

## On Two Methods for Computing the Non-Rigid Group of Molecules

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**ABSTRACT.** In this paper, two methods are described, by means of which it is possible to calculate the non rigid group of molecules consisting of a number of  $XH_3$  groups attached to a rigid framework. The first method is a combination of the wreath product formalism of Balasubramanian and modern computer algebra and the second method is a computational approach by using group theory package GAP. We apply these methods on 2,3,6,7,10,11-hexanitrotriphenylene (HNT) to compute its non-rigid group.

**Keywords:** Non-rigid group, the Computer Algebra System GAP, Character table, HNT.

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### 1. INTRODUCTION

A rigid molecule is defined as being such that the barriers between its versions are insuperable and there are no observable tunneling splittings. For non-rigid molecules, there are one or more contortional large amplitude vibrations such as

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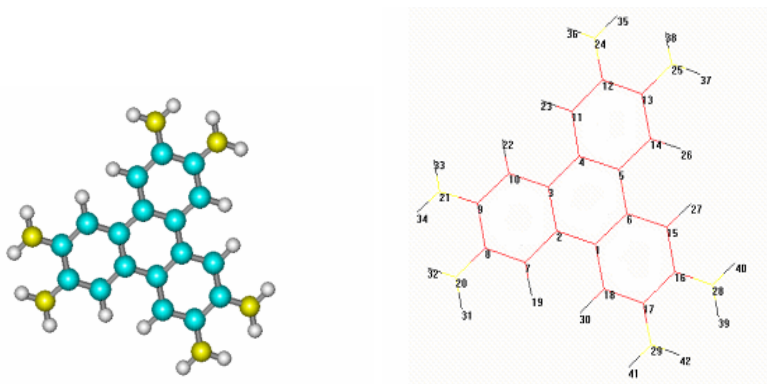
inversion or internal rotation that give rise to tunneling splittings. Because of this deformability, the non-rigid molecules exhibit some interesting properties of intramolecular dynamics which can be studied more easily resorting to group theory.

Following Y.G. Smeyers [23], the non-rigid molecule group (NRG) will be strictly defined as the complete set of the molecular conversion operations, which commute with a given nuclear Hamiltonian operator, limited to large amplitude motions. In addition, these molecular conversion operations will be expressed in terms of physical operations, such as rotations, internal rotations, inversions, similarly as in the Altmann's theory, rather than in terms of permutations and permutations-inversions [24 and 25].

The molecular symmetry group is first defined by Longuet-Higgins [21]. Although there have been earlier works that suggested the need for such a framework. Bunker and Papouek extended the definition of the molecular symmetry group to linear molecules using an extended molecular symmetry.

Computing the NRGs using wreath product formalism was first introduced by Balasubramanian [6]. He then found some methods for computing the character table of wreath product of groups and applied his method to solve some problems related to the enumeration of molecules.

The present authors [1-4,7-16 and 19], applied the Computer Algebra System GAP [22] to find symmetry and non-rigid group of some molecules. Here, we combine wreath product formalism of Balasubramanian and a computational method to obtain a powerful method for computing non-rigid group of molecules. We apply this method on 2,3,6,7,10,11-hexanitrotriphenylene (HNT), Fig. 1. Then we apply another method for computing NRG of HNT. It is shown that the non-rigid group of this molecule has order 384 with 28 conjugacy classes and so irreducible characters. The character table of HNT is also computed. The notation we use is standard and the reader may consult references [20 and 26]. The non-rigid group theory also finds applications in the enumeration of isomers [5] and substituted aromatics [17 and 18].



**Figure 1.** Two Different Models for the Geometry of HNT

## 2. RESULTS AND DISCUSSION

In this section we first describe some notation which will be kept throughout. Suppose  $X$  is a set. The set of all permutations on  $X$ , denoted by  $SX$ , is a group which is called the symmetric group on  $X$ . In the case that,  $X = \{1, 2, \dots, n\}$ , we denote  $SX$  by  $S_n$  or  $\text{Sym}(n)$ . Also, for a group  $G$  and a subset  $A$  of  $G$ ,  $\langle A \rangle$  is the subgroup of  $G$  generated by  $A$ .

