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The Isometric Group
of Nonrigid Molecules

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H. Møllendal
Structure of Molecules with
Large Amplitude Motion as
Determined from Electron-Diffraction
Studies in the Gas Phase



Large Amplitude Motion in Molecules I

Springer-Verlag Berlin Heidelberg New York

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**Springer-Verlag****Berlin Heidelberg New York 1979**

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ISBN 3-540-09310-9 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-09310-9 Springer-Verlag New York Heidelberg Berlin

Library of Congress Cataloging in Publication Data. Main entry under title: Large amplitude motion in molecules I. (Topics in current chemistry ; 81) Bibliography: p. Includes index. 1. Molecular structure – Addresses, essays, lectures. I. Series. QDL.F58 · vol. 81 [QD461] · 540'.8s [541'.22] · 79-4221

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Typesetting and printing: Schwetzingen Verlagsdruckerei GmbH, 6830 Schwetzingen. Bookbinding: Konrad Tritsch, Graphischer Betrieb, 8700 Würzburg
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ISBN 3-540-09311-7

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The Isometric Group of Nonrigid Molecules

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1 Introduction

At the present time the conventional concept of molecular structure is appropriately based on the Born-Oppenheimer approximation¹⁾. Molecular structure is commonly understood as relative nuclear configuration, which may be considered as stable in the sense of one criterion or another. Many such structures may be characterized by a continuous set of nuclear configurations, which deviate only infinitesimally from each other (quasirigid molecules, sometimes called rigid molecules). Experimental research has revealed a large number of molecular structures which have to be described by a continuous set of nuclear configurations defined by structural parameters (bond length, bond angles, dihedral angles, etc.), some of which vary over finite domains. Molecules of this type will be called nonrigid molecules.

For quasirigid molecules a symmetry concept has been used very early in some branches of molecular research, e.g. stereochemistry^{2, 3)}. This symmetry concept was based on the concept of isometric mappings⁴⁾ and formed the basis of extended applications to molecular dynamics since 1930, developed first by Wigner⁵⁾.

Attempts to construct symmetries of nonrigid molecules have first been made by Hougen⁶⁾, Longuet-Higgins⁷⁾, and Altmann^{8, 9)}. All these procedures were based on the symmetries of the molecular Born-Oppenheimer operator, i.e. on the Schrödinger operator for a system of nuclei and electrons. In particular the Longuet-Higgins concept uses the intuitive concept of feasibility, which says that a permutation of nuclei corresponds to a feasible operation, if the permutation corresponds to a path on the Born-Oppenheimer surface involving only points of low potential energy. Hence, the elements of the Longuet-Higgins group are permutations and formal combinations of permutations and inversion. The whole concept lacks well defined mathematical tools for determination of transformation properties of energy operators, multipole operators and functions of the dynamical coordinates. Nevertheless, the concept has been applied to a number of specific examples, typical cases have been discussed by Hougen¹⁰⁾, but since its publication, the Longuet-Higgins concept has not been cast into a rigorous tool. Already before the Longuet-Higgins approach the symmetry of the rotation-internal motion problem of nonrigid molecules has been studied by direct investigation of the symmetry group of the rotation-internal motion hamiltonian. Typical examples of this direct approach have been given by Howard¹¹⁾, Wilson¹²⁾, Wilson et al.¹³⁾.

The method presented here has been motivated by the desire to find a method which starts from the geometrical description of nuclear configurations and replaces the feasibility concept by rigorous mathematical definitions. Furthermore, it allows the determination of transformation properties of operators and functions by the methods used generally in applications of group theory to quantum mechanical problems in strict analogy to the treatment of quasirigid molecules within the framework of the covering symmetry group (molecular point symmetry group).

The approach presented in this contribution is a review of a method published in papers by Bauder et al.¹⁴⁾ and Frei et al.^{15, 16)}. It is based on the concept of the isometry of nuclear configurations and therefore may be considered as a natural generalization of the concept of covering symmetry of rigid point sets to nonrigid point sets.

