Computer Generation of the Symmetry Elements of Nonrigid Molecules

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Algorithms and computer programs are developed for generating the symmetry elements of nonrigid molecules. These programs are based on the wreath product formalism for the symmetry groups of nonrigid molecules developed by the present author. Several examples are given to illustrate the procedures. Applications to weakly bound van der Waal complexes synthesized by supersonic beam expansion are also presented.

I. INTRODUCTION

The symmetry groups of nonrigid molecules contain permutation and inversion operations (PI operations) induced by large-amplitude motions. This permutation–inversion group approach to describe the symmetry of nonrigid molecules was essentially formulated by Longuet-Higgins. Since this formulation, several other authors have developed equivalent formulations. The present author has shown that the symmetry groups of molecules that exhibit internal rotations can be represented by wreath product groups or in general, generalized wreath product groups. The symmetry groups of nonrigid molecules have several applications in chemical physics. A review of these applications can be found in the author's article and several other articles that appear in ref. 13.

The symmetry of permutation processes in nonrigid molecules can be represented by associated diagrams known as isomerization graphs. Randić, Randić and Klein, and Balaban studied the symmetry properties of these graphs. The symmetry groups of some of these graphs are wreath product groups. For example, the symmetry group of the isomerization graph of propane is a generalized wreath product group as recently shown by Randić. A computer program to generate the symmetry elements of these groups will be of great use in understanding these permutation processes.

The number of symmetry elements of nonrigid molecules increases in an exponential order, the exponent being the number of internal rotors in the molecule. Even a simple nonrigid molecule like isobutane has 162 symmetry elements. Therefore, it will be advantageous to have a computer program that will generate the symmetry elements of nonrigid molecules. We develop a computer program which generates the symmetry elements of nonrigid molecules (with symmetry groups that can be embedded into wreath products) from the symmetry groups of much smaller orders. For example, the symmetry group of isobutane can be generated by this program using the symmetry elements of the group. The wreath product groups have several elegant applications to nuclear magnetic resonance (NMR) spectroscopy, nuclear spin statistics, symmetry of chemical graphs, configuration interaction (CI) calculations, etc. For these reasons we undertake the present investigation.

Section II describes the basic algorithm, computer programs, and illustrative examples. Section III gives applications, such as application to symmetry groups of weakly bound van der Waal complexes generated by supersonic molecular beam expansion.

II. COMPUTER GENERATION OF THE SYMMETRY ELEMENTS OF NONRIGID MOLECULES

A. Preliminaries and Definitions

Before we consider computer algorithms, we will first review our formulation of the symmetry
Symmetry Elements of Nonrigid Molecules

Consider the nonrigid hydrazine molecule. This molecule is nonrigid in that at room temperature the protons of each nitrogen atom are rapidly permuted by a twisting operation. This nonrigid molecule can be modeled by a particle-in-box model as shown in Figure 1. The protons attached to each nitrogen atom can be thought of as particles in a box. The particles in each box can be permuted by the twisting operation. The boxes can also be permuted as a consequence of the symmetry of the rigid molecule. The resulting operations generated by switching the particles and boxes are shown in Figure 1. Suppose $G$ to be the permutation group of boxes and $H$ the permutation group of particles in each box; then the permutation group of all the particles and boxes is simply the wreath product of $G$ and $H$, denoted as $G \wr H$. It is formally defined as follows. Let $Q$ be the set $\{1, 2, \ldots, n\}$, the number of elements in the set $Q$. In this article we develop computer programs which generate the symmetry elements of nonrigid molecules using the wreath product formalism.

Figure 1. Particle-in-box model for hydrazine. The permutation group of the nonrigid molecule is a wreath product of the permutation group of boxes ($S_2$) with the permutation group of particles in a box ($S_2$).

Groups of nonrigid molecules as generalized wreath product groups. The present author showed that the symmetry groups of nonrigid molecules exhibiting internal rotation are expressible as wreath product groups.

The map $\pi_{2g_1}$ is defined as follows

$$\pi_{2g_1}(i) = \pi_2(g_1^{-1}i), \quad i \in \Omega$$

It can be shown that the above set forms a group, called the wreath product of $G$ and $H$. For the hydrazine molecule, $G$ and $H$ are both the symmetric group $S_2$ so that the permutation group of the nonrigid molecule is $S_2 \wr S_2$. Several illustrative examples of wreath product groups can be found elsewhere.