Let  $H$  be a subgroup of  $SX$ , i.e., a permutation group on  $X$ , and let  $G$  be a group. The set of all mappings  $X \rightarrow G$  is denoted by  $G^X$ , i.e.  $G^X = \{f \mid f : X \rightarrow G\}$ . It is clear that  $|G^X| = |G|^{|X|}$ . We put  $G \wr H = G^X \times H = \{(f; \pi) \mid f \in G^X, \pi \in H\}$ . For  $f \in G^X$  and  $\pi \in H$ , we define  $f\pi \in G^X$  by  $f\pi = f \circ \pi^{-1}$ , where “ $\circ$ ” denotes the composition of functions. It is easy to check that the following law of composition:

$$(f; \pi) (f'; \pi') = (ff'; \pi \pi'),$$

makes  $G \wr H$  into a group. This group is called the wreath product of  $G$  by  $H$ .

### 2.1. Computing Non Rigid Group of HNT Using Wreath Product.

In this section, the non-rigid group of HNT molecule is computed using wreath product formalism. Before going into the details of the computations of hexanitrotripheny, we should mention that we consider the speed of rotations of nitro groups sufficiently high so that the mean time dynamical symmetry of the molecules makes sense. In order to characterize the NRG of HNT, we first note that each dynamic symmetry operation of hexanitrotripheny, considering the rotations of  $NO_2$  groups, is composed of two sequential physical operations. We first have a physical symmetry of the framework (as we have to map the  $NO_2$  groups on  $NO_2$  groups which are on vertices of the framework). Such operations form the group  $H$  of order 6, which as is well known, is isomorphic to  $S_3$  or  $\text{Sym}(3)$ , the group of permutations on three distinct symbols. After

accomplishing the first framework symmetry operation we have to map each of the six  $NO_2$  group on itself which forms the two element group  $C_2$ . The number of all such operations is  $26 \times 6 = 384$ .

Let's use numbers  $\{1,2,3,4,5,6\}$  to indicate the central carbon atoms. Then  $H = \{(), (1,2)(3,6)(4,5), (1,3,5)(2,4,6), (1,4)(2,3)(5,6), (1,5,3)(2,6,4), (1,6)(2,5)(3,4)\}$  is the symmetry group of rigid framework and the NRG group of HNT is of the form  $G = C_2 \wr H$ , which is a group of order 384. It is shown by Balasubramanian [6] that the conjugacy classes of such a group can be obtained by the matrix types and its character table can also be generated using the matrix generator. We now apply GAP to obtain the conjugacy classes and character table of the group  $G$ , Tables 1 and 2.

## 2.2. Computing Non Rigid Group of HNT Using Computer Algebra System GAP.

In this section we apply a computational approach to compute the non-rigid group of HNT. To do this, we consider the point group of hexanitrotripheny in the case of rigid framework. From Fig. 1, it is clear that the following permutations are elements of non-rigid group of HNT:

$$\alpha_1 := (1, 3, 5)(2, 4, 6)(7, 11, 15)(10, 14, 18)(8, 12, 16)(9, 13, 17)(20, 24, 28)(21, 25, 29) \\ (31, 36, 40)(32, 35, 39)(33, 37, 41)(34, 38, 42)(19, 23, 27)(22, 26, 30),$$

$$\beta_1 := (1, 3, 5)(2, 4, 6)(7, 11, 15)(10, 14, 18)(8, 12, 16)(9, 13, 17)(20, 24, 28)(21, 25, 29) \\ (31, 36, 40, 32, 35, 39)(33, 37, 41, 34, 38, 42)(19, 23, 27)(22, 26, 30),$$

$$\alpha_2 := (1, 2)(3, 6)(4, 5)(7, 18)(8, 17)(9, 16)(10, 15)(11, 14)(12, 13)(23, 26)(27, 22)(19, 30) \\ (20, 29)(21, 28)(24, 25)(31, 41)(32, 42)(34, 39)(33, 40)(36, 37)(35, 38),$$

$$\beta_2 := (1, 2)(3, 6)(4, 5)(7, 18)(8, 17)(9, 16)(10, 15)(11, 14)(12, 13)(23, 26)(27, 22)(19, 30) \\ (20, 29)(21, 28)(24, 25)(31, 41, 32, 42)(34, 39, 33, 40)(36, 37, 35, 38).$$

Suppose  $H = \langle \alpha_1, \alpha_2 \rangle$  and  $G = \langle \alpha_1, \alpha_2, \beta_1, \beta_2 \rangle$  are groups generated by  $A = \{\alpha_1, \alpha_2\}$  and  $B = \{\alpha_1, \alpha_2, \beta_1, \beta_2\}$ , respectively. Obviously,  $H$  is the symmetry group of rigid framework and has order six. Since  $H$  is not abelian, it

is isomorphic to the symmetric group  $S_3$ . On the other hand, the NRG group  $G$  of HNT is generated by the generating set  $A$  of  $H$  and permutations of the non-rigid group of HNT related to  $\alpha_1$  and  $\alpha_2$ . Therefore  $G = \langle B \rangle$  is NRG group of HNT.