In Chap. 2 the construction of the isometric group of semirigid nuclear configurations is presented, starting from the geometrical definitions of a semirigid model. Furthermore, the relation between isometric groups and the permutation-inversion group will be discussed. A number of applications of isometric groups, in particular to the dynamics of the rotation-large amplitude internal motion problem in classical and quantum mechanical formulation, to transformation properties of irreducible tensor operators and selection rules for irreducible tensor operators up to rank 2 (Wigner-Eckart theorem) are discussed in Chap. 3. Use of the isometric group to stereochemical problems of nonrigid molecules is presented, in particular for questions of chirality and classification of stereoisomers. In Chap. 4 relations of the isometric groups of semirigid models to the familiar symmetry approach for quasirigid molecules and to the symmetry groups of the associated nonrigid molecules are discussed.

For Chaps. 2 and 3 a number of examples will be given. Furthermore, techniques used for practical calculation of isometric groups and their application to problems of molecular geometry and dynamics will be collected in a series of appendices.

2 Construction of Isometric Groups

2.1 Definitions

By a nuclear configuration (NC) we understand the set of informations $\text{NC}\{\mathbf{X}_k, Z_k, M_k\}$ consisting of the coordinates \mathbf{X}_k , the masses M_k and charge numbers Z_k of the nuclei $1, 2, \dots, K$ of a molecular system. The coordinate vectors will be referred to a coordinate system, which will be defined when required. Important coordinate systems will be the laboratory system (LS, basis $\tilde{\mathbf{e}}^l$) and the frame system (FS, basis $\tilde{\mathbf{e}}^f$). The latter is attached to the nuclear configuration by a prescription to be defined in each case. The relation between $\tilde{\mathbf{e}}^l$ and $\tilde{\mathbf{e}}^f$ may be expressed by

$$\{\tilde{\mathbf{e}}^f \mathbf{X}^f\} = \{\tilde{\mathbf{e}}^l \mathbf{O}\} \cdot \begin{bmatrix} D(\epsilon) & \mathbf{X}^f \\ 0 & 1 \end{bmatrix} \quad (2.1)$$

where $D(\epsilon) = \tilde{\mathbf{R}}(\epsilon)$ is a rotation matrix parametrized by the eulerian angles $\alpha\beta\gamma$ (abbreviated by ϵ), as defined in Appendix 1. \mathbf{X}^f stands for the origin of the FS with respect to the LS. For the dynamical problem \mathbf{X}^f will be chosen as center-of-mass coordinate of the NC.

The relative nuclear configuration $\text{RNC}\{\mathbf{X}_k(\xi), Z_k, M_k\}$ is defined as the set of informations determining a NC up to translations and rotations in \mathcal{R}_3 , i.e. invariant with respect to transformations of the inhomogeneous three-dimensional rotation group $\text{IO}(3)$. Conveniently the RNC is determined by internal structural parameters $\xi_1, \xi_2, \dots, \xi_{3K-6}$ which are invariant with respect to (w.r.t.) $\text{IO}(3)$.

A molecule will be called rigid (quasirigid) if its internal structural parameters are constant (may vary only infinitesimally). The term semirigid model (SRM) will be used for a molecular model, whose nuclear configurations are defined by

1, 2, ..., $f \leq 3K-6$ internal coordinates which vary over finite domains, whereas the remaining $3K-6-f$ coordinates remain constant. The introduction of the SRM is motivated by the fact that its isometric group is isomorphic to the symmetry group of the associated nonrigid molecule (NRM), i.e. to the molecule with the same f finite and $3K-6-f$ infinitesimal internal coordinates (cf. Chap. 4). In practical cases the number of finite internal coordinates does not exceed 3 or 4 and remains always small in comparison to $3K-6$.

