

Strategies for advanced applications of permutation–inversion groups to the microwave spectra of molecules with large amplitude motions

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ABSTRACT

This article presents permutation–inversion group-theoretical strategies and recipes aimed at helping a high-resolution molecular spectroscopist use the existing pedagogical literature to carry out their own treatment of the basic symmetry questions in rotating molecules with large-amplitude vibrational motions. Topics addressed include: determination of the feasible permutation–inversion group and its symmetry species and character table; a general equation defining coordinates that can describe translation, overall rotation, large-amplitude vibrations and small-amplitude vibrations for a large class of floppy molecules; and the determination of symmetry species for basis functions and selection rules for operators written in these coordinates. The article is intended to be more advanced than existing pedagogical works, but it still leaves many important topics untreated.

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1. Introduction

The purpose of this article is to present a set of strategies and recipes for do-it-yourself applications of permutation–inversion (PI) groups to the high-resolution rotational spectra of molecules with large-amplitude motions. Vibrations will be divided into small-amplitude vibrations (SAVs), which are usually nearly harmonic and well behaved, and large-amplitude motions (LAMs), which are usually very anharmonic and often give rise to tunneling splittings, very large LAM–rotation interactions, and/or other complications. The treatment of SAVs in molecules that also have LAVs requires consideration of a number of subtle questions. Some of these questions are mentioned below, but SAVs are not discussed in detail.

The material covered can be grouped into four main tasks: (i) Postulate the molecular structure and its LAMs. Select from the full PI group those elements which correspond to feasible motions in the Longuet–Higgins sense [1]. Determine the molecular symmetry group [2]. (ii) Determine the class structure of the PI group obtained. From the class structure and some guessed basis set functions determine the character table [3–5]. (iii) Fix in some way an axis system in the molecule. The orientation of this axis system in the laboratory will define the rotational angles. Define in some mathematical way the LAM coordinate(s) of interest. Then find the transformation properties of the rotational angles and the LAM coordinates that correspond to each element of the PI group.

(iv) From these transformation properties determine the symmetry species of various functions, e.g., determine the symmetry species of the basis functions, interaction terms in the Hamiltonian operator, the electric dipole moment operator, the total angular momentum operator, etc. Tasks (i), (ii), and (iv) are frequently discussed in the pedagogical literature, so the main emphasis here will be on task (iii). General principles are discussed in the main part of the text. Tips for improving speed in the numerous mathematical manipulations needed for any actual application are given in the appendices.

The reader is assumed to be relatively familiar with the feasible permutation–inversion ideas in Longuet–Higgins' original article [1] and/or in the book by Bunker and Jensen [2], and with the mathematical fundamentals of the theory of finite groups [3–5]. Basic concepts associated with these topics are not repeated here. In addition, the references are not exhaustive, but instead cite representative works the author is familiar with.

The reader is assumed to be quite familiar with point groups and their application to molecular spectroscopic problems. The PI groups for many molecules with LAMs contain a number of operations that correspond exactly to point-group operations for some equilibrium conformation of the molecule or for some intermediate conformation along the LAMs. For such PI operations it is convenient to make use of the very familiar language and ideas of point-groups. Even for PI operations that do not correspond to point-group operations, the author (when trying to think intuitively) finds it convenient to visualize them as "point-group operations applied to only part of the molecule," i.e., as rotations and reflections applied to only certain functional groups. Thus, while

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permutation–inversion operations and their algebraic consequences are taken as the fundamental and definitive symmetry operations in this article, pictorial and intuitive understanding can be gained by discussing some properties of the PI operations using point-group ideas.

The words “strategies and recipes” are shorthand expressions meant to indicate that: (i) This article does not contain a collection of ready-to-use group-theoretical results for various molecules, but rather attempts to describe how to obtain such results. (ii) Only the author's preferred way of thinking and preferred schemes for avoiding mathematical inconsistencies are presented. Many other ways of approaching this problem can be found in the literature, but they are not discussed here. (iii) Only the procedures themselves will be presented. For mathematical underpinnings, the reader must consult the references. (iv) Some qualitative discussion is given of what can go wrong, and why the author therefore favors a given way of doing things.

The complexity and ambiguity of the general problem addressed here is illustrated by the following statements: (i) The same feasible PI group, G_{36} , is derived for the molecules $\text{CH}_3\text{--C}\equiv\text{C--CH}_3$ (dimethylacetylene), $\text{CH}_3\text{--O--CH}_3$ (dimethylether), and $\text{CH}_3\text{--NH--CH}_3$ (dimethylamine). (ii) As can be seen more clearly using ball-and-stick models, dimethylacetylene, with its linear carbon chain and coaxial methyl rotors, has one LAM (an internal rotation of one methyl group against the other); dimethylether, with its bent C–O–C skeleton, has two LAMs (the internal rotation of each methyl group against the C–O–C plane); and dimethylamine, with its pyramidal nitrogen bonds, has three LAMs (the internal rotation of each methyl group against the C–N–C plane and an “inversion” motion taking the amino hydrogen from one side of this plane to the other). (iii) The quantum mechanical (SAV–LAM–rotation) energy levels and their associated tunneling splittings, etc. will obviously be very different for these three molecules, so how do we “go beyond” the G_{36} character table to obtain spectroscopically useful symmetry labels, selection rules, etc. For example, how do we obtain symmetry labels and selection rules for the LAM problem by itself and for the rotational problem by itself.

The answer to this question is complicated, because: (i) The bulk of our spectroscopic experience is based on the fact that it is possible to set up a general vibration–rotation formalism for essentially all molecules containing only SAVs by: (a) locking a molecule-fixed axis system to the principal-axis directions of the equilibrium structure [6], and then (b) treating all displacements from the equilibrium configuration as infinitesimal [7]. The orientation of the molecule-fixed axis system in the laboratory defines the rotational (Eulerian) angles. The vibrational displacements, because they are infinitesimal, can all be lumped together and treated simultaneously by a set of linear algebra techniques, e.g., Wilson's FG matrix formalism [7]. The mathematical simplicity of this SAV-rotation problem, and the universality of many of its main results, gives us a false sense of security. (ii) When LAMs are present, the principal moments of inertia are in general no longer nearly constant in direction or magnitude, so the concept of a molecule-fixed principal axis system loses some of its usefulness. This prompts different investigators to define their molecule-fixed axis systems in different ways. The group-theoretical symmetry properties of the components of the total angular momentum operator in the molecule-fixed axis system depend on how a given investigator chooses to lock this axis system to the molecule, so these symmetry properties become investigator-dependent. The pure rotational selection rules will therefore also be investigator-dependent. While this appears at first to be ridiculous, it must be remembered that interaction of the LAMs with rotation often gives rise to large contributions to the energy levels (via tunneling splittings, Coriolis interactions, etc.), so that the concept of pure rotational selection rules also loses some of its usefulness in molecules with LAMs.

(iii) LAMs are almost never well described by a perturbed harmonic oscillator formalism, either because the displacements are so large that anharmonic “perturbations” become comparable to harmonic effects, or because tunneling through various barriers leads to a splitting of the LAM vibrational energy levels. These difficulties mean, at least at the present time, that almost every new combination of LAMs in a molecule must be treated quantum mechanically as a special case, and that group-theoretical symmetry considerations will often be investigator-dependent, even when the same PI group is used.

2. Recipe for applying permutation–inversion operations

Many spectroscopists reading this article will already have carried out Task (i) in the introduction, i.e., they will already have a good guess for the feasible PI group appropriate for their molecule, either because the molecule has been discussed before in the literature, or because they have read parts of Ref. [2]. Since the effects of PI operations are central to the whole discussion here, we define various conventions needed for concrete applications of PI group operations before discussing determination of the PI group.