Let $H_i$ be the group defined as follows.

$$H_i = \{(e;\pi) | \pi(j) = 1H, \quad j \neq i\}$$

where $1H$ is the identity of $H$. Note that $H_i$ is isomorphic to $H$. Let $G'$ be the group defined as follows.

$$G' = \{(g;e') | e'(j) = 1H, \quad \forall j\}$$

Then the wreath product of $G[H]$ has the following permutation representation.

$$G[H] = (H_1 \times H_2 \times \cdots \times H_n)G'$$

where $n = |\Omega|$, the number of elements in the set $\Omega$. In this article we develop computer programs which generate the symmetry elements of nonrigid molecules using the wreath product formalism.

We will use the following notation for a permutation. Any permutation of $n$ objects is characterized by a $2 \times n$ matrix such that the first row contains the elements $1, 2, \ldots, n$ in their natural position, and the second row contains the elements to which they are permuted. To illustrate, the permutation $(123)$ takes the following form.
An element $i$ in the first row goes to the element $P(i)$ in the second row. We will use the right-to-left multiplication convention. For example, the product of (123) and (12) is shown below in this convention.

\[
\begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix}
\]

For the sake of convenience, we will omit the first row in which the column $j$ is always $j$. For example, the permutation (123) can simply be denoted as 231.

**B. Algorithms**

This section outlines the basic algorithms used to generate the symmetry elements of nonrigid molecules. First we describe the algorithm PROPER which generates the product of $m$ permutations of the same length $n$. Let $\{P_{ij}\} \ (j = 1, m; i = 1, n)$ be the set of $m$ permutations.

**Algorithm PROPER:**

Initialize: $N_i \leftarrow i$, for $i = 1, n$.

\[
\begin{align*}
& \text{for } j = 1, m \text{ DO} \\
& \quad \text{for } i = 1, n \text{ DO} \\
& \quad \quad k \leftarrow P_{ij} \\
& \quad \quad q_i \leftarrow N_k \\
& \quad \text{for } i = 1, n \text{ DO} \\
& \quad \quad N_i \leftarrow q_i \\
& \end{align*}
\]

The final array $(q_i)(i = 1, n)$ obtained after the execution of the algorithm gives the permutation which is the product of $m$ permutations in the array $\{(P_{ij})\}$.

We will now illustrate this algorithm with an example of the product of two permutations, 231 and 213, used in an earlier example. Thus $m$ and $n$ are 2 and 3, respectively. The array $N$ is initialized to 123. With this value the various steps of the algorithm are now executed.

**P1:** $j = 1$

\[
\begin{align*}
& i = 1, k = P_{11} = 2, q_1 = N_2 = 2 \\
& i = 2, k = P_{21} = 3, q_2 = N_3 = 3 \\
& i = 3, k = P_{31} = 1, q_3 = N_1 = 1 \\
& N_1 = q_1 = 2, N_2 = q_2 = 3, N_3 = q_3 = 1 \\
& \end{align*}
\]

The final result is contained in the array $(q)$ which is 321. Thus the product of two permutations 231 and 213 is 321. In cycle notation, this corresponds to $(123)(12)(3) = (13)(2)$.

Now we describe the algorithm WREATH which generates the elements of the symmetry group of the nonrigid molecule. Let $G$ and $H$ be the groups whose wreath product $G[H]$ is under consideration. Let $G$ act on $\Omega$, and $H$ act on $T$. Let $h_{ij}$ and $g_{ij}$ be the permutations of $G$ and $H$. Let $|S|$ denote the number of elements in the set $S$. Let $n$ be the total number of nuclei in the molecule.

\[
\begin{align*}
& \text{for } k = 1, |G|, \text{ DO} \\
& \quad \text{for } j \in [\Omega], |G|, \text{ DO} \\
& \quad \quad \text{for } i \in [\Omega], |H|, \text{ DO} \\
& \quad \quad \quad \text{for } i = 1, n \text{ DO} \\
& \quad \quad \quad \quad f \leftarrow (i - 1)!|T| + 1 \\
& \quad \quad \quad \quad t \leftarrow (f - 1) T \\
& \quad \quad \quad \quad ik \leftarrow l - t \\
& \quad \quad \quad \quad P_{il} \leftarrow h_{ik,if} + t \\
& \quad \quad \text{CALL PROPER} \\
& \text{for } i = 1, n \text{ DO} \\
& \quad P_{11} \leftarrow q_i \\
& \quad P_{12} \leftarrow g_{ik} \\
& \quad \text{CALL PROPER} \\
& \text{PRINT } (q_i, i = 1, n)
\end{align*}
\]
Symmetry Elements of Nonrigid Molecules

