and  $Y - X - Z_3$  respectively. The subgroups of  $C_{3v}$  are the following:

$$\begin{aligned} C_1 &= \{e\} \\ C_3 &= \{e, C_3^1, C_3^2\} \\ C_s(1) &= \{e, \sigma_1\} \\ C_s(2) &= \{e, \sigma_2\} \\ C_s(3) &= \{e, \sigma_3\} \\ C_{3v} &= \{e, C_3^1, C_3^2, \sigma_1, \sigma_2, \sigma_3\} \end{aligned}$$

**Fig. 1** Internal coordinates for the  $XYZ_3(C_{3v})$  molecule



**Table 1** Table of marks of the group  $C_{3v}$

	$C_1$	$C_s$	$C_3$	$C_{3v}$
$C_{3v}/C_1$	6	0	0	0
$C_{3v}/C_s$	3	1	0	0
$C_{3v}/C_3$	2	0	2	0
$C_{3v}/C_{3v}$	1	1	1	1

**Table 2** Burnside matrix of the group  $C_{3v}$

	$C_{3v}/C_1$	$C_{3v}/C_s$	$C_{3v}/C_3$	$C_{3v}/C_{3v}$
$C_1$	1/6	0	0	0
$C_s$	-1/2	1	0	0
$C_3$	-1/6	0	1/2	0
$C_{3v}$	1/2	-1	-1/2	1

where  $C_s(1)$ ,  $C_s(2)$  and  $C_s(3)$  are conjugate subgroup.

The table of marks and the Burnside matrix of the group  $C_{3v}$  are shown in Tables 1 and 2 respectively.

**Table 3** Partitions of  $X$  into  $H$ -orbits

Subgroup	Partition
$C_{3v}$	$X = \{R\} \cup \{L_1, L_2, L_3\} \cup \{\vartheta_1, \vartheta_2, \vartheta_3\} \cup \{\varphi_1, \varphi_2, \varphi_3\}$
$C_3$	$X = \{R\} \cup \{L_1, L_2, L_3\} \cup \{\vartheta_1, \vartheta_2, \vartheta_3\} \cup \{\varphi_1, \varphi_2, \varphi_3\}$
$C_s(1)$	$X = \{R\} \cup \{L_1\} \cup \{L_2, L_3\} \cup \{\vartheta_1\} \cup \{\vartheta_2, \vartheta_3\} \cup \{\varphi_1\} \cup \{\varphi_2, \varphi_3\}$
$C_1$	$X = \{R\} \cup \{L_1\} \cup \{L_2\} \cup \{L_3\} \cup \{\vartheta_1\} \cup \{\vartheta_2\} \cup \{\vartheta_3\} \cup \{\varphi_1\} \cup \{\varphi_2\} \cup \{\varphi_3\}$

The partitions of  $X$  into  $H$ -orbits are shown in Table 3. According to these partitions, Eq. 2 gives the following functions  $f_H(t)$ :

$$f_{C_{3v}}(t) = \frac{1}{(1-t)(1-t^3)^3}$$

$$f_{C_3}(t) = \frac{1}{(1-t)(1-t^3)^3}$$

$$f_{C_s}(t) = \frac{1}{(1-t)^4(1-t^2)^3}$$

$$f_{C_1}(t) = \frac{1}{(1-t)^{10}}$$

The substitution of the above expressions and the coefficients of Table 2 into Eq. 3 gives:

$$\Phi(C_{3v}) = 1 + t + t^2 + 4t^3 + 4t^4 + 4t^5 + 10t^6 + 10t^7 + 10t^8 + 20t^9 + \dots$$

$$\Phi(C_3) = 0$$

$$\Phi(C_s) = 3t + 12t^2 + 28t^3 + 67t^4 + 136t^5 + 249t^6 + 438t^7 + 732t^8 + 1156t^9 + \dots$$

$$\Phi(C_1) = 3t^2 + 22t^3 + 85t^4 + 265t^5 + 708t^6 + 1686t^7 + 3684t^8 + 7522t^9 + \dots$$

According to the above, the partitions into orbits of the sets  $S^n(X)$  are:

$$S^1(X) = (C_{3v}/C_{3v}) + 3(C_{3v}/C_s)$$

$$S^2(X) = (C_{3v}/C_{3v}) + 12(C_{3v}/C_s) + 3(C_{3v}/C_1)$$

$$S^3(X) = 4(C_{3v}/C_{3v}) + 28(C_{3v}/C_s) + 22(C_{3v}/C_1)$$

$$S^4(X) = 4(C_{3v}/C_{3v}) + 67(C_{3v}/C_s) + 85(C_{3v}/C_1)$$

$$S^5(X) = 4(C_{3v}/C_{3v}) + 136(C_{3v}/C_s) + 265(C_{3v}/C_1)$$

$$S^6(X) = 10(C_{3v}/C_{3v}) + 249(C_{3v}/C_s) + 708(C_{3v}/C_1)$$

$$S^7(X) = 10(C_{3v}/C_{3v}) + 438(C_{3v}/C_s) + 1686(C_{3v}/C_1)$$

$$S^8(X) = 10(C_{3v}/C_{3v}) + 732(C_{3v}/C_s) + 3684(C_{3v}/C_1)$$

$$S^9(X) = 20(C_{3v}/C_{3v}) + 1156(C_{3v}/C_s) + 7522(C_{3v}/C_1)$$

$$\dots$$



Thus we obtain that, for example, the molecule has  $4 + 67 + 85 (= 156)$  quartic force constants whose stabilizers are  $C_{3v}$ ,  $C_s$  and  $C_1$  respectively.

The above results are consistent with those obtained using the Molien series, which in our example is given by:

$$\begin{aligned} M(t) &= \frac{1 + 3t^2 + 7t^3 + 6t^4 + 6t^5 + 10t^6 + 3t^7}{(1-t)^4(1-t^2)^3(1-t^3)^3} \\ &= 1 + 4t + 16t^2 + 54t^3 + 156t^4 + 405t^5 + 967t^6 + 2134t^7 \\ &\quad + 4426t^8 + 8698t^9 + \dots \end{aligned}$$

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