Permutations are conveniently represented by cycles of the form (1245); the inversion is represented by a “star” [1]. The precise meaning of these symbols in the present article is illustrated by their application to the following functions, where X_i , Y_i , Z_i are variables representing the laboratory-fixed Cartesian coordinates of atom i .

$$(1245)f(X_1, Y_1, X_2, Y_3, Z_5) \equiv f(X_2, Y_2, X_4, Y_3, Z_1) \quad (1a)$$

$$(357)^*f(X_1, Y_1, X_2, Y_3, Z_5) \equiv f(-X_1, -Y_1, -X_2, -Y_3, -Z_5) \quad (1b)$$

$$(1245)[X_2 + X_1^2 - Y_3^3 + Z_5^4 - Y_1^5] \equiv [X_4 + X_2^2 - Y_3^3 + Z_1^4 - Y_5^5] \quad (1c)$$

$$(357)^*[X_2 + X_1^2 - Y_3^3 + Z_5^4 - Y_1^5] \equiv [-X_2 + X_1^2 + Y_3^3 + Z_7^4 + Y_1^5]. \quad (1d)$$

In Eqs. (1a) and (1b) the variables are ordered by atom subscript; in Eqs. (1c) and (1d) they are ordered by increasing exponent, to illustrate the point that (1245) seeks out variables with atom 1 subscripts wherever they may be in the original function and replaces them by variables with atom subscript 2, seeks out all atom 2 subscripts in the original function and replaces them by the subscript 4, etc.

If several permutations are to be applied in succession, e.g., (123)(124)(23), we first apply the permutation on the right, then apply the permutation in the middle, and finally the permutation on the left, in the same way that sequences of other operators are conventionally applied to a function. A recipe for quickly carrying out multiplications is given in Appendix A.

The procedure illustrated in Eqs. (1) applies to drawings as well as to functions. If the original configuration had atoms 1,2,3,4 on the coordinate axes in the XY plane as shown in Fig. 1(a), then this figure can be represented by the function $\text{Fig}(X_1 = -1, Y_1 = 0, X_2 = 0, Y_2 = -1, X_3 = +1, Y_3 = 0, X_4 = 0, Y_4 = +1)$, in which the various Cartesian-coordinate variables are given numerical values. The figure obtained after applying (1234) is

$$\begin{aligned} (1234)\text{Fig}(X_1 = -1, Y_1 = 0, X_2 = 0, Y_2 = -1, X_3 = +1, \\ Y_3 = 0, X_4 = 0, Y_4 = +1) \\ = \text{Fig}(X_2 = -1, Y_2 = 0, X_3 = 0, Y_3 = -1, X_4 = +1, \\ Y_4 = 0, X_1 = 0, Y_1 = +1) \\ = \text{Fig}(X_1 = 0, Y_1 = +1, X_2 = -1, Y_2 = 0, X_3 = 0, \\ Y_3 = -1, X_4 = +1, Y_4 = 0). \end{aligned} \quad (2)$$

Note that changing the order in which the “pieces between commas” (i.e., $X_i = \text{constant}$, etc.) are written in the function defined in Eq. (2) does not change the figure to be drawn. Eq. (2) leads to Fig. 1(b), where atom 2 has gone to the position originally occupied by atom 1. The replacement of the coordinate variables of atom 1 by

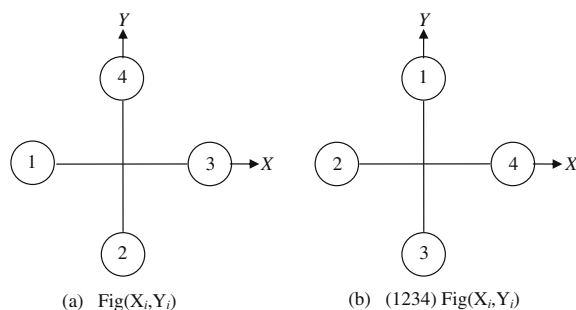


Fig. 1. Illustration of the effect of (1234) on a function of the laboratory-fixed coordinates X_i , Y_i of the atoms $i = 1, 2, 3, 4$, which for this example is the function describing how to draw the figure shown in (a): $\text{Fig}(X_1 = -1, Y_1 = 0, X_2 = 0, Y_2 = -1, X_3 = +1, Y_3 = 0, X_4 = 0, Y_4 = +1)$. The permutation (1234) as defined in Eq. (2) involves a cyclic exchange of the coordinate variables, i.e., $(1234) \text{Fig}(X_1 = -1, Y_1 = 0, X_2 = 0, Y_2 = -1, X_3 = +1, Y_3 = 0, X_4 = 0, Y_4 = +1) = \text{Fig}(X_2 = -1, Y_2 = 0, X_3 = 0, Y_3 = -1, X_4 = +1, Y_4 = 0, X_1 = 0, Y_1 = +1) = \text{Fig}(X_1 = 0, Y_1 = +1, X_2 = -1, Y_2 = 0, X_3 = 0, Y_3 = -1, X_4 = +1, Y_4 = 0)$. This has the effect of sending atom 1 to the previous position of atom 4, etc., as shown in (b), which is the opposite of what would be obtained if coordinate values (parameters) were exchanged instead of coordinate variables.

the coordinate variables of atom 2, as required by the present definition of (1234), turns out to be equivalent to the replacement of *numerical values* for the coordinates of atom 2 by the numerical values for atom 1. This result is just opposite to that defined for (1234) in many other works.

Why would one want to use a seemingly counter-intuitive definition? The answer to this question concerns the interplay between geometrical (pictorial) and algebraic thinking for problems of symmetry. The author strongly believes that geometrical thinking, which essentially involves permuting *numerical values* for the atom position variables, i.e., moving an atom from $(x, y) = (1, 0)$ to $(x, y) = (2, 3)$, should be used only for inspirational hints of what to do next, and that algebraic operations on the *variables* of the problem, as defined in Eqs. (1) and (2), should be used for the derivation of all theoretical results. This is the approach that will be followed here. Many spectroscopists express mild or strong disapproval of favoring algebra over geometry, but: (i) It is nearly impossible for two investigators, each waving his/her own arms in some ostensibly geometrically meaningful way in multidimensional space, to understand in precise mathematical detail what the other one is saying. It is, however, almost trivial to check another investigator's algebra against one's own. (ii) Much of the derivation of selection rules and energy splitting patterns in the presence of multidimensional tunneling paths, etc. depends on paying close attention to phase factors. It is difficult to keep track of complicated phase-factor changes across a set of pictures. It is almost trivial to keep track of such things with the help of equations corresponding to a sequence of variable transformations. (iii) The principal use of group theory in quantum mechanics is to determine selection rules by examining the behavior of a multi-dimensional definite integral after some change of variables in that integral. If these variable changes are to be useful, one must in general insure that both the Hamiltonian operator and the definite integral operator remain invariant. This is best demonstrated algebraically, particularly for Hamiltonians and integrals involving the complicated, relatively unfamiliar, and sometimes multiply valued curvilinear coordinates that often arise when treating LAM problems.

3. Recipe for finding the permutation-inversion group [1,2]

3.1. Long procedure

Make two identical ball-and-stick models of the equilibrium configuration and tape numbers or letters to each atom as labels.

Keep one model as the reference and put the second model along side it in "the same orientation," i.e., so that the two models and all their atom labels are related by a simple translation. Ball-and-stick models can be replaced by careful drawings with labeled atoms, though care must be taken to properly indicate the locations of atoms above and below the plane of the paper.

It is simplest to begin by finding the PI equivalents of all point-group operations of the equilibrium configuration. (i) Carry out each proper rotation from the point-group character table for this equilibrium shape on the second model, and then write down, from an inspection of how the atom labels have changed, the appropriate permutation cycles. In principle, great care should be taken to write down the permutation cycles so that they are consistent with Eq. (2). But in practice, if all PI operations are eventually to be found and verified, such care is not needed, since lack of care at this stage will only lead to "confusing" a PI-group element with its inverse. (ii) Carry out each sense-reversing operation from the point-group character table on the second model, which will often require taking the model partially apart and putting it back together again in a new, mirror-image or inverted configuration. Write down the resultant permutation cycles and add a *. There are no sense-reversing operations in the point group for a chiral molecule.