Table I. Computer program for the symmetry elements of nonrigid molecules.

```
*DECK WREATH
PROGRAM WREATH(INPUT, OUTPUT, TAPES=INPUT, TAPE=OUTPUT)
INTEGER PG(100, 50), PH(100, 100), P(100, 13), INV(100), PRO(1000), JL(1C)
C, TITLE(10)
READ(5, 80) TITLE(I), I=1, 10
WRITE(6, 90) TITLE(I), I=1, 10
FORMAT(10)
WRITE(6, 81)
FORMAT(8X, *NG, *X, *PI OPERATIONS*)
READ(5, 90) N, MOD, MODT, MODG, MODD
FORMAT(20)
READ(5, 93) (PG(I, J), I=1, N), J=1, MODG
READ(5, 92) (INV(I), I=1, MODG)
READ(5, 90) ((PH(I, J), I=1, MODG), J=1, MODD)
DO 700 II=1, 10
700 JL(II)=1
DO 850 J=1, MODCM
850 JL(J)=MODCM
JL(10)=JL(10) SJL9=JL(9) SJL8=JL(8) SJL7=JL(7) SJL6=JL(6) SJL5=JL(5)
JL4=JL(4) SJL3=JL(3) SJL2=JL(2) SJL1=JL(1)
IND=0
DO 200 K=1, MODG
DO 100 J10=1, JL10
DO 100 J9=1, JL9
DO 100 J8=1, JL8
DO 100 J7=1, JL7
DO 100 J6=1, JL6
DO 100 J5=1, JL5
DO 100 J4=1, JL4
DO 100 J3=1, JL3
DO 100 J2=1, JL2
DO 100 J1=1, JL1
DO 800 J=1, MODCM
DO 800 I=1, N
30) P(I, J)=1
DO 50 I1=1, N
IFACT=I-I+1/MOD*(I
IT=(IFACT-I)*MOD
IK=I-IT
GO TO 21, 22, 23, 24, 25, 26, 27, 28, 29, 30 IFACT
21 P(I, IFACT)=PH(IK, JL)+IT
GO TO 50
22 P(I1, IFACT)=PH(IK, J2)+IT
GO TO 50
23 P(I1, IFACT)=PH(IK, J3)+IT
GO TO 50
24 P(I1, IFACT)=PH(IK, J4)+IT
GO TO 50
25 P(I1, IFACT)=PH(IK, J5)+IT
GO TO 50
26 P(I1, IFACT)=PH(IK, J6)+IT
GO TO 50
27 P(I1, IFACT)=PH(IK, J7)+IT
GO TO 50
28 P(I1, IFACT)=PH(IK, J8)+IT
GO TO 50
29 P(I1, IFACT)=PH(IK, J9)+IT
GO TO 50
30 CALL PROPER(PN, MOD, PRO)
DO 250 I1=1, N
P(I1, 2)=PRO(I)
250 P(I1, 2)=PG(I, K)
CALL PROPER(PN, 2, PRO)
IND=IND+1
WRITE(6, 93) IND, INV(I), (PRO(I), I=1, N)
FORMAT(2X, I6, 2X, A1, 104)
100 CONTINUE
200 CONTINUE
STOP
END

*DECK PROPER
SUBROUTINE PROPER(PN, JK, PRO)
INTEGER P(100, 10), PRO(1000), NPRO(1000)
DO 50 I=1, N
```

```
The array \( (q_i) \) of length \( n \) printed every time is a permutation in the symmetry group of the nonrigid molecule.

The two algorithms described above can be coded into Fortran. A Fortran program thus obtained is shown in Table I. This program requires the elements of \( G' \) and \( H \) as input, and it generates the elements of nonrigid molecules. The program can handle both permutation and permutation inversion operations. The program actually reads in the elements of \( G' \) (cf. sec DA) rather than \( G \) since this is more convenient. Nevertheless, \( G' \) is isomorphic to \( G \). Table II gives the input description for this program.

We will now illustrate the use of this program with two examples. First consider the nonrigid isobutane molecule. The symmetry group of this molecule contains 162 operations. The input to generate the symmetry elements of this molecule is shown in Table III. The first 12 entries of the output corresponding to this input are shown in Table IV. Note that the tertiary proton (10) is not permuted by any operation of the symmetry group of the nonrigid molecule. Hence it is omitted from the list. Note that although there are 162 elements in this group, we have shown in Table IV only the first 12 elements.

### III. APPLICATIONS

The programs described have applications in several areas. First, of course, in characterizing the symmetry of molecules exhibiting large amplitude motions, this program will be of use. Second, this program will be of use in computer generation of the character tables of the symmetry groups of nonrigid molecules, their projection operators, etc.

Topological representation of isomerization processes and the elucidation of modes of rearrangements, etc. are of great interest to several workers such as Randić, Klein, Balaban, and the

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**Table I** (continued from previous page)

<table>
<thead>
<tr>
<th>Card</th>