There are several methods for computing the character table of permutation groups. It is interesting to notice that small group library of GAP contains all groups of order  $\leq 2000$ , except from 1024. So we can apply GAP to find the conjugacy classes and character table of the group  $G$ , Tables 1 and 2. Our calculations with GAP shows that this group has 28 conjugacy classes and so irreducible characters. In Table 2,  $n_x$  denotes a conjugacy class of elements of order  $n$  in  $G$  and,  $A = -i\sqrt{3}$ .

**Table 1.** Conjugacy Classes of the Group  $G$

<i>No.</i>	<i>Representatives</i>	<i>Sizes</i>
1	( e, e, e, e, e, e, () )	1
2	( e, e, e, e, e, e, (1,2)(3,6)(4,5) )	24
3	( e, e, e, e, e, e, (1,3,5)(2,4,6) )	32
4	( e, e, e, e, e, f, () )	6
5	( e, e, e, e, e, f, (1,2)(3,6)(4,5) )	24
6	( e, e, e, e, e, f, (1,3,5)(2,4,6) )	32
7	( e, e, e, e, e, f, (1,4)(2,3)(5,6) )	24
8	( e, e, e, e, e, f, (1,5,3)(2,6,4) )	32
9	( e, e, e, e, e, f, (1,6)(2,5)(3,4) )	24
10	( e, e, e, e, f, f, () )	3
11	( e, e, e, e, f, f, (1,2)(3,6)(4,5) )	24
12	( e, e, e, e, f, f, (1,3,5)(2,4,6) )	32
13	( e, e, e, f, e, f, () )	6
14	( e, e, e, f, e, f, (1,4)(2,3)(5,6) )	24
15	( e, e, e, f, e, f, (1,6)(2,5)(3,4) )	24
16	( e, e, e, f, f, e, () )	3
17	( e, e, e, f, f, f, () )	6
18	( e, e, e, f, f, f, (1,6)(2,5)(3,4) )	24
19	( e, e, f, e, e, f, () )	3
20	( e, e, f, e, f, f, () )	6
21	( e, e, f, f, f, f, () )	3
22	( e, f, e, f, e, f, () )	2
23	( e, f, e, f, f, e, () )	6
24	( e, f, e, f, f, f, () )	6
25	( e, f, f, e, f, f, () )	3
26	( e, f, f, f, f, e, () )	3
27	( e, f, f, f, f, f, () )	6
28	( f, f, f, f, f, f, () )	1

## 3. CONCLUDING REMARKS

The small group library of GAP contains the structure and character table of all groups with order  $\leq 2000$  except from 1024, groups of order 55, 74 and groups of orders  $p^2q$  and  $pqr$ , where  $p$ ,  $q$  and  $r$  are primes. Thus GAP is very useful for research and education in chemistry.

Our discussion in Section 2.3 shows that it is reasonable to accept the universe is infinite. We have several examples which show that the symmetry group of a molecule is depended critically to our accuracy in computing the Cartesian coordinates of atoms in the molecule under consideration.