If a NC of a SRM is considered from a suitably defined FS the coordinate vectors may be expressed as functions of the internal coordinates $\xi_1, \xi_2, \dots, \xi_f$. The RNC $\{X_k(\xi), Z_k, M_k\}$ is then completely defined by the values of ξ_1, \dots, ξ_f and the constant structural parameters. Further classification of SRMs may be based on the 2, 3, ... rigid parts, whose relative positions are determined by the finite coordinates ξ_1, ξ_2, \dots . Such parts are often denoted as frame (F), top (T), inverter (I), etc. Moreover each part may have its own local covering symmetry and the complete NC $\{X_k(\xi), Z_k, M_k\}$ may have a proper covering symmetry group $\mathcal{G}(\xi)$ for arbitrary values of the internal coordinates. Typical SRMs are listed in Tables 1, 2 and 3.

To each NC we associate a graph $\mathcal{N} \{P(\pi_k(Z_k, M_k)), K(d_{kk'})\}$, consisting of the set P of vertices π_k valued by charge and mass number of the nucleus k and the set K of edges $(\pi_k, \pi_{k'})$, valued by the internuclear distance $d_{kk'}(\xi)$

$$d_{kk'}(\xi) = |X_k(\xi) - X_{k'}(\xi)| \quad (2.2)$$

\mathcal{N} is a complete (universal) valued graph. In many cases it is sufficient to consider the graph $\mathcal{N} \{P(\pi_k(Z_k)), K(d_{kk'})\}$ in which the vertices π_k are valued by the nuclear charge only. This is appropriate in all cases in which isotope effects within the Born-Oppenheimer approximation may be neglected.

2.2 Isometric Group of a SRM

The isometric group of a SRM will be constructed from two subgroups:

- (i) internal isometric group $\mathcal{F}(\xi)$
- (ii) covering group $\mathcal{G}(\xi)$

Since most of the nonrigid molecules treated so far may be described by a SRM whose covering group is the improper group C_1 , the internal isometric group is treated first.

2.2.1 Internal Isometric Group $\mathcal{F}(\xi)$

From the definition (2.2) it is seen that the distances $d_{kk'}$ are functions of the internal coordinates. The set of transformations

$$\xi' = F(\xi) \quad (2.3)$$

which map the graph \mathcal{N} onto itself, conserving incidence, forms a group $\mathcal{F}(\xi)$, the group law being the usual composition of functions. Mappings of the graph \mathcal{N} onto itself are defined as

6 Table 1. Isometric groups of semirigid models $f = 1^a$, $\mathcal{G}(\xi) = C_1^b$

System	Type of int. motion	Covering symmetry		Symmetry groups			Typical molecule
		Frame	Top/invertor	$\Gamma^{(3)} \{ \nu \}$	$\mathcal{K}(\xi)$	$\mathcal{P}(\xi)$	
C_3F-C_3vT	Int. rotation	C_s	C_{3v}	C_s	ϑ_3	ϑ_3	CH_3CHO
C_3F-C_2vI	Int. rotation	C_s	C_{2v}	C_s	ϑ_4	ϑ_4	$CH_2:CHNO_2$
C_3F-C_sT	Int. rotation	C_s	C_s	C_s	ϑ_2	ϑ_2	$CH_2:CHCHO$
$C_{2v}F-C_{3v}T$	Int. rotation	C_{2v}	C_{3v}	C_{2v}	ϑ_6	$\vartheta_6[E, T]^c$	CH_3NO_2
C_3F-C_3I	Inversion	C_s	C_s	C_s	ϑ_2	ϑ_2	$CHONHD$
$C_3F-C_{2v}I$	Inversion	C_s	C_{2v}	C_s	ϑ_2	ϑ_2	$\overline{CH_2CR_2NH}$

^a Number of finite degrees of freedom.
^b Covering group for arbitrary values of ξ .
^c T commutes with all other elements.