<th>5</th>
<th>10A8</th>
<th>53</th>
<th>NPRO(I)=I</th>
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<tr>
<td></td>
<td>DO 200 J=1JK</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DO 100 I=1N</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>PPRO(I)=NPRO(P(I,J))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DO 150 I=1N</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>NPRO(I)=PPRO(I)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>CONTINUE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>RETURN</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>END</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table II.** Input description for the program WREATH which generates the symmetry elements of nonrigid molecule.

<table>
<thead>
<tr>
<th>Card</th>
<th>Format</th>
<th>Input Variables</th>
<th>Description</th>
</tr>
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<tr>
<td>1</td>
<td>10A8</td>
<td>N</td>
<td>Total number of Nuclei</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MORDM</td>
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<td></td>
<td></td>
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<td>MODH</td>
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<tr>
<td></td>
<td></td>
<td>MDOD</td>
<td>(</td>
</tr>
<tr>
<td>3</td>
<td>2014</td>
<td>PG(I,J)</td>
<td>Permutations of the group ( G' )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J=1,</td>
<td>G</td>
</tr>
<tr>
<td>4</td>
<td>80A1</td>
<td>INV(I)</td>
<td>Inversion variable. If the ( i )th operation in ( G ) is a pure permutation, ( INV(i) = ) blank. If it is a permutation-inversion operation ( INV(i) = * )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I=1,</td>
<td>G</td>
</tr>
<tr>
<td>5</td>
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<td>PH(I,J)</td>
<td>Permutations of the group ( H )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J=1,</td>
<td>H</td>
</tr>
</tbody>
</table>

* The elements of \( G \) and \( H \) may need more than one card, depending on the number of elements in them.

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**Table III.** Input for generating the symmetry elements of nonrigid isobutane.

<table>
<thead>
<tr>
<th>Card</th>
<th>Symmetry Elements of Non-rigid Isobutane</th>
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<td>9 3 3 3 6</td>
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<td>1 2 3 4 5 6 7 8</td>
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<tr>
<td>4</td>
<td>9 1 2 3 4 5 6 7 8</td>
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<tr>
<td>5</td>
<td>9 8 4 6 8 4 5 6 7 8</td>
</tr>
<tr>
<td>6</td>
<td>E E E E * * * *</td>
</tr>
<tr>
<td>7</td>
<td>E E E E E E E E</td>
</tr>
</tbody>
</table>

* / denotes blank.
Table IV. Symmetry elements of nonrigid isobutane.

<p>| No. |</p>
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<td>9</td>
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</tbody>
</table>

Finally, we give an application to molecular beam deflection experiments of weakly bound van der Waal complexes. It is possible to generate weakly bound complexes of molecules like NH₃, H₂O, C₆H₆, etc., by a supersonic jet expansion. Molecules created this way are nonrigid in that they exhibit rapid tunneling motions at room temperature since they are very weakly bound polymers. It is important to know the nature of their symmetry groups in order to analyze their spectra, etc. We will use benzene dimer (C₆H₆)₂ as an example to illustrate the use of our program. The output corresponding to this molecule can be obtained from the author.

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