A convenient check on the PI operations found above can be described using the concept of a "framework." A framework is a ball-and-stick model with each atom having a different number painted on it. Two frameworks are different if their ball-and-stick models cannot be superimposed with all atom numbers matching. Two frameworks are chemically equivalent (and isoenergetic) if they are indistinguishable when the atom numbers are removed. It turns out that PI operations corresponding to point-group operations for a molecule in a given framework never take the molecule from that framework to another. This fact is obvious for the proper rotations of the point group, since they are defined to be nothing more than overall rotations of the given framework. This fact is less obvious for the sense-reversing operations, because they are defined to be exactly those point-group operations which do in fact generate a mirror image of the original object. Indeed, the permutation part of the PI operation associated with a given sense-reversing point-group operation will also generate a mirror image of the original framework, but the required * then generates a mirror image of the mirror image, which takes the molecule back to its original framework. After checking to make sure that no new frameworks are generated by the PI operations found in steps (i) and (ii) above (changing frameworks is not a feasible operation for "rigid" molecules), we are finished with the point-group considerations appropriate for the equilibrium configuration.

We must now deal with the LAMs. In most molecules of interest to high-resolution molecular spectroscopists, the LAMs correspond to tunneling processes (occasionally with almost no barrier) between different, but chemically equivalent, frameworks, and these are the only types of LAMs considered in this article (an example of LAMs not satisfying this criterion are those associated with chemical isomerizations). Thus: (iii) Carry out the first of the chemically feasible large-amplitude tunneling motions on the second model. If the LAM-transformed shape can still be superimposed on the original by only an overall rotation plus translation, do this and write down the resultant permutation of atom labels. The permutation found in this way will not be unique if more than one overall rotation brings the "pre-LAM" and "post-LAM" shapes into coincidence. When the umbrella motion is carried out in ammonia, for example, with hydrogens numbered 1, 2, 3, the rule above will yield the three permutations (12), (23) and (31), corresponding to the fact that any one of these permutations takes ammonia from its "left-handed" framework to its "right-handed" framework. For chiral equilibrium configurations, some large-amplitude motions may

result in a post-LAM shape that is a non-superimposable mirror image of the pre-LAM shape. In that case, make a mirror image of the post-LAM framework, compare atom labels after superposing the post-LAM's mirror image on the original framework, write down the appropriate permutation and add a *. Continue the procedure for all large-amplitude tunneling motions that are “feasible” in the Longuet-Higgins sense [1].

After finishing the pictorially driven steps (i)–(iii), find all remaining PI operations in the group by examining algebraically all powers and products of the PI operations found in steps (i)–(iii).

3.2. Short procedure

(See the example in Appendix B) Try to guess a set of generators (generating operations) for the PI group, and determine PI operations as in steps (i)–(iii) above, but only for the generators. Then generate the whole group of PI operations by taking all algebraic powers and products of the generators, using the multiplication procedure of Eq. (A.1). Make sure (by chemical intuition) that you have not forgotten a feasible permutation–inversion or included a non-feasible one.

3.3. Shortest procedure

It is tempting to avoid the hassle of making two ball-and-stick models or the tedium of making a large number of carefully labeled molecular drawings, by deciding to investigate all of these PI operations in one's head. This procedure does not work well for the author.

4. Recipe for finding the character table of the PI group [3–5]

Task (ii) of the introduction begins in this section. This task can in principle be avoided entirely. If the resultant PI group is isomorphic to a point group, we can use the character table for that point group. If the resultant PI group is not a point group, but has been considered before in the literature, we can use the character table in the literature. A paper by Groner [8], for example, contains information on a number of larger PI groups. If the PI group is new (or apparently new) to the molecular spectroscopy literature, we can use the publically available GAP software package [9] to find the character table for that PI group as well as the nuclear-spin statistical weights for the particular isotopolog of the molecule under consideration. The author has not personally used the GAP package (which was kindly brought to his attention by a referee), but according to its developers [9], the input information consists of the generators of the PI group to be considered and the nuclear spins of the atoms in the molecule, and only a few seconds is required on a personal computer to go from this input to an output containing the character table and statistical weights. If one of the options in this paragraph is chosen, the reader can skip the rest of this section and go directly to Section 5.

Only if one wishes to check someone else's character table (which is sometimes a good idea), or if one wishes to understand in more detail what is going on in the black boxes of the previous paragraph (which is sometimes enjoyable), will it be necessary to follow the various steps outlined in the rest of this section for making an old-fashioned hand calculation (the example in Appendix B illustrates these steps in more detail).

Determine the classes of your PI group by computing all triple products of the form

$$P = X^{-1}QX. \quad (3)$$

Start with a given element Q and let X run through all elements of the group. Then Q and all the elements P generated by Eq. (3) are in

the same class. This is a very laborious procedure when carried out by brute force. It is often much easier to accomplish if one makes use of the generating equations associated with the generating operations, as in Appendix B.

From the class structure of the group, one can determine the structure of the character table. The number of irreducible representations (i.e., the number of symmetry species) is equal to the number of classes. The dimensions d_i of the irreducible representations must satisfy the equation

$$\sum_i d_i^2 = g, \quad (4)$$

where the summation index i runs over all species and g is the number of elements in the group. Sometimes the integers d_i satisfying this equation are unique. Sometimes they are not. For the example in Appendix B, the number of classes in the group is 6 and the number of elements is 12, so we are looking for six integers d_i . Since $g = 12$, $d_i \geq 4$ is impossible. One $d_i = 3$ and one $d_i = 2$ is also impossible. Even one $d_i = 3$ and five $d_i = 1$ is not possible. By considering various combinations of $d_i = 2$ and $d_i = 1$, we find that only the combination of two $d_i = 2$ and four $d_i = 1$ satisfies Eq. (4), so we are looking for four one-dimensional (1D) and two 2D irreducible representations.

We seek the characters of these six irreducible representations by guessing at small basis sets that might span an irreducible representation. The elements of the example group G_{12} in Appendix B are listed at the top of Table 1. As a first guess, let us see what the characters for a 1D basis set consisting of a single numerical constant might be. Since a constant is invariant to all PI elements of the group (which, as mentioned earlier, act only on variables), the character must be +1 for all elements of the group. This species is normally called the totally symmetric representation and is often represented by the symbol A_1 , as shown in the first row of Table 1. As a guess for the basis of another 1D representation, we might try the symmetrical sum of the laboratory-fixed X coordinates of the three hydrogens in CH_3F : $X_1 + X_2 + X_3$. This function obviously has the character +1 for permutations of G_{12} with no * and the character –1 for permutations with a *, as shown for the irreducible representation A_2 in Table 1. As a guess for a 2D basis set, try the pair of “rather symmetrical” sums involving $\varepsilon \equiv \exp(2\pi i/3)$, i.e., $X_1 + \varepsilon X_2 + \varepsilon^2 X_3$ and $X_1 + \varepsilon^2 X_2 + \varepsilon X_3$. We find for E the character +2, for (123) and (132) the character –1, and for (12), (23), and (31) the character 0. Similarly, for E^* the character is –2, for (123)* and (132)* the character is +1, and for (12)*, (23)* and (31)* the character is 0. This species is called E_1 in the third row of Table 1.

All these characters pass the test for an irreducible representation, i.e., the sum of the squares of the characters for a given species taken over all elements of the group is equal to the order g of the group. It is necessary to perform this test on every set of characters obtained from the guessed basis sets. If the test fails, the basis set contains too many, too few, or poorly designed functions and must be discarded.

Looking for another species, without guessing at a new basis set, see if the direct product $A_2 \times E_1$ gives a new irreducible representation. Indeed, it gives the characters shown for E_2 in the fourth row of Table 1. We are still missing two 1D irreducible representations. As a guess (using a second method that does not involve designing a new basis set), see what the 4D reducible representation corresponding to $E_1 \times E_1$ contains. It contains the already found A_1 and E_2 irreducible representations each once, but also contains a new one, shown as A_3 in the fifth row of Table 1. As another guess, try $A_2 \times A_3$, which indeed gives the last 1D irreducible representation, shown as A_4 in the last row of Table 1. Comparison of this character table with those for known point groups shows that G_{12} of this example is isomorphic with C_{6v} , D_6 , D_{3h} , and D_{3d} .

Table 1
Character table for G_{12} ^a.