Table 2. Isometric groups of semirigid models $f \geq 2^a$, $\mathcal{G}(\xi) = C_1^b$

f^a	System	Type of motion ^c	Covering symmetry		Symmetry groups		Typical molecule
			Frame	Top 1	Top 2/ inverter	$\mathcal{H}(\xi)$	
2	$C_{2v}F(C_{3v}T)_2$	RIR	C_{2v}	C_{3v}	C_{3v}	\mathcal{H}_{36}	CH_3COCH_3
2	$C_8F(C_{3v}T)(C_{3v}T)'$	RIR	C_8	C_{3v}	C_{3v}	\mathcal{H}_{18}	$CH_3CH:NCH_3$
2	$C_8F(C_{3v}T)(C_{2v}T)$	RIR	C_8	C_{3v}	C_{2v}	\mathcal{H}_6	$CH_3CH_2NO_2$
2	$C_8F(C_{3v}T)(C_sT)$	RIR	C_8	C_{3v}	C_s	\mathcal{H}_3	CH_3CH_2CHO
2	$C_{2v}F(C_{2v}T)_2$	RIR	C_{2v}	C_{2v}	C_{2v}	$\mathcal{H}_{16} = \mathcal{H}_4[E, T]^d$	$CH_2(NO_2)_2$
2	$C_8F(C_{2v}T)(C_{2v}T)'$	RIR	C_8	C_{2v}	C_{2v}	$\mathcal{H}(2, 2, 2)$	$NO_2CH:CFNO_2$
2	$C_8F(C_{2v}T)(C_sT)$	RIR	C_8	C_{2v}	C_s	\mathcal{H}_4	$NO_2CH_2CH_2F$
2	$C_{2v}F(C_sT)_2$	RIR	C_{2v}	C_s	C_s	\mathcal{H}_4	$O(CHO)_2$
2	$C_8F(C_sT)(C_sT)'$	RIR	C_8	C_s	C_{2v}	\mathcal{H}_2	CH_2FCH_2CHO
2	$C_{2v}F(C_{3v}T)(C_{2v}I)$	RIRINV	C_{2v}	C_{3v}	C_{2v}	\mathcal{H}_6	CH_3NH_2
3	$C_2(\tau)F(C_sT)_2$	RIR	$C_2(\tau)$	C_s	C_s	\mathcal{H}_4	CH_2OHCH_2OH

^a Number of finite degrees of freedom.^b Covering group for arbitrary values of ξ .^c RIR = rotation-internal rotation, INV = inversion.^d T commutes with all other elements.

8 Table 3. Isometric Groups of Semirigid Models $f = 1^a$, $\mathcal{G}(\xi)^b$ proper

System	Type of int. motion	Symmetry groups					Fixed points	Typical molecule
		$\mathcal{F}(\xi)$	$\overline{\mathcal{F}}(\xi)$	$\mathcal{G}(\xi)$	$\mathcal{H}(\xi)$	$\overline{\mathcal{H}}(\xi)$		
$D_{\infty h}F(C_{2v}T)_2$	Int. rot.	$\vartheta_2 \stackrel{\text{is}}{=} \mathcal{F}_4$	ϑ_4	D_2	$\vartheta_4 [E, T]^c$	\mathcal{G}_{32}	D_{2h}, D_{2d}	$(C_6H_5)_2$
$C_{2v}F-C_{2v}T$	Int. rot.	$\vartheta_2 \stackrel{\text{is}}{=} \mathcal{F}_4$	ϑ_2	C_2	$\mathcal{A}(2, 2, 2)$	$\mathcal{A}(2, 2, 2)$	C_{2v}	$C_6H_5NO_2$
$D_{\infty h}F(C_sT)_2$	Int. rot.	\mathcal{F}_2	\mathcal{F}_4	C_2	\mathcal{F}_4	$\mathcal{A}(2, 2, 2)$	C_{2v}, C_{2h}	CHOCHO
$C_{2v}F-C_{2v}I$	Inversion	\mathcal{F}_2	\mathcal{F}_2	C_s	\mathcal{F}_4	\mathcal{F}_4	C_{2v}	$\overline{CH_2CH_2NH}$
$C_{3v}I$	Inversion	\mathcal{F}_2	\mathcal{F}_4	C_{3v}	ϑ_6	$\vartheta_6 [E, T]^c$	D_{3h}	NH_3

^a Number of finite degrees of freedom.
^b Covering group for arbitrary values of ξ .
^c T commutes with all other elements.