**Table 2.** The Character Table of the Group G

	1a	2a	2b	2c	2d	2e	2f	2g	2h	2i	2j	2k	2l	2m	2n	2o	2p	4a
$\chi_1$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\chi_2$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-1
$\chi_3$	1	-1	1	1	1	-1	1	-1	1	-1	-1	1	1	1	-1	1	1	-1
$\chi_4$	1	-1	1	1	1	-1	1	-1	1	-1	-1	1	1	1	-1	1	-1	1
$\chi_5$	2	-2	2	2	2	-2	2	-2	2	-2	2	2	2	2	-2	2	0	0
$\chi_6$	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	0	0
$\chi_7$	2	0	-2	2	-2	0	-2	0	2	0	0	-2	2	2	0	-2	0	0
$\chi_8$	2	0	-2	2	-2	0	-2	0	2	0	0	-2	2	2	0	-2	0	0
$\chi_9$	2	0	-2	2	-2	0	-2	0	2	0	0	-2	2	2	0	-2	0	0
$\chi_{10}$	3	-1	3	-1	-1	-1	-1	-1	3	3	3	-1	-1	-1	-1	3	-1	1
$\chi_{11}$	3	-1	3	-1	-1	-1	-1	-1	3	3	3	-1	-1	-1	-1	3	1	-1
$\chi_{12}$	3	1	3	-1	-1	1	-1	1	3	-3	-3	-1	-1	-1	1	3	-1	-1
$\chi_{13}$	3	1	3	-1	-1	1	-1	1	3	-3	-3	-1	-1	-1	1	3	1	1
$\chi_{14}$	3	-1	-1	-1	-1	3	3	-1	-1	3	-1	-1	3	-1	-1	3	-1	1
$\chi_{15}$	3	-1	-1	-1	-1	3	3	-1	-1	3	-1	-1	3	-1	-1	3	1	-1
$\chi_{16}$	3	-1	-1	-1	3	-1	-1	3	-1	3	-1	-1	-1	3	-1	3	-1	-1
$\chi_{17}$	3	-1	-1	-1	3	-1	-1	3	-1	3	-1	-1	-1	3	-1	3	1	1
$\chi_{18}$	3	1	-1	-1	-1	-3	3	1	-1	-3	1	-1	3	-1	1	3	-1	-1
$\chi_{19}$	3	1	-1	-1	-1	-3	3	1	-1	-3	1	-1	3	-1	1	3	1	1
$\chi_{20}$	3	1	-1	-1	3	1	-1	-3	-1	-3	1	-1	-1	3	1	3	-1	1
$\chi_{21}$	3	1	-1	-1	3	1	-1	-3	-1	-3	1	-1	-1	3	1	3	1	-1
$\chi_{22}$	6	-4	2	2	2	0	2	0	-2	0	0	-2	-2	-2	4	-6	0	0
$\chi_{23}$	6	4	2	2	2	0	2	0	-2	0	0	-2	-2	-2	-4	-6	0	0
$\chi_{24}$	6	-2	-2	2	-2	2	-2	2	-2	-6	2	2	-2	-2	-2	6	0	0
$\chi_{25}$	6	2	-2	2	-2	-2	-2	-2	-2	6	-2	2	-2	-2	2	6	0	0
$\chi_{26}$	6	0	2	-2	-6	0	2	0	-2	0	0	2	-2	6	0	-6	0	0
$\chi_{27}$	6	0	2	-2	2	0	-6	0	-2	0	0	2	6	-2	0	-6	0	0
$\chi_{28}$	6	0	-6	-2	2	0	2	0	6	0	0	2	-2	-2	0	-6	0	0

## Continue of Table 2.

	4b	4c	4d	4e	4f	4g	3a	6a	6b	6c
$\chi_1$	1	1	1	1	1	1	1	1	1	1
$\chi_2$	-1	-1	-1	-1	-1	-1	1	1	1	1
$\chi_3$	-1	1	-1	1	1	-1	1	-1	-1	1
$\chi_4$	1	-1	1	-1	-1	1	1	-1	-1	1
$\chi_5$	0	0	0	0	0	0	-1	1	1	-1
$\chi_6$	0	0	0	0	0	0	-1	-1	-1	-1
$\chi_7$	0	0	0	0	0	0	2	0	0	-2
$\chi_8$	0	0	0	0	0	0	-1	A	-A	1
$\chi_9$	0	0	0	0	0	0	-1	-A	A	1
$\chi_{10}$	1	-1	-1	1	1	-1	0	0	0	0
$\chi_{11}$	-1	1	1	-1	-1	1	0	0	0	0
$\chi_{12}$	-1	-1	1	1	1	1	0	0	0	0
$\chi_{13}$	1	1	-1	-1	-1	-1	0	0	0	0
$\chi_{14}$	-1	1	1	-1	1	-1	0	0	0	0
$\chi_{15}$	1	-1	-1	1	-1	1	0	0	0	0
$\chi_{16}$	1	1	1	1	-1	-1	0	0	0	0
$\chi_{17}$	-1	-1	-1	-1	1	1	0	0	0	0
$\chi_{18}$	1	1	-1	-1	1	1	0	0	0	0
$\chi_{19}$	-1	-1	1	1	-1	-1	0	0	0	0
$\chi_{20}$	-1	1	-1	1	-1	1	0	0	0	0
$\chi_{21}$	1	-1	1	-1	1	-1	0	0	0	0
$\chi_{22}$	0	0	0	0	0	0	0	0	0	0
$\chi_{23}$	0	0	0	0	0	0	0	0	0	0
$\chi_{24}$	0	0	0	0	0	0	0	0	0	0
$\chi_{25}$	0	0	0	0	0	0	0	0	0	0
$\chi_{26}$	0	0	0	0	0	0	0	0	0	0
$\chi_{27}$	0	0	0	0	0	0	0	0	0	0
$\chi_{28}$	0	0	0	0	0	0	0	0	0	0

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