	E	(123) (132)	(12) (23) (31)	E [*]	(123) [*] (132) [*]	(12) [*] (23) [*] (31) [*]	How obtained ^b
A ₁	1	1	1	1	1	1	Basis set = {1}
A ₂	1	1	1	−1	−1	−1	Basis set = {X ₁ + X ₂ + X ₃ }
E ₁	2	−1	0	−2	1	0	Basis set = {X ₁ + εX ₂ + ε ² X ₃ , X ₁ + ε ² X ₂ + εX ₃ } ^c
E ₂	2	−1	0	2	−1	0	A ₂ × E ₁
A ₃	1	1	−1	1	1	−1	E ₁ × E ₁ − A ₁ − E ₂
A ₄	1	1	−1	−1	−1	1	A ₂ × A ₃

^a See Section 4 and Appendix B.

^b See Section 4 for more explanation.

^c $\varepsilon \equiv \exp(2\pi i/3)$, so that $\varepsilon^2 = \varepsilon^{-1} = \varepsilon^*$ and $\varepsilon^3 = 1$.

One should therefore seriously consider using the symmetry species symbols and character table arrangement from one of these common point groups, rather than devising an entirely new character table of one's own, as we have done here.

For checking purposes, if each element of the PI group is in the same class as its inverse, then all characters for the irreducible representations will be real. In the author's experience [10–12], this condition is sometimes not fulfilled, and then some characters are complex (as for the point groups C_3 or C_{3h} , for example). Under these conditions it is often convenient to use separable (reducible) representations with real characters for many molecular symmetry applications, but this topic will not be discussed here.

5. Definition of molecule-fixed coordinates

So far we have been working only with laboratory-fixed Cartesian coordinates for the atoms in the molecule. Task (iii), which involves finding the algebraic connection necessary to go from the easily understood laboratory-fixed Cartesian coordinates (X_i , Y_i , Z_i) for each particle in the molecule to some set of translational, rotational, LAM, and SAV coordinates that are spectroscopically appropriate for the molecule under consideration, begins in this section. This set will be referred to here by the shorthand expression “molecule-fixed coordinates.” Task (iii) is probably the most important and the most difficult challenge in any advanced application of PI groups.

For readers wanting more detail on how the general ideas associated with tasks (iii) and (iv) can be applied to a concrete example, it may be helpful to refer to Section 4.2 of Ref. [12], which deals with the case of three equivalent methyl rotors in $(CH_3)_3SnCl$, or to Section 3 of Ref. [10], which deals with the case of two equivalent methyl rotors and one “generalized inversion motion” (see Section 13.4 below) in $(CH_3O)_2P(=O)CH_3$. Note, however, that the full group-theoretical treatment of both of these molecules requires use of some general ideas not covered in this paper (see Section 17 below).

Speaking simply, we want at this point to find the equation that gives the correspondence between coordinates in the laboratory-fixed Cartesian axis system and coordinates “attached” to the molecule. With such an equation in hand, which in fact defines the molecule-fixed coordinates mathematically, we can check the transformation properties of different molecule-fixed coordinates under the symmetry operations and, if desired, derive the exact kinetic energy operator in the molecule-fixed coordinates. We can also: (i) determine the symmetry species of our chosen basis set functions, (ii) generate symmetry-allowed LAM-rotation Hamiltonian operators; and (iii) determine selection rules for the Hamiltonian and dipole-moment operator in our chosen basis set.

Why is it so desirable to find the equation described above? As seen in Section 2, the recipe for applying PI operations to laboratory-fixed Cartesian coordinates is simple, and involves only

exchanging particle subscripts with or without a change of sign of the Cartesian coordinates for all particles. As will be seen below, the much more complicated recipe for the effects of PI operations on a given choice of molecule-fixed coordinates can be determined with confidence only after these coordinates have been mathematically related to the laboratory-fixed Cartesian coordinates. This is equivalent to saying that symmetry properties of vibrational and rotational basis functions expressed in molecule-fixed coordinates can be determined only after these coordinates have been precisely defined. In the author's opinion (though this opinion is not universal), dealing in some mathematically precise way with the concepts in the rest of this section is the barrier that must be crossed if a practicing spectroscopist wishes to progress from “applications” to “advanced applications” of PI group theory to his/her molecule.

Since molecule-fixed coordinates for LAM problems can become very complicated, we content ourselves here with some compromise between convenience of mathematical definition, and accuracy of description of the true LAM. This reflects the general philosophy of carrying out group theoretical algebra on relatively simply defined molecule-fixed coordinates, and then compensating in later energy level calculations for any inaccuracies in LAM description by introducing into the Hamiltonian operator appropriate symmetry-allowed “higher-order” distortion and interaction terms.

In spite of the emphasis on algebraic methods in this article, there is still a place for pictorial thinking at the beginning of Task (iii), as summarized by the following outline. (i) Keep the molecule-fixed axis system at the instantaneous center of mass. Otherwise you cannot separate off translations of the molecule. (ii) Look at the LAMs to see if any part of the molecule is unaffected by them. If there is such a part, consider locking the molecule-fixed axis system to that part. (iii) If there is no part of the molecule that does not change, see if some symmetry element is preserved during one of the LAMs (we are studying symmetry, after all), e.g., for internally rotating HO–OH a C_2 axis is always present, for inverting NH_3 a C_3 axis is always present, for H transfer in malonaldehyde, a C_s plane is always present. Consider putting one of the molecular axes along a C_n axis or perpendicular to a symmetry plane, etc. (iv) If some “transition state” has high symmetry, consider locking the molecular axes in a symmetrical way to that transition state. (v) For near prolate rotors try to keep the z axis pointing nearly along the principal a axis during most of the LAMs. We consider next how these pictorial ideas can be represented by algebraic equations.

6. Recipe for defining the center-of-mass coordinates R

For spectroscopic study of an isolated molecule in free space it is convenient to separate off the motion of the center of mass. As is

well known, this is conveniently done by defining three linear combinations of the Cartesian coordinates, which are then collected in one vector equation

$$\mathbf{R} \equiv (1/M) \sum_i m_i \mathbf{R}_i. \quad (5)$$

In this equation \mathbf{R} is a 3×1 vector containing the laboratory-fixed X, Y, Z coordinates of the molecular center of mass, M is the total mass of the molecule, m_i is the mass of atom i , and \mathbf{R}_i is a 3×1 vector containing the laboratory-fixed X_i, Y_i, Z_i coordinates of atom i .

In p -H₂ crystals or other matrix hosts, it may not be advisable to separate off translation of the center-of-mass, since this motion then takes place in a cage, and thus affects the host's phonon spectrum, i.e., the three translations of the guest molecule in general mix with various phonons of the host matrix, and via that mixing, with various low-frequency modes of the molecule itself. We will not consider this complication here.

7. Recipe for defining the overall rotational coordinates χ, θ, ϕ

For an isolated molecule in free space it is often convenient to separate overall rotation from the other motions by defining a molecule-fixed axis system whose orientation with respect to the laboratory-fixed axis system determines the molecular rotational angles. Again, this may not be advisable in matrix hosts, since the overall molecular rotations are then hindered, and form part of the librational phonon spectrum, with the consequent possibility of mixing with low-frequency molecular vibrations. Even for a molecule in free space, the concept of overall molecular rotation may lose its meaning if the bonds between atoms are not long-lasting enough or not sufficient in number to define a “molecular shape.” This can happen, for example, in a very loosely bound bimolecular complex A–B or in a metal droplet. In the former case, it may be convenient to use two rotating molecular axis systems, one fixed in A and one fixed in B, with vector addition used to define the total angular momentum components. In the latter case, the total angular momentum should probably be treated as it is in atoms, i.e., without introducing a molecule-fixed axis system at all.

In this article we restrict consideration to molecules where the number of long-lasting bonds is large enough that picturing the subset of tightly bonded atoms in the molecule as a rotating nearly rigid body still has some meaning. The problems of this subsection are thus: (i) to somehow define an axis system fixed in the molecule, and then (ii) to relate its orientation to the orientation of the laboratory-fixed axis system.