$$\hat{F} : P \rightarrow P, K \rightarrow K$$

$$\hat{F}(\pi_k(Z_k, M_k)) = \pi_{\bar{k}}(Z_{\bar{k}}, M_{\bar{k}}) \in P, \quad k, \bar{k} \in [1, K] \quad (2.4)$$

$$\text{where } Z_{\bar{k}} = Z_k, M_{\bar{k}} = M_k$$

$$\hat{F}(d_{kk'}(\xi)) = d_{\bar{k}\bar{k}'}(\xi) \in K(d_{kk'}), \quad \forall d_{kk'}(\xi) \quad (2.5)$$

The transformations $\xi' = F(\xi)$ will be called internal isometric transformations. They transform any NC to a NC with the same set of distances. In many cases they may be expressed as linear inhomogeneous transformations

$$\begin{pmatrix} \xi' \\ 1 \end{pmatrix} = \begin{pmatrix} A(F) & a(F) \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \xi \\ 1 \end{pmatrix} = \mathcal{A}(F) \begin{pmatrix} \xi \\ 1 \end{pmatrix} \quad (2.6)$$

To the isometric transformation (2.3) we will associate the operator \hat{P}_F , defined by

$$\hat{P}_F h(\xi) = h(F^{-1}(\xi)) \quad (2.7)$$

where $h(\xi)$ is any admissible function of ξ . Application of \hat{P}_F to the substrate $\{\widetilde{d_{kk'}}(\xi)\}$, i.e. to the set of distances $d_{kk'}$ ordered in a row yields

$$\hat{P}_F \{\widetilde{d_{kk'}}(\xi)\} = \{\widetilde{d_{kk'}}(F^{-1}(\xi))\} = \{\widetilde{d_{kk'}}(\xi)\} \Gamma^{(\mathcal{N}^{\mathcal{C}})}(F) \quad (2.8)$$

The last equation expresses the fact that the set of distances is mapped by \hat{P}_F onto itself, therefore the matrix $\Gamma^{(\mathcal{N}^{\mathcal{C}})}(F)$ is a permutation matrix of dimension $\binom{K}{2}$, i.g. intransitive. The matrix group

$$\Gamma^{(\mathcal{N}^{\mathcal{C}})}\{\mathcal{F}\} := \{\Gamma^{(\mathcal{N}^{\mathcal{C}})}(F) \mid F, F_2, F_3, \dots\} \quad (2.9)$$

is a representation of the isometric substitutions $\xi' = F(\xi)$ by permutation matrices. The symbol $\mathcal{F}(\xi)$ will henceforward be used as the abstract group $\mathcal{F}(\xi) := \{E, F_2, \dots\}$ represented either by

$$\mathcal{A}\{\mathcal{F}\} := \left\{ \begin{pmatrix} A(F) & a(F) \\ 0 & 1 \end{pmatrix} \mid \forall F \in \mathcal{F}(\xi) \right\} \quad (2.10)$$

$$\text{or by } \Gamma^{(\mathcal{N}^{\mathcal{C}})}\{\mathcal{F}\} := \{\Gamma^{(\mathcal{N}^{\mathcal{C}})}(F) \mid \forall F \in \mathcal{F}(\xi)\}$$

If the distances $d_{kk'}(\xi) \in K(d_{kk'})$ possess a common primitive period p w.r.t. the internal coordinates

$$d_{kk'}(\xi + p) = d_{kk'}(\xi), \quad \forall k, k' \in [1, K], \quad (2.11)$$

the coordinates involved in the transformations (2.6) have to be taken modulo their respective primitive periods. The implication of the existence of primitive periods will be discussed in Sect. 2.2.2.

The operators $\hat{P}_F, F \in \mathcal{F}(\xi)$ will next be applied to the basis $\{\tilde{X}_k(\xi)\}$, i.e. to the (transposed) coordinate vectors referred to the frame system \tilde{e}^f ordered in a row:

$$\begin{aligned}\hat{P}_F\{\tilde{X}_k(\xi)\} &= \{\tilde{X}_k(F^{-1}(\xi))\} = \{\tilde{X}_k(\xi)\} \Pi(F) \otimes \Gamma^{(3)}(F) \\ &= \{\tilde{X}_k(\xi)\} \cdot \Gamma^{(\text{NCf})}(F)\end{aligned}\quad (2.12)$$

Thereby the matrix $\Pi(F)$ denotes a K -dimensional permutation matrix and $\Gamma^{(3)}(F)$ a 3 by 3 orthogonal matrix. The form of this representation follows from the fact that each isometric transformation maps the NC $\{X_k, Z_k, M_k\}$ onto a NC which by definition has the same set of distances, i.e. is isometric to NC $\{X_k, Z_k, M_k\}$. Expressed alternatively, the nuclear configurations NC $\{X_k(\xi), Z_k, M_k\}$ and NC $\{X_k(F^{-1}(\xi)), Z_k, M_k\}$ are properly or improperly congruent up to permutations of nuclei with equal charge and mass for any $F \in \mathcal{F}(\xi)$. The set of matrices Eq. (2.12) forms a representation of $\mathcal{F}(\xi)$ by linear transformations and will furtheron be denoted by

$$\Gamma^{(\text{NCf})}\{\mathcal{F}\} := \{\Pi(F) \otimes \Gamma^{(3)}(F) \mid \forall F \in \mathcal{F}(\xi)\} \quad (2.13)$$

the index f indicating reference to the frame system. In general $\Gamma^{(\text{NCf})}\{\mathcal{F}\}$ decomposes into transitive systems, since each subset of identical nuclei, which is mapped by all elements of \mathcal{F} onto itself gives rise to such a system. The group theoretical relation between $\mathcal{A}\{\mathcal{F}\}$ and $\Gamma^{(\text{NCf})}\{\mathcal{F}\}$ is an isomorphism

$$\mathcal{A}\{\mathcal{F}\} \stackrel{\text{is}}{=} \Gamma^{(\text{NCf})}\{\mathcal{F}\} \quad (2.14)$$

The isomorphism strictly holds for SRMs without primitive period isometric transformations only (cf. Sect. 2.2.2). However, as will be shown in Sect. 2.2.2, the group theoretical relations derived in this section also apply for SRMs with primitive period transformations if \mathcal{F} is replaced by an appropriately extended group $\overline{\mathcal{F}}$. The sets

$$\Pi\{\mathcal{F}\} := \{\Pi(F) \mid \forall F \in \mathcal{F}(\xi)\} \quad (2.15)$$

$$\text{and } \Gamma^{(3)}\{\mathcal{H}\} := \{\Gamma^{(3)}(F) \mid \forall F \in \mathcal{F}(\xi)\} \quad (2.16)$$

form each a representation of $\mathcal{F}(\xi)$. The first set consisting of all permutation factors of $\Gamma^{(\text{NCf})}\{\mathcal{F}\}$ is isomorphic to the permutation group $\Gamma^{(\mathcal{N}^{\mathcal{C}})}\{\mathcal{F}\}$; this follows from a theorem given by Harary¹⁷, relating vertex and edge group of a complete graph.

The group $\Gamma^{(3)}\{\mathcal{H}\}$ (abstract group \mathcal{H}), consisting of all different rotational parts of $\Gamma^{(\text{NCf})}$ is a finite group of orthogonal matrices in \mathcal{R}_3 and must be a subgroup of $O(3)$. It therefore must be one of the point symmetry groups $C_n, S_n, D_n, C_{nv}, C_{nh}, D_{nh}, D_{nd}, T, T_d, T_h, O, O_h$. $\Gamma^{(3)}\{\mathcal{H}\}$ will play an important role in most applications of isometric groups. It pictures the set of all orthogonal matrices, which map a reference NC on to all possible isometric NCs.

In general the group theoretical relation between $\Gamma^{(\text{NCf})}\{\mathcal{F}\}$ and $\Gamma^{(3)}\{\mathcal{H}\}$ is a homomorphism $\hat{\eta}$:

$$\hat{\eta} : \Gamma^{(\text{NCf})}\{\mathcal{F}\} \longrightarrow \Gamma^{(3)}\{\mathcal{H}\} \quad (2.17)$$

whose kernel is given by