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On the symmetry properties of non-rigid molecules
Semifactorizability of the isometric group

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A recent theorem states that the complete isometric symmetry group of a non-rigid molecule is a semi-direct product of the point group and the internal isometric group. It is shown that, although the point group is an invariant subgroup of the complete isometric group, the theorem is not generally valid. A counter-example is presented and a necessary condition is given for the validity of the general theorem. The counter-example is also discussed in terms of the symmetry group of the molecular model.

1. INTRODUCTION

Irrespective of the details of the particular approach adopted, a study of the symmetry properties of non-rigid molecules (NRMs) soon leads to the appearance of large (typically 10–10^3 elements) and relatively unfamiliar groups [1–3]. This fact then opens up the following interesting question : what, if any, are the characteristic structural features of these large NRM groups ?

The search for methods to systematize and to simplify the group theory has led to several investigations of the possibility of formulating NRM symmetry groups as *semi-direct products*, notably those of Altmann [4, 5], Woodman [6] and Günthard *et al.* [7–9] (see also [10, 11]). We have recently discussed this problem from a unified point of view [12].

When present, this type of group factorization has many important implications. Thus, semi-direct product structure provides the basis for a detailed and physically significant nomenclature for the irreducible representations (IRs) of NRM groups [5, 6, 13]. Moreover, there is available a systematic procedure for construction of the associated character tables, which utilizes the properties of the smaller component groups to the maximum extent [5, 13]. We mention also that the formulation of interrelations between NRM groups, the construction of group chains and homomorphisms, and the correlation of NRM states with various rigid molecule geometries are all facilitated by the recognition of semi-direct product structure [14].

It is therefore pertinent to consider the extent to which one may expect to encounter this important feature in any treatment of NRM symmetry. In other words, for a given approach to the NRM problem, are there any general results that can be proved concerning the occurrence of semi-direct products ?

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In a recent paper on the *isometric* theory of the symmetry properties of NRMs, Günthard *et al.* proposed the following theorem concerning the structure of the complete isometric group $\mathscr{H}(\gamma)$ (notation and definitions are briefly reviewed in § 2).

Theorem The (abstract) complete isometric group $\mathscr{H}$ is a semi-direct product of the point group $\mathscr{G}$ and the internal isometric group $\mathscr{F}$, where the point group $\mathscr{G}$ is the invariant subgroup.

An analogous theorem was proposed for the group $\bar{\mathscr{H}}$, the extension of the complete isometric group to include primitive period transformations [8, 9].

In view of the significance of semi-direct product structure as emphasized above, the availability of such a strong result would be of considerable importance. However, in this paper we show by means of a counterexample that the theorem on the isometric group is not strictly valid and that the proof given in [8] breaks down on a fundamental point.

The non-existence of the general theorem on the structure of the isometric group is entirely in accord with our recent discussion of NRM symmetry [12]. There we attempted to develop a unified approach to the problem and were able to provide a consistent framework for previous treatments of NRM groups as semi-direct products [4–10]. It was shown that, for the particular class of NRMs considered (those for which the dynamical picture introduced by Sayvetz [15] and the associated use of a *semi-rigid molecular model* is appropriate), it is possible under certain conditions to identify two particular invariant subgroups of the NRM symmetry group, the *point group* and the *intrinsic group*. However, it does not necessarily follow that the NRM group can always be written as a semi-direct product with these groups as invariant subgroups.

These negative conclusions leave open an important question concerning the possibility of obtaining a correct (albeit weaker) version of the theorem of Günthard *et al.* Although we provide a necessary condition for the validity of the theorem here, the reformulation is discussed in the paper by Günthard *et al.* following this one.

Before turning to the details concerning possible semi-direct product structure of the isometric group in § 3, the isometric approach is briefly reviewed in § 2.

2. Review of the isometric theory

In this section we outline the isometric approach to the symmetry properties of NRMs. Detailed accounts may be found in the original papers [7, 8] and a recent review article [9].

We begin by considering the semi-rigid molecular model (SRMM) [7, 12, 16]. The utility of this concept derives from the fact that, at least for certain classes of NRM, the nuclear dynamics are best described in terms of the intuitive picture introduced by Sayvetz [15], in which the nuclei execute rapid, small-amplitude (*vibrational*) motion about a reference configuration that is itself performing some sort of slow, large-amplitude (*internal* or *contortional* [3]) motion, as well as undergoing overall rotation. The internal motion embodied in the specification of the SRMM may involve some form of large-amplitude bending [17], internal rotation [18], inversion at (for example) a nitrogen atom [19] and a more complex type of motion such as pseudorotation [20].

The SRMM underlies the description of vibrational motion in NRMs in precisely the same way that the *static molecular model* [21] does in the dynamics of conventional quasi-rigid molecules [8, 12, 16, 21]. For NRMs the reference structure is embedded into an arbitrary spatial configuration of nuclei using the Eckart-Sayvetz conditions [15], which are a natural generalization of the usual Eckart conditions [21] to non-rigid systems. We note that Natanson and Jørgensen [22] have given a least-squares criterion for orientation of the Eckart–Sayvetz frame that is particularly useful, while a detailed discussion of the dynamical implications of the use of the Eckart–Sayvetz constraints has recently been given by Sørensen [16].

Formally, the SRMM is a set of triples [7, 12, 16]

$$\mathscr{A} \equiv \{(\mathbf{a}^\alpha(\gamma), m_\alpha, z_\alpha)\,; \quad \alpha = 1, 2 \ldots N\} \tag{1}$$

defining N vectors $\mathbf{a}^\alpha(\gamma)$ as functions of a set of parameters collectively denoted γ, where each vector $\mathbf{a}^\alpha(\gamma)$ is associated with a nucleus of charge z_α and mass m_α, γ is a representative point in a parameter domain Γ, and we shall suppose that there are $T(\leqslant 3N-6)$ independent parameters, so that γ stands for the vector $(\gamma_1 \ldots \gamma_t \ldots \gamma_T)$. Here, each γ_t is a coordinate, such as a torsional angle or angle of pucker, describing a particular large-amplitude motion and each has a finite range defined in a suitable fashion [7]. The γ_t are therefore *curvilinear* coordinates in the sense of [16].

The $3N$ components of the SRMM vectors

$$a^\alpha(\gamma)_i \equiv \hat{\mathbf{e}}_i \cdot \mathbf{a}^\alpha(\gamma), \quad i = x, y, z \tag{2}$$

are defined by introducing a coordinate frame $\{\hat{\mathbf{e}}_i\}$ into the SRMM, where $\{\hat{\mathbf{e}}_i\}$ may be a principal axis frame for a particular value of γ. The actual definition of the $\{a^\alpha(\gamma)_i\}$ as functions of the parameters γ_t requires careful consideration when we come to the problem of formulating a multiplication rule in the symmetry group of the molecular model [12, 13] (see also [16, equation (4.9)]); for the moment, however, we note that it is convenient to require that the centre of mass condition

$$\sum_\alpha m_\alpha a^\alpha(\gamma)_i = 0 \quad \forall\gamma\,; \quad i = x, y, z \tag{3}$$

be satisfied.

Consider a transformation τ of internal parameters [7, equation (3.1)]

$$\tau : \gamma \to \tau(\gamma) \equiv \gamma' \in \Gamma \quad \forall\gamma \tag{4}$$

which, although there is no necessary restriction, is usually an inhomogeneous linear transformation on the components of the vector $(\gamma_1 \ldots \gamma_t)$ [7, 8]

$$\tau : \gamma_t \to \gamma'_t = \sum_{\tilde{t}} \eta(\gamma)_{t\tilde{t}} \gamma_{\tilde{t}} + \tau_t \tag{5}$$

and has the induced action upon the SRMM vectors

$$\hat{P}_\tau : a^\alpha(\gamma)_i \to a^\alpha(\tau^{-1}(\gamma))_i. \tag{6}$$

The transformation τ is said to be an *internal isometric transformation* if the resulting SRMM $\{\mathbf{a}^\alpha(\tau^{-1}(\gamma))\}$ is related to the original $\{\mathbf{a}^\alpha(\gamma)\}$ by an isometry, that is, if the resulting nuclear configuration can be superimposed upon the original by a (finite) rotation or rotation–inversion, the net result being simply

some permutation of SRMM vectors associated with identical nuclei. The set of all such transformations forms a group, the *internal isometric group*, denoted $\bar{\mathscr{F}}$ (see [7, §3.1]; note that the distinction between $\mathscr{F}$ and $\bar{\mathscr{F}}$, the extension of $\mathscr{F}$ to include primitive period isometric transformations [8], is ignored henceforth)

$$\bar{\mathscr{F}}(\gamma) \equiv \{\tau | \{\mathbf{a}^\alpha(\gamma)\} \overset{\text{isometry}}{\longleftrightarrow} \{\mathbf{a}^\alpha(\tau^{-1}(\gamma))\}\}. \tag{7}$$

According to the above definition of an isometry, for all elements of the internal isometric group, it is possible to write [7, equation (3.7); 12, equation (2.8)]

$$\forall \tau \in \bar{\mathscr{F}}, \hat{p}_\tau : a^\alpha(\gamma)_i \to a^\alpha(\tau^{-1}(\gamma))_i = \sum_\beta a^\beta(\gamma)_j S(\tau)_{\beta\alpha} R(\tau)_{ji}, \tag{8}$$

where $R(\tau)$ defines a finite rotation or rotation–inversion associated with the isometry and $S(\tau)$ is an N by N matrix permuting identical nuclei. The representation of $\bar{\mathscr{F}}$ on the nuclear configuration $\{a^\alpha(\gamma)_i\}$ is denoted [8]

$$\Gamma^{(\mathrm{NCI})}\{\bar{\mathscr{F}}\} \equiv \{R(\tau) \otimes S(\tau) | \tau \in \bar{\mathscr{F}}\}. \tag{9}$$

Thus, in the isometric method we are explicitly interested in the set of solutions to equation (8) and the corresponding set of perrotations (permutation–rotations [23]) (9). The molecular potential energy is manifestly invariant under an isometry and Günthard *et al.* have shown that the rotation/internal-motion kinetic energy operator is also invariant under the induced action of the group of internal isometric transformations [7].

Should the SRMM possess any non-trivial covering symmetry for arbitrary γ, there is an indeterminacy in the association of perrotations with a given internal isometric transformation τ. In fact, if the point group for arbitrary γ, denoted $\mathscr{G}(\gamma)$, has order $|\mathscr{G}(\gamma)|$, then the solutions of the isometry equation (8) are $|\mathscr{G}(\gamma)|$-valued. To see this, we consider the properties of $\mathscr{G}(\gamma)$ in more detail.

A covering operation $g \in \mathscr{G}$ is a rotation or rotation–inversion of the SRMM resulting in a permutation of SRMM vectors associated with identical nuclei

$$\forall g \in \mathscr{G}, \quad g : a^\alpha(\gamma)_i \to R(g)_{ij} a^\alpha(\gamma)_j = \sum_\beta a^\beta(\gamma)_i S(g)_{\beta\alpha} \tag{10}$$

so that [8, equation (2.19″)]

$$\forall g \in \mathscr{G}, \quad a^\alpha(\gamma)_i = \sum_\beta a^\beta(\gamma)_j S(g)_{\beta\alpha} R(g)_{ji} \tag{11}$$

and the point group $\mathscr{G}$ can be characterized by the set of all perrotations that are equivalent to the identity operation when acting upon the nuclear configuration $\{a^\alpha(\gamma)_i\}$. Hence, if the perrotation $S(\tau) \otimes R(\tau)$ is a solution of the isometry equation (8) associated with the internal isometric transformation τ, then so is $S(g)S(\tau) \otimes R(g)R(\tau)$ for any element g in $\mathscr{G}(\gamma)$.

In order to formulate a definition of NRM symmetry overcoming this indeterminacy and encompassing both the notion of point symmetry and of internal isometric transformation, Günthard *et al.* define the *complete isometric group* $\bar{\mathscr{H}}(\gamma)$ as the abstract group (complex)

$$\bar{\mathscr{H}}(\gamma) \equiv \mathscr{G}(\gamma) \cdot \bar{\mathscr{F}}(\gamma), \tag{12}$$

where, in practice, a faithful representation of $\bar{\mathscr{H}}$ is constructed as a set of perrotations $\Gamma^{(\mathrm{NCI})}\{\mathscr{H}\}$ on the SRMM configuration $\{a^\alpha(\gamma)_i\}$ [7, §3.3.2.3].

In the next section, we consider the problem of the structure of the complete isometric group.

3. The structure of the isometric group

In [8] the following theorem is proposed : the (abstract) complete isometric group $\bar{\mathscr{K}}(\gamma)$ is a semi-direct product of the point group $\mathscr{G}(\gamma)$ and the internal isometric group $\bar{\mathscr{F}}(\gamma)$, where $\mathscr{G}(\gamma)$ is the invariant subgroup.

Recall that, in order to prove that a group is a semi-direct product, two results must be established [5] : first, the presence of an invariant subgroup must be demonstrated : second, it must be shown that the coset generators of the invariant subgroup can be chosen in such a way that they close to form a group, necessarily isomorphic with the factor group.

Consider the first step. We wish to show that the point group $\mathscr{G}(\gamma)$ is invariant under the action of the internal isometric group $\bar{\mathscr{F}}$ and hence an invariant subgroup of $\bar{\mathscr{K}}$. However, this result follows from the definition of the point group $\mathscr{G}(\gamma)$. Thus, $\mathscr{G}(\gamma)$ is a *global* property of the molecular model, being defined as the highest common symmetry over the whole parameter range [7]. This global specification of $\mathscr{G}(\gamma)$ ensures that

$$\mathscr{G}(\tau(\gamma)) = \mathscr{G}(\gamma) \quad \forall \tau \in \bar{\mathscr{F}}, \tag{13}$$

so that

$$\mathscr{G} \lhd \bar{\mathscr{K}}, \tag{14}$$

that is $\mathscr{G}$ is an invariant subgroup.

Although problems do not normally arise concerning the definition of $\mathscr{G}(\gamma)$, since SRMMs can usually be defined to have a given, fixed (with respect to $\{\hat{\mathbf{e}}_i\}$) covering symmetry for all values of γ except for a few isolated points, we would note the subtle problems discussed by Nourse and Mislow in connection with correlated ring rotations in the teraphenylmethane molecule [24]. Even though the molecular model is assumed to have non-trivial S_4 covering symmetry at all times, it turns out that the group S_4 is not an invariant subgroup of the symmetry group of the molecular model (which is the semi-direct product $(C_2 \otimes C_2 \otimes C_2 \otimes C_2) \textcircled{\wedge} T_d$ of order 384). This is because there are three distinct S_4 groups involved, having the unique S_4-axes aligned along orthogonal x-, y- and z-axes respectively, and the intersection of these groups is C_1, the trivial point symmetry. The point group associated with this model is therefore C_1. We note also that a global specification of the point group is implicit in the definition of $\mathbb{G}^P$ given in [12], equation (24).

Given that $\mathscr{G}$ is an invariant subgroup, it must then be shown that the coset generators of the (abstract) complete isometric group with respect to the point group can be chosen to form a group, isomorphic with the internal isometric group. However, in their treatment of this aspect of the theorem Günthard *et al.* proceed by a less direct route. Thus, they choose to determine the representations of $\bar{\mathscr{K}}$ on various substrates of interest (molecular model vectors, rotation coordinates, internal parameters, etc.) and attempt to demonstrate semi-direct product for each case [8].

The validity of this approach depends crucially upon the assertion [8, equation (2.35)] that all point groups can be written as the semi-direct product of two covering (point) groups. However, this is not true in general [5] : for

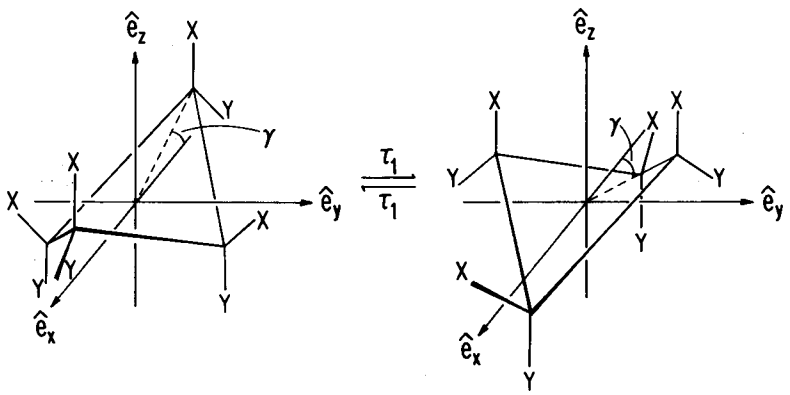

Figure 1. The C_{4v}–C_{2v} rotation/ring-puckering semi-rigid molecular model.

example, the cyclic group of order $4n$, although possessing a proper invariant subgroup C_{2n}, cannot be written as the semi-direct product of its invariant subgroup and another subgroup of order 2, and the counter-example presented in the next section will exploit this fact.

4. The counter-example

Consider first the SRMM for the substituted cyclobutadiene $(CXY)_4$ (atomic X, Y) shown in figure 1, which has covering symmetry $\mathscr{G}(\gamma)=C_{2v}$. In this example, there is a single internal parameter, the angle of pucker $\gamma(0\leqslant\gamma<\pi/2)$, and the transformation

$$\tau_1:\gamma\rightarrow-\gamma \quad \text{(pucker)} \tag{15}$$

shown is an isometry. This molecular model is a useful starting point for our discussion, since it obeys the assertions of the general theorem.

The properties of the isometric group for this SRMM are summarized as follows ($\tau_0:\gamma\rightarrow\gamma$)

$$\bar{\mathscr{F}}=\{\tau_0,\tau_1\}\overset{\text{iso}}{=}\mathscr{V}_2, \tag{16a}$$

$$\mathscr{G}(\gamma)=C_{2v}\overset{\text{iso}}{=}\Gamma^{(3)}\{\mathscr{G}\}, \tag{16b}$$

$$\bar{\mathscr{H}}=C_{2v}\cdot\mathscr{V}_2, \tag{16c}$$

$$C_{2v}\lhd\bar{\mathscr{H}}, \tag{16d}$$

$$\Gamma^{(3)}\{\bar{\mathscr{P}}\}\overset{\text{iso}}{=}C_{4v}, \tag{16e}$$

$$C_{2v}\lhd C_{4v} \tag{16f}$$

and

$$\mathscr{K}\equiv\Gamma^{(3)}\{\bar{\mathscr{P}}\}/\Gamma^{(3)}\{\mathscr{G}\}=C_{4v}/C_{2v}\overset{\text{iso}}{=}\mathscr{V}_2. \tag{16g}$$

Thus, the internal isometric group is of order 2, the point group is C_{2v} and $\bar{\mathscr{H}}$ is of order 8.

The set $\Gamma^{(3)}\{\mathscr{G}\}$ is the defining representation of $\mathscr{G}(\gamma)$

$$\Gamma^{(3)}\{\mathscr{G}\} \equiv \{R(g) | g \in \mathscr{G}(\gamma)\} \tag{17}$$

isomorphic with C_{2v}, while $\Gamma^{(3)}\{\bar{\mathscr{P}}\}$ is the set of all 3 by 3 orthogonal matrices associated with the complete isometric group $\bar{\mathscr{H}}$ and is isomorphic with C_{4v}, which is the effective point symmetry of a puckering 4-ring. The SRMM of figure 1 can therefore be denoted $(CXY)_4C_{4v} - C_{2v}$.

In this case, the effective point group C_{4v} can be written as a semi-direct product of the point group C_{2v} with the reflection group generated by $\hat{\sigma}_d$, the reflection in a dihedral plane

$$C_{4v} = C_{2v} \textcircled{S} C_s(\sigma_d), \tag{18}$$

that is

$$\Gamma^{(3)}\{\bar{\mathscr{P}}\} = \Gamma^{(3)}\{\mathscr{G}\} \textcircled{S} \Gamma^{(3)}\{\mathscr{K}\}, \tag{19 a}$$

where

$$\Gamma^{(3)}\{\mathscr{K}_v\} \equiv \{R(E), R(\sigma_d)\} \overset{\text{iso}}{=} \mathscr{V}_2. \tag{19 b}$$

The essential condition on the structure of the effective point group $\Gamma^{(3)}\{\bar{\mathscr{P}}\}$ is therefore satisfied, so we can conclude from [8] that representations of $\bar{\mathscr{H}}$ for the $(CXY)_4C_{4v} - C_{2v}$ model exhibit semi-direct product structure and that the complete isometric group is a semi-direct product $(CXY)_4C_{4v} - C_{2v}$,

$$\bar{\mathscr{H}} = C_{2v} \textcircled{S} \mathscr{V}_2 \overset{\text{iso}}{=} C_{4v}. \tag{20}$$

Note that it is only possible to find the group $\Gamma^{(3)}\{\mathscr{K}\}$ of orthogonal matrices isomorphic with the factor group $\mathscr{K}$ because of the presence of the involute reflection $\hat{\sigma}_d$. There is then a 1 : 1 correspondence between the elements of $\bar{\mathscr{F}}$ and $\Gamma^{(3)}\{\mathscr{K}\}$.

With this in mind we see that in order to exhibit a counterexample to the theorem we must find a model where (for example) $\mathscr{K} \overset{\text{iso}}{=} \mathscr{V}_2 \overset{\text{iso}}{=} \bar{\mathscr{F}}$, but $\Gamma^{(3)}\{\bar{\mathscr{P}}\}$ cannot be generated from $\Gamma^{(3)}\{\mathscr{G}\}$ by a self-inverse element. This can be done by removing the reflection symmetries from the previous example ; the required

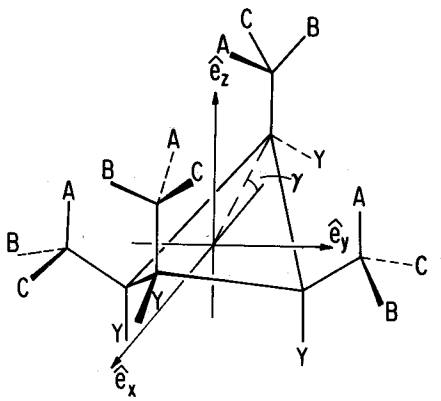

Figure 2. The C_4–C_2 rotation/ring-puckering semi-rigid molecular model.

substitution of chiral groups X, Y produces the C_4-C_2 molecular model shown in figure 2, whose properties are as follows

$$\bar{\mathscr{F}} = \{\tau_0, \tau_1\} \overset{\text{iso}}{=} \mathscr{V}_2, \tag{21 a}$$

$$\mathscr{G}(\gamma) = C_2 \overset{\text{iso}}{=} \Gamma^{(3)}\{\mathscr{G}\}, \tag{21 b}$$

$$\bar{\mathscr{H}} = C_2 \cdot \mathscr{V}_2, \tag{21 c}$$

$$C_2 \lhd \bar{\mathscr{H}}, \tag{21 d}$$

$$\Gamma^{(3)}\{\bar{\mathscr{P}}\} \overset{\text{iso}}{=} C_4, \tag{21 e}$$

$$C_2 \lhd C_4 \tag{21 f}$$

and

$$\mathscr{K} = C_4/C_2 \overset{\text{iso}}{=} \mathscr{V}_2. \tag{21 g}$$

The internal isometric group $\bar{\mathscr{F}}$ is the same as before, being generated by the puckering transformation τ_1 (the C–A bonds being constrained always to lie, for example, in the vertical plane). Here, the effective point symmetry is C_4, the cyclic group of order 4 and $\bar{\mathscr{H}}$ is also of order 4. The point group C_2 is an invariant subgroup of C_4. However, in contrast to the previous example, it is not possible to construct C_4 as a semi-direct product of C_2 and another group of order 2, so that the proof of the second part of the theorem attempted in [8] fails at this point.

We therefore have a counter-example to the theorem of Günthard *et al.*; for the C_4–C_2 molecular model shown in figure 2, the complete isometric group $\bar{\mathscr{H}}$ is not a semi-direct product.

Having established this particular counter-example, it is appropriate to inquire more deeply into the general reasons for the failure of this aspect of the proof of the theorem. It appears that the definition of the group $\Gamma^{(3)}\{\mathscr{K}\}$ is of central importance here. In their work, Günthard *et al.* define the group $\Gamma^{(3)}\{\mathscr{K}\}$ as follows [8, equation (2.12)]

$$\Gamma^{(3)}\{\mathscr{K}\} \equiv \{R(\tau) | \forall \tau \in \bar{\mathscr{F}}(\gamma)\}, \tag{22}$$

that is the set of all different rotational parts $R(\tau)$ of the representation $\Gamma^{(\mathrm{NCI})}\{\bar{\mathscr{F}}\}$ (equation (9)), and assert that there is in general a homomorphism from $\Gamma^{(\mathrm{NCI})}\{\bar{\mathscr{F}}\}$ onto the matrix group $\Gamma^{(3)}\{\mathscr{K}\}$ [8, equation (2.13)],

$$\hat{\eta} : \Gamma^{(\mathrm{NCI})}\{\bar{\mathscr{F}}\} \to \Gamma^{(3)}\{\mathscr{K}\} \tag{23 a}$$

such that

$$\Gamma^{(\mathrm{NCI})}\{\bar{\mathscr{F}}\}/(\mathrm{Ker}\ \hat{\eta}) \overset{\text{iso}}{=} \Gamma^{(3)}\{\mathscr{K}\}. \tag{23 b}$$

However, we would argue that this begs the question of the possible semi-factorization of $\Gamma^{(3)}\{\bar{\mathscr{P}}\}$ (and hence $\bar{\mathscr{H}}$) as a semi-direct product with invariant subgroup $\mathscr{G}$. Thus, in general *only* the following entities are well defined: the matrix group $\Gamma^{(3)}\{\bar{\mathscr{P}}\}$; the matrix group $\Gamma^{(3)}\{\mathscr{G}\}$; the *factor group* $\mathscr{K}$

$$\mathscr{K} \equiv \Gamma^{(3)}\{\bar{\mathscr{P}}\}/\Gamma^{(3)}\{\mathscr{G}\}. \tag{24}$$

It follows that *if* a matrix group $\Gamma^{(3)}\{\mathscr{K}\}$, isomorphic with $\mathscr{K}$, exists such that $\Gamma^{(3)}\{\bar{\mathscr{P}}\}$ can be written as a semi-direct product

$$\Gamma^{(3)}\{\bar{\mathscr{P}}\} = \Gamma^{(3)}\{\mathscr{G}\} \circledS \Gamma^{(3)}\{\mathscr{K}\} \tag{25}$$

then it is true that there is a homomorphism from $\Gamma^{(\mathrm{NCf})}\{\bar{\mathscr{F}}\}$ (the kernel of which is the intrinsic group (cf. [12, § 3]) on to $\Gamma^{(3)}\{\mathscr{K}\}$ and that $\bar{\mathscr{K}}$ is also a semi-direct product. We therefore have a necessary condition for the validity of the theorem. An exhaustive examination of the semi-factorizability condition (25) for molecular covering groups is given by Günthard *et al.* in the following paper [25] (see also [5]).

The problem with the discussion in [8] is that, in the absence of the relation (25) between $\Gamma^{(3)}\{\bar{\mathscr{P}}\}$, $\Gamma^{(3)}\{\mathscr{G}\}$ and $\mathscr{K}$, it is not necessarily possible to find the many : one correspondence between elements of $\bar{\mathscr{F}}$ and $\mathscr{K}$ implied by the definitions (22) and (23). This is confirmed by the existence of the C_4–C_2 counter-example.

5. The symmetry group of the molecular model

In [12] (to which we refer for detailed discussion) we have proposed a unified formalism for the symmetry properties of a class of non-rigid molecules and have introduced the *symmetry group of the semi-rigid molecular model*, denoted $\mathbb{H}$. For these molecules the group $\mathbb{H}$ is identified as *the* NRM symmetry group and determines the transformations of molecular (Born–Oppenheimer) variables induced by *feasible* permutations of nuclei (cf. also [26]). The C_4–C_2 counter-example is now discussed briefly in terms of this approach.

Elements of the symmetry group of the molecular model $\mathbb{H}$ are ordered pairs of transformations of the form

$$h \equiv (\rho, \tau), \tag{26}$$

where ρ is an element of the group 0(3) (a rotation or rotation–inversion) and τ is a transformation of internal parameters (cf. (4)). The group $\mathbb{H}$ consists of all operations h that permute position vectors of the molecular model corresponding to equivalent nuclei and, provided that the specification of the rotation ρ is independent of the values of the internal parameters, has the simple multiplication rule

$$\begin{aligned} h_1 \cdot h_2 &= (\rho_1, \tau_1) \cdot (\rho_2, \tau_2) \\ &= (\rho_1\rho_2, \tau_1\tau_2). \end{aligned} \tag{27}$$

This well defined rule enables us to investigate whether or not $\mathbb{H}$ has semi-direct product structure using standard methods involving manipulation of the group elements themselves.

The symmetry group $\mathbb{H}$ of the C_4–C_2 molecular model of § 3 is the set of 4 elements

$$\mathbb{H} = \{(\hat{E}, \tau_0), (\hat{C}_{4z}, \tau_1), (\hat{C}_{2z}, \tau_0), (\hat{C}_{4z}^{\,3}, \tau_1)\}, \tag{28 a}$$

$$\overset{\text{iso}}{=} C_4 \tag{28 b}$$

isomorphic, as is the permutation–inversion group for the problem, with the cyclic group of order 4 (cf. (21 *c*)). The subgroup $\mathbb{G}^P$ (corresponding to $\mathscr{G}$) is the set of 2 elements

$$\mathbb{G}^P = \{(\hat{E}, \tau_0), (\hat{C}_{2z}, \tau_0)\}, \tag{29 a}$$

$$\overset{\text{iso}}{=} C_2 \tag{29 b}$$

isomorphic with the cyclic group of order 2. It follows from the multiplication rule (27), which is valid here, that $\mathbb{G}^P$ is an invariant subgroup of $\mathbb{H}$ (cf. (21 *d*))

$$\mathbb{G}^P \lhd \mathbb{H} \tag{30}$$

and that the factor group is the abstract group of order two (cf. (21 *e*))

$$\mathbb{H}/\mathbb{G}^P = \mathscr{V}_2. \tag{31}$$

Decomposing $\mathbb{H}$ into cosets with respect to the invariant subgroup $\mathbb{G}^P$

$$\mathbb{H} = \{(\hat{E}, \tau_0), (\hat{C}_{2z}, \tau_0)\} \cup \{(\hat{C}_{4z}, \tau_1), (\hat{C}_{4z}^3, \tau_1)\} \tag{32}$$

it can easily be seen that it is not possible to find coset generators that form a group of order two and thereby construct $\mathbb{H}$ as a semi-direct product. Thus, for the C_4–C_2 model of figure (2), $\mathbb{H}$ is not a semi-direct product of $\mathbb{G}^P$ and another group of order 2 and this corresponds to the conclusion concerning the isometric group.

We would stress, however, that for the symmetry group of the molecular model this result is manifest directly in the coset decomposition (32). In order to specify an element of $\mathbb{H}$, we must give *both* an (internal isometric) transformation τ *and* a rotation ρ; using the multiplication rule (27), the elements of $\mathbb{H}$ can then be manipulated directly. It is this feature of our approach that gives us a firm hold on the structure of the NRM symmetry group and which leads to a relatively simple formulation of the problem.

6. Summary

A theorem proposed recently by Günthard *et al.* states that the complete isometric group of a non-rigid molecule is a semi-direct product [8]. In this paper, we show that the theorem is not always strictly valid. A counter-example is presented and the reason for the failure of the general theorem discussed. The crucial point is that it is not always possible to semi-factorize an arbitrary molecular covering group with respect to a given invariant subgroup, a result which emphasizes the importance of distinguishing between a proof of the invariance of a subgroup and a demonstration of strict semi-factorization. We thereby establish a necessary condition for the validity of the theorem, namely that it should be possible to write the effective covering symmetry group of the non-rigid molecule (realized as the set of orthogonal matrices $\Gamma^{(3)}\{\mathscr{P}\}$) as a semi-direct product of the point group $\mathscr{G}$ (realized as the matrix group $\Gamma^{(3)}\{\mathscr{G}\}$) and a covering group $\Gamma^{(3)}\{\mathscr{K}\}$, where $\Gamma^{(3)}\{\mathscr{K}\}$ is isomorphic with the factor group $\mathscr{K} \equiv \Gamma^{(3)}\{\mathscr{P}\}/\Gamma^{(3)}\{\mathscr{G}\}$.

Semi-direct product groups have many useful properties, since they are only roughly an order-of-magnitude more complicated than direct products [13]. Although the theorem on the structure of the complete isometric group does not hold in general, semi-direct product structure will arise whenever the above condition is satisfied. This conclusion is in accord with our recent discussion of the symmetry groups of non-rigid molecules as semi-direct products [12]. An exhaustive treatment of the semi-factorizability of molecular covering groups is given by Günthard *et al.* in the following paper, where the theorem on the isometric group is reformulated in a slightly weaker version and a generalization of the usual so-called minimal semi-factorizability is discussed [25].

Our counter-example is also discussed here in terms of the formalism developed in [12]. Using a straightforward coset decomposition of the symmetry group of the molecular model [12], a result corresponding to that for the isometric group is obtained in a very direct fashion.

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