The second goal, which we consider first, is traditionally accomplished via the definition of a direction-cosine matrix. The complication here is that a very large number of direction cosine matrices have been defined in the scientific literature of various countries, disciplines, and eras, each with a slightly different arrangement of sines, cosines, and minus signs, and with slightly different symbols for the three Eulerian angles. To avoid inconsistencies over the course of a long career (and thereby a trail of incorrect results) a spectroscopist should ideally make the choice of direction cosine matrix only once in his/her lifetime and then stick with it. In this article we use the direction cosine matrix given in Appendix I of the book by Wilson et al. [7], which then makes all of the vibration-rotation results (equations) in that book usable without change. We thus choose:

$$S^{-1}(\chi, \theta, \phi) = \begin{bmatrix} +c\chi c\theta c\phi - s\chi s\phi & -s\chi c\theta c\phi - c\chi s\phi & +s\theta c\phi \\ +c\chi c\theta s\phi + s\chi c\phi & -s\chi c\theta s\phi + c\chi c\phi & +s\theta s\phi \\ -c\chi s\theta & +s\chi s\theta & +c\theta \end{bmatrix}, \quad (6)$$

where $c\chi$ and $s\chi$ represent $\cos\chi$ and $\sin\chi$, respectively, etc. The rows of this direction cosine matrix are labeled by laboratory-fixed axes X, Y, Z . The columns are labeled by the molecule-fixed axes x, y, z . This matrix does not have a standard name in the spectroscopic literature, but we call it $S^{-1}(\chi, \theta, \phi)$, as indicated in Eq. (6). We interpret it to mean that if the molecule-fixed components x, y, z of a given vector are contained in the column vector \mathbf{v} , then the laboratory-fixed components X, Y, Z of that same vector are contained in the column vector $\mathbf{V} = S^{-1}(\chi, \theta, \phi) \mathbf{v}$. This is another example of the algebraic approach used here (the geometric approach would tend to first visualize S^{-1} using the several intersecting planes in Fig. I-2 of [7], and then interpret S^{-1} as rotating a vector pointing in one direction into a vector pointing in some other direction). Note for future use, that because the determinant of S^{-1} is +1, it can only relate the coordinates in one right-handed (left-handed) coordinate system to those in another right-handed (left-handed) system. We consider here only right-handed coordinate systems. A collection of useful mathematical properties of the direction cosine matrix in Eq. (6) is given in Appendix C.

Returning to the first goal, i.e., the question of how best to fix an axis system in the molecule (which often deserves a reasonable amount of thought), we note that two possible definitions are easy to understand: (i) We can use an instantaneous principal axis system. (ii) We can use the instantaneous bond between two chosen atoms to define the z axis, and the instantaneous bond from one of these to a third atom to define the xz plane. For most microwave studies, all SAVs are removed from explicit consideration, and their effects are taken into account by some sort of (usually implicit) contact transformation followed by (again usually implicit) small-amplitude vibrational averaging of all coefficients for the LAM-rotation terms. When SAVs are ignored and when none of the three atoms chosen for special treatment in (ii) are exchanged by the PI operations with other atoms, then the two coordinate systems described above can be quite useful. When SAVs are explicitly considered, however, as is necessary when symmetry species, selection rules, etc. are desired for infrared spectra involving SAV excited states, then the two coordinate systems defined above have the conceptual disadvantage that the SAVs introduce a high-frequency vibrational jitter into the rotational variables.

8. Reasons for restricting consideration to LAM-rotation problems at this point

It turns out that a slight generalization of the Eckart condition [13] together with the Sayvetz conditions [14] can be used to define the molecule-fixed axis system when SAVs (and especially their excited states) are to be considered, but there is a fundamental problem associated with the SAV displacement vectors [15], as well as with molecular orbitals for the electrons in molecules with LAMs, that leads to group-theoretical ambiguities. Consider as an example the vibrational displacement vector for the carbon atom in methanol CH₃OH [16]. Should this displacement vector be defined so that it remains constant in direction with respect to the COH plane as the methyl top rotates, or should it be defined to remain constant in direction as viewed from the rotating CH₃ top? It turns out that PI group theory is flexible enough to deal with either definition for this and other displacement vectors in the molecule, but the symmetry species determined for the SAV vibrational degrees of freedom change when the definition changes. This change in symmetry species is easier to imagine in the somewhat exotic molecule CH₃–C≡C–C≡C–CHO. We can then ask if the best zeroth-order small-amplitude vibrational basis set for the stretches of the methyl group should consist of one non-degenerate A and one degenerate E vibration, as would make sense if the methyl group cannot feel any effects from the distant aldehyde group, or

should this basis set consist of two in-plane A' stretches and one out-of-plane A'' stretch, as would be appropriate if the methyl group can clearly feel effects of the planar aldehyde group.

A similar problem obviously arises for molecular orbitals expressed as a linear combination of atomic p orbitals, since the direction of a p orbital in a molecule with two parts rotating against each other can be defined to follow one part or the other.

While it will be disappointing to many readers to abandon infrared (vibrational) and visible/UV (electronic) transitions at this point, it is necessary to limit this already long pedagogical article by excluding electronic motions and SAVs from in-depth consideration.

9. Recipe for a general equation

It is possible to write a widely applicable general equation relating laboratory-fixed (\mathbf{R}_i) and molecule-fixed coordinates under the four assumptions that: (i) we want to separate off translation of the center of mass (\mathbf{R}), (ii) we want to define a unique molecule-fixed x, y, z axis system, whose orientation is described by the Eulerian angles χ, θ, ϕ in the direction cosine matrix of Eq. (6), (iii) we want to define some LAMs, represented by the curvilinear coordinates γ_j , and (iv) we want to define some SAVs, described by infinitesimal Cartesian atomic displacement vectors \mathbf{d}_i in the molecule-fixed axis system. Spectroscopists faced with a molecule not satisfying these four assumptions will require a modified version of the formalism below (as examples of molecules that do not satisfy one or more of these four assumptions, we recall here the three types briefly discussed in Sections 6 and 7, i.e., molecules in a matrix cage, bimolecular complexes A-B within which the A and B molecules each carry out nearly-free three-dimensional rotation, and atomic droplets with no long-lasting interatomic bonds). Many of the general principles can still be applied, but the details of the rest of this paper are only applicable to LAM-rotation problems satisfying the four requirements in this paragraph.

The following two expressions are suggested by assumptions (i) and (ii) above:

$$\mathbf{R}_i = \mathbf{R} + \text{laboratory-fixed Cartesian coordinates relative to the center of mass} \quad (7a)$$

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi)[\text{molecule-fixed Cartesian coordinates in a center-of-mass system}] \quad (7b)$$

The molecule-fixed Cartesian coordinates of each atom i in a center-of-mass system in Eq. (7b) are then further separated into a reference configuration part \mathbf{a}_i (LAMs), which describes the (frequently large) changes in atom position as a function of the LAMs, and a SAV infinitesimal displacement vector part \mathbf{d}_i .

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi)[\mathbf{a}_i(\gamma_j) + \mathbf{d}_i] \quad (8)$$

As mentioned above, by ignoring the SAVs, we can simplify Eq. (8) to read

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi)\mathbf{a}_i(\gamma_j). \quad (9)$$

At this point a little mathematical cheating occurs, because the number of degrees of freedom on the left of Eq. (9) does not match the number of degrees of freedom on the right. We normally think of this as just setting all $\mathbf{d}_i = 0$ and then ignoring them. The uncertainty principle then requires, however, that all momenta in the molecular Hamiltonian conjugate to the \mathbf{d}_i become infinite, and these infinities should in principle be shown mathematically to be harmless before proceeding. A treatment of the \mathbf{d}_i which avoids

setting them to zero requires the introduction of constraints, as briefly discussed in Appendix D. We shall be concerned for most of the rest of this article only with definitions and transformations of the “ \mathbf{d}_i -free” variable set ($\mathbf{R}, \chi, \theta, \phi, \gamma_j$) on the right of Eq. (9).

One may be tempted to ask at about this point: Can’t we just skip this tedious discussion of coordinates and go straight to the desired group-theoretical results? Such a simplified and direct approach may indeed exist, but the author doesn’t know how to find it, so the formulation of that approach is left as an exercise for the reader.

Before proceeding, it is necessary to emphasize what is meant mathematically by the word “variable” in this article. Consider putting all symbols in every equation into one of three mutually exclusive categories, i.e., consider classifying all symbols as “variables,” “parameters,” or “functions of the variables and/or parameters.” Variables are then the degrees of freedom with respect to which differentiation is carried out by the momentum operators in the Hamiltonian, or equivalently the degrees of freedom with respect to which integration is carried out in the definite integrals arising when quantum mechanical matrix elements are evaluated. Parameters is a shorthand term meant to include true constants (like π) as well as molecular constants occurring in the Hamiltonian (like equilibrium bond lengths and atomic masses). The group-theoretical variable transformations in the partial differential operator representing the quantum mechanical Hamiltonian and in the definite integrals representing matrix elements, do not ever involve transforming the parameters. Essentially no one would be tempted to change π into 2 during some group theoretical operation, but the temptation is significantly greater when both quantities are represented by letters. For example, we should consider changing b_1 into b_2 as part of a group-theoretical transformation only if both are variables.

We note in passing, that this same distinction between parameter and variable is made when one says that the electronic wavefunction of a diatomic molecule contains the internuclear distance r as a parameter. The mathematical implication is that the fixed-nucleus electronic Hamiltonian problem does not involve differentiation or integration with respect to r . The internuclear distance only becomes a variable in the second stage of the Born–Oppenheimer approximation, when the vibrational Hamiltonian is considered.

10. Generalized recipe for transformation of the variables in a function

Before considering PI variable transformations for the molecule-fixed coordinates in detail we must give a precise definition of the recipe for how a given transformation of variables T is to be carried out on a given function f of these variables. This is necessary because a number of different conventions exist (which we do not discuss here). To describe the recipe used here, which is just a generalization of that described in section 2, it is convenient to distinguish between old (pre-transformation) variables, and new (post-transformation) variables. Begin with a function of the old variables

$$f(\mathbf{w}_{old}, \mathbf{x}_{old}, \mathbf{y}_{old}, \mathbf{z}_{old}). \quad (10)$$

Define the variable transformation T by equations of the form

$$\begin{aligned} \mathbf{w}_{new} &= \mathbf{g}_w(\mathbf{w}_{old}, \mathbf{x}_{old}, \mathbf{y}_{old}, \mathbf{z}_{old}) \\ \mathbf{x}_{new} &= \mathbf{g}_x(\mathbf{w}_{old}, \mathbf{x}_{old}, \mathbf{y}_{old}, \mathbf{z}_{old}) \\ \mathbf{y}_{new} &= \mathbf{g}_y(\mathbf{w}_{old}, \mathbf{x}_{old}, \mathbf{y}_{old}, \mathbf{z}_{old}) \\ \mathbf{z}_{new} &= \mathbf{g}_z(\mathbf{w}_{old}, \mathbf{x}_{old}, \mathbf{y}_{old}, \mathbf{z}_{old}). \end{aligned} \quad (11)$$

Then define

$$\begin{aligned}
Tf(w_{old}, x_{old}, y_{old}, z_{old}) &\equiv f(w_{new}, x_{new}, y_{new}, z_{new}) \\
&= f[g_w(w_{old}, x_{old}, y_{old}, z_{old}), g_x(w_{old}, x_{old}, y_{old}, z_{old}), \\
&\quad g_y(w_{old}, x_{old}, y_{old}, z_{old}), g_z(w_{old}, x_{old}, y_{old}, z_{old})] \\
&= h(w_{old}, x_{old}, y_{old}, z_{old}), \quad (12)
\end{aligned}$$

i.e., every place that w_{old} occurs in f , it must be replaced by w_{new} , as given by $g_w(w_{old}, x_{old}, y_{old}, z_{old})$, etc. This replacement then yields a (frequently different) function of $w_{old}, x_{old}, y_{old}, z_{old}$, which is ready either for comparison with the original function or for a subsequent variable transformation using exactly the same procedure, but for a different transformation T_1 .

When we speak of determining variable transformations in this article, we mean constructing a table like Table 2 of [12]. The first row of the table contains the unchanged “old” variables, corresponding to (the lack of) transformation caused by applying the identity operation. These old variables are in fact the translational, rotational, and large-amplitude variables on the right of Eq. (9) (which are represented above by the four variables w, x, y, z). Each of the other rows contains the “new” variables for some given PI operation expressed explicitly in terms of the “old” (not symbolically as on the right of Eq. (11)). For the purpose of determining symmetry species, the rows in the table can be limited to one representative PI operation from each class.

11. Review of molecule-fixed coordinate transformations for rigid molecules

In this section, we work through the details of coordinate transformations caused by PI operations applied to “rigid” molecules, i.e., to molecules with no LAMs, because: (i) these transformations can be described by simple fixed rules, (ii) these transformations can be used almost without change in molecules with LAMs for PIs that correspond to point-group operations, and (iii) these transformations can serve as the basis for intuitive guesses in molecules with LAMs when we consider PI operations that correspond to point-group-like operations for only some part of the molecule.

Because the infinitesimal displacement vectors \mathbf{d}_i of SAVs in rigid molecules cause no special group-theoretical complications, we retain them in our discussion of coordinate transformation properties in this section. We do this not only for instructional purposes, but also because a knowledge of the transformation properties of the \mathbf{d}_i for the equilibrium (or other specially chosen) configuration of a molecule with LAMs (i.e., a knowledge of the point-group vibrational symmetry species and transformation properties for that configuration) frequently permits rather accurate intuitive guesses for the transformation properties of the LAM coordinates under the subset of PI operations corresponding to point-group operations for the chosen configuration.

For rigid molecules, pure permutations (i.e., permutations with no $*$) always correspond to proper rotations. In fact, permutation cycles of order n correspond to C_n about some axis, e.g., $(12) \rightarrow C_2$, $(345) \rightarrow C_3$, $(1234) \rightarrow C_4$, etc. Proper rotations are represented in this section by the letter C . Permutation–inversions (i.e., permutations with a final $*$) always correspond (for rigid molecules) to improper rotations (also often called sense-reversing operations). Sense-reversing point-group operations come in three types: mirror reflections σ in a plane, inversion i with respect to a point, and rotation–reflections S_n . In this section we represent all of these by the letter B . Unlike the case for proper rotations, the relation between permutation–inversions and improper rotations is not unique, e.g., hypothetical rigid molecules can be drawn such that $(12)(34)(56)$ corresponds to either σ or i .

For a rigid molecule, the analog of Eq. (8) becomes

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi)[\mathbf{a}_i + \mathbf{d}_i], \quad (13)$$

where the \mathbf{a}_i are constant parameters describing the equilibrium structure in its principal axis system. The algebraic formulation of transformations of the variables on the right of this equation under point-group operations is the subject of the rest of this section.

11.1. Recipe for a proper-rotation point-group operation C

For the transformation of the SAV displacements \mathbf{d}_i in Eq. (13), we follow Ref. [7], i.e., we rotate a given \mathbf{d}_i (together with the tightly attached vector connecting it to the molecular center of mass) about the center of mass until we can attach it to some other identical atom. Mathematically, the first part of the recipe is then $(\mathbf{d}_i)_{new} = C(\mathbf{d}_j)_{old}$ for some appropriate j . But how do we choose j for given i , i.e., how are the atoms i and j related, or equivalently, how do we define the integer function $j(i)$? The second part of the \mathbf{d}_i recipe is to pick j from an examination of the equation $\mathbf{a}_j = C^{-1}\mathbf{a}_i$. (If this equation cannot be satisfied, then C is not a point-group symmetry operation for the equilibrium configuration described by the \mathbf{a}_i , and C should be dropped from consideration).

For the transformation of rotational variables we follow the recipe in Refs. [17,18] and seek some triple of Eulerian angles $\chi_{new}, \theta_{new}, \phi_{new}$ such that $S^{-1}(\chi_{new}, \theta_{new}, \phi_{new}) = S^{-1}(\chi_{old}, \theta_{old}, \phi_{old})C^{-1}$. This equation can always be solved for $\chi_{new}, \theta_{new}, \phi_{new}$ (albeit sometimes only implicitly [18,19]), since the product of two rotations on the right is always a third rotation, which can then be represented by the direction cosine matrix on the left.

For the transformation of the center of mass we use the simple recipe [17,18] $\mathbf{R}_{new} = +\mathbf{R}_{old}$.

Consider for simplicity the example of a function only of $(\mathbf{R}_i)_{old}$ for atom i ,

$$f\{(\mathbf{R}_i)_{old}\} \equiv f\{\mathbf{R}_{old} + S^{-1}(\chi_{old}, \theta_{old}, \phi_{old})[\mathbf{a}_i + (\mathbf{d}_i)_{old}]\}. \quad (14)$$

The recipe above then yields for the transformation T

$$Tf\{(\mathbf{R}_i)_{old}\} \equiv Tf\{\mathbf{R}_{old} + S^{-1}(\chi_{old}, \theta_{old}, \phi_{old})[\mathbf{a}_i + (\mathbf{d}_i)_{old}]\} \quad (15a)$$

$$= f\{\mathbf{R}_{new} + S^{-1}(\chi_{new}, \theta_{new}, \phi_{new})[\mathbf{a}_i + (\mathbf{d}_i)_{new}]\} \quad (15b)$$

$$= f\{\mathbf{R}_{old} + S^{-1}(\chi_{old}, \theta_{old}, \phi_{old})C^{-1}[\mathbf{a}_i + C(\mathbf{d}_i)_{old}]\} \quad (15c)$$

$$= f\{\mathbf{R}_{old} + S^{-1}(\chi_{old}, \theta_{old}, \phi_{old})[\mathbf{a}_j + (\mathbf{d}_j)_{old}]\} \quad (15d)$$

$$= f\{(\mathbf{R}_j)_{old}\} \quad (15e)$$

Eq. (15a) is just a statement that we are going to apply the transformation T to both sides of Eq. (14). Eq. (15b) replaces old variables by new variables on the right hand side of Eq. (15a). Eq. (15c) expresses the new variables in terms of the old , using the recipe for T given at the beginning of this section. Eq. (15d) gives the results of letting C^{-1} act on the quantities in square brackets. Eq. (15e) notes that the expression in braces in Eq. (15d) is equal to the expression for $(\mathbf{R}_j)_{old}$.

Consider now a set of $n > 2$ atoms arranged symmetrically around a circle, i.e., atoms at the vertices of a regular n -gon, and numbered such that $C_n^{-1}\mathbf{a}_i = \mathbf{a}_{i+1}$. The reader can then easily show that the effect of T on a function of the molecule-fixed variables is equivalent to the effect of the PI operation $(123 \dots n)$ on a function of the laboratory-fixed Cartesian coordinates of the atoms. As mentioned, close analogs of this procedure can be used in molecules with LAMs to treat many cyclic permutations of the form $(123 \dots n)$.

11.2. Recipe for a sense-reversing point-group operation B

For the transformation of the SAV displacement variables, we again follow Ref. [7], i.e., we “reflect, invert, or rotation-reflect” a given \mathbf{d}_i vector to some symmetrically related atom, so that $(\mathbf{d}_i)_{new} = B(\mathbf{d}_j)_{old}$ for some appropriate j . The integer function $j(i)$ is defined by the equation $\mathbf{a}_j = B^{-1}\mathbf{a}_i$.

For the transformation of rotational variables, one is at first tempted to seek values for $\chi_{\text{new}}, \theta_{\text{new}}, \phi_{\text{new}}$ such that $S^{-1}(\chi_{\text{new}}, \theta_{\text{new}}, \phi_{\text{new}}) = S^{-1}(\chi_{\text{old}}, \theta_{\text{old}}, \phi_{\text{old}}) B^{-1}$. But this equation has no solution, since the determinants of the two S^{-1} direction cosine matrices are +1, while the determinant of the 3×3 matrix corresponding to the sense-reversing operation B is -1 . We again follow the recipe in Refs. [17,18] and seek $\chi_{\text{new}}, \theta_{\text{new}}, \phi_{\text{new}}$ such that $S^{-1}(\chi_{\text{new}}, \theta_{\text{new}}, \phi_{\text{new}}) = S^{-1}(\chi_{\text{old}}, \theta_{\text{old}}, \phi_{\text{old}}) [iB^{-1}]$. The product of the inversion i times B^{-1} is now a 3×3 rotation matrix with determinant +1, so that this equation always has a solution for $\chi_{\text{new}}, \theta_{\text{new}}, \phi_{\text{new}}$. Note that the inversion i must be considered when dealing with rotational-angle transformations for all sense-reversing operations of a rigid molecule, whether or not i is an element of the point group for that molecule. Note further that iB takes rather simple forms, since $i\sigma(xy) = C_2(z)$, $ii = E$ (the identity), and $iS_n(z) = C_2(z)C_n(z)$.

For sense-reversing operations we take [17–19] $\mathbf{R}_{\text{new}} = -\mathbf{R}_{\text{old}}$.

The recipe above then yields the following analog of Eq. (15)

$$Tf\{(\mathbf{R}_i)_{\text{old}}\} \equiv Tf\{\mathbf{R}_{\text{old}} + S^{-1}(\chi_{\text{old}}, \theta_{\text{old}}, \phi_{\text{old}})[\mathbf{a}_i + (\mathbf{d}_i)_{\text{old}}]\} \quad (16a)$$

$$= f\{\mathbf{R}_{\text{new}} + S^{-1}(\chi_{\text{new}}, \theta_{\text{new}}, \phi_{\text{new}})[\mathbf{a}_i + (\mathbf{d}_i)_{\text{new}}]\} \quad (16b)$$

$$= f\{-\mathbf{R}_{\text{old}} + S^{-1}(\chi_{\text{old}}, \theta_{\text{old}}, \phi_{\text{old}})[iB^{-1}][\mathbf{a}_i + B(\mathbf{d}_i)_{\text{old}}]\} \quad (16c)$$

$$= f\{-\mathbf{R}_{\text{old}} + S^{-1}(\chi_{\text{old}}, \theta_{\text{old}}, \phi_{\text{old}})[i][\mathbf{a}_i + (\mathbf{d}_i)_{\text{old}}]\} \quad (16d)$$

$$= f\{(-\mathbf{R}_i)_{\text{old}}\} \quad (16e)$$

Eq. (16) has essentially the same meaning in words as Eq. (15), with the main difference arising in (16d), where the 3×3 inversion matrix $i = -E$ coming from iB^{-1} changes both vectors in square brackets into negatives.

The reader can easily show for a pair of atoms 1,2 related by the inversion ($B = i$) or by a reflection ($B = \sigma$), that the transformation T on the molecule-fixed variables is equivalent to the PI operation $(12)^*$ acting on the laboratory-fixed Cartesian coordinates. A proof that S_n has the PI form $(12 \dots n)^*$ (for some atom numbering) is only slightly more complicated. The procedure above can often be used essentially without change for atoms in non-rigid molecules that do not participate in the LAMs.

The 3×3 rotation matrix associated with C^{-1} in Eq. (15) or iB^{-1} in Eq. (16) is called the equivalent rotation in Ref. [2]. Equivalent rotations are important because, as we shall see below, they determine the symmetry species of the molecule-fixed components of the electric dipole moment operator and of the total angular momentum operator, as well as the symmetry properties of the symmetric-top and asymmetric-rotor rotational basis functions.

12. Strategies for guessing equivalent rotations for molecules with LAMs

Before determining equivalent rotations, it is necessary to choose a molecule-fixed axis system for the molecule. One common method is to use the principal axes (or nearly the principal axes) of the equilibrium configuration of the molecule. For the C_s equilibrium configuration of CH_3OH , three variants of this method would correspond to putting the y axis perpendicular to the plane of symmetry, and the z axis along: (i) the principal a axis, (ii) the CH_3 symmetry axis, or (iii) the C–O bond. Another common method is to use the principal axes of a “highly symmetrical transition state” for one of the LAMs, e.g., the principal axes of the planar D_{3h} configuration of NH_3 at the top of its inversion barrier. In these cases, and in any others where some initial “reference” configuration is chosen, equivalent rotations for all PI operations contained in the point group of the chosen reference configuration can be found as described for rigid molecules in the preceding section. We consider below general strategies for determining equivalent

rotations for internal-rotation-like LAMs and for inversion-like LAMs.

The PI operation corresponding to internal rotation of a top with n symmetrically equivalent atoms is $(123 \dots n)$. If the molecule-fixed axis system is fixed to some part of the molecule external to the top, the equivalent rotation can usually be taken to be the identity E .

Some LAM motions (e.g., umbrella motions, H-transfer motions, etc.) are “of order 2,” in the sense that one application of the LAM takes the molecule from framework A to B and a second application takes the molecule from B back to A. Under these circumstances, the corresponding PI operation is also of order 2, and the equivalent rotation must therefore be either the identity or a C_2 rotation about some axis. For the C_2 case, clever choice of orientation for the molecule-fixed axes may put the C_2 axis along the x , y , or z axis, allowing use of the simple equations in Appendix C.

From the above two paragraphs, it is clear that if the PI operation for a given LAM is of order n , then the equivalent rotation must have the form of C_p about some axis, where p is one of the factors of n (including 1 and n).

For PI groups with many elements (e.g., G_{162} [12]), it will save considerable time (usually a factor equal to the ratio of the number of elements in the group to the number of generators) if one tries to find equivalent rotations only for the generators of the PI group (see Appendix B).

13. Strategies for finding LAM transformations

The guesses for equivalent rotations in the previous section must be verified by a two-step process. (i) Each equivalent rotation must be associated with a transformation of the LAMs. (ii) The combined transformation must then be substituted into the right side of Eq. (9) to verify that their combined effect does indeed produce the desired PI operation on the left of Eq. (9), analogous to what was done in Section 11 for rigid molecules. But before determining LAM transformations, we have to define the LAM coordinates. In this section we discuss strategies for defining the LAMs and for guessing at their transformations, as well as the algebraic procedure for verifying these guesses.

We note in passing, that it is possible to write small computer programs to check the algebraically derived results for changes caused by any transformation of variables on one side of an equation. It should also be possible to do and/or check much of the algebra described in this paper with software designed to carry out algebraic manipulations (provided one recognizes that possessing such software does not eliminate all necessity for careful thought and detailed understanding, as implied by the well known “garbage-in, garbage-out” warning).

13.1. Internal rotation in a one-top molecule

Internal rotations are particularly simple. To specifically indicate such LAMs we replace γ_j by the internal rotation angle α . In general we would like each of the $i = 1$ to n atoms in the top to follow the same trajectory as its neighbors, but with an angular offset of some appropriate multiple of $2\pi/n$. This can be expressed algebraically as

$$\mathbf{a}_i(\alpha) = \mathbf{a}_1[\alpha + 2\pi(i-1)/n]. \quad (17)$$

This trajectory can be made more explicit (but less general) as follows. We first choose a constant reference position \mathbf{a}_i^0 for each atom i (frequently corresponding to the equilibrium configuration in its principal axis system). Then we select the subset of atoms ($i \leq n$) that is to be rotated and define their \mathbf{a}_i^0 and their LAM-dependent positions $\mathbf{a}_i(\alpha)$ to satisfy

$$\mathbf{a}_i^0 = S^{-1}[2\pi(i-1)/n, 0, 0]\mathbf{a}_1^0 \quad (18a)$$

$$\mathbf{a}_i(\alpha) = S^{-1}(\alpha, 0, 0)\mathbf{a}_i^0. \quad (18b)$$

All other atoms ($i > n$) are defined to be unaffected by α , so that for them

$$\mathbf{a}_i(\alpha) \equiv \mathbf{a}_i^0. \quad (19)$$

As it happens, the rotations in Eq. (18) are about the z axis, which will in general not be the direction of the single bond about which internal rotation actually takes place. We have two choices. The first approach, which seems simpler to the author when the effects of numerous symmetry operations must be determined and which is therefore the approach followed in this paper, is to always start with a set of constant reference positions \mathbf{a}_i^0 that put the internal rotation axis along the z axis. We can then first do the internal rotation $R(\alpha)$ of the top about the z axis, and afterwards rotate atoms in the whole molecule (i.e., atoms in both the top and frame) to their true positions in our chosen molecule-fixed axis system using some (frequently constant) matrix Q . This procedure can be represented symbolically (although somewhat imprecisely) by defining the \mathbf{a}_i^0 structure as $|\text{top}\rangle_0 + |\text{frame}\rangle_0$, the structure with the internally rotated top as $R(\alpha)|\text{top}\rangle_0 + |\text{frame}\rangle_0$, and the rotated whole molecule as $Q[R(\alpha)|\text{top}\rangle_0 + |\text{frame}\rangle_0]$.

The other approach would be to start from constant reference positions \mathbf{a}_i^{0Q} that already have the molecule correctly oriented in our chosen molecule-fixed axis system, i.e., to start symbolically from $|\text{top}\rangle_{0Q} + |\text{frame}\rangle_{0Q}$. Since this starting point can be expressed in terms of the \mathbf{a}_i^0 structure with z along the top axis as $Q|\text{top}\rangle_0 + Q|\text{frame}\rangle_0$, it is obvious that we need to apply the rotation matrix $QR(\alpha)Q^{-1}$ to $|\text{top}\rangle_{0Q}$ to arrive at our internally rotated and correctly oriented structure $QR(\alpha)Q^{-1}|\text{top}\rangle_{0Q} + |\text{frame}\rangle_{0Q}$.

13.2. Example: One-top molecule with a plane of symmetry

Consider a C_s molecule with all atoms lying in the plane, except for a C_{3v} methyl top, which has its symmetry axis in the plane [20,21]. Choose as the reference configuration one of the three equivalent equilibrium configurations of the molecule, with the y axis perpendicular to the plane of symmetry and the z axis along to the top axis. Number the methyl top atoms as H_1, H_2, H_3, C_4 , and all other atoms as A_n with $n = 5, 6, 7$, etc. The PI group for this molecule is G_6 and its generators are (123) and (23)^{*}. If two of the other atoms A_p and A_q are out of plane, but symmetrically placed above and below the plane so they preserve C_s symmetry, then the generators of G_6 would be (123) and (23)(pq)^{*}.

The problem now is to define a functional form for $\mathbf{a}_i(\alpha)$ and then determine the equivalent rotations and transformations of α corresponding to the two generating operations.

Since the z axis lies along the top axis we can use Eqs. (18) and (19) above to describe the internal rotation motion. A complication arises because a z axis along the top axis will in general not pass through the center of mass, and Eq. (9) requires that the $\mathbf{a}_i(\alpha)$ be in a center-of-mass system. This is easily remedied by defining a center of mass vector $\mathbf{A}(\alpha)$ as

$$\mathbf{A}(\alpha) = (1/M)\sum_i m_i \mathbf{a}_i(\alpha), \quad (20)$$

and subtracting it from the $\mathbf{a}_i(\alpha)$, leading to a modified Eq. (9) which must be used in this example.

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi)[\mathbf{a}_i(\alpha) - \mathbf{A}(\alpha)]. \quad (21)$$

For the simple internal-rotation LAM considered here $\mathbf{A}(\alpha)$ is actually independent of α , but for more complicated LAMs, the center of mass will have the form $\mathbf{A}(\text{LAMs})$.

We now insert Eqs. (18b) and (19) simultaneously into Eq. (21) by putting a subscript i on the $S^{-1}(\alpha, 0, 0)$ matrix to indicate that it

has the form $S^{-1}(\alpha, 0, 0)$ for $i = 1, 2, 3, 4$, and the form $S^{-1}(0, 0, 0)$ for $i \geq 5$:

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi)[S_i^{-1}(\alpha, 0, 0)\mathbf{a}_i^0 - \mathbf{A}]. \quad (22)$$

We can stop here if we are willing to work in a center-of-mass axis system with z parallel to the methyl top axis. Frequently we want to work in a PAM or RAM system [21], which have z along the principal a axis or along the ρ direction, respectively, and which therefore require introducing an additional direction cosine matrix $S^{-1}(0, \beta, 0)$ to rotate the whole molecule about the y axis, leading to a final equation of the form

$$\mathbf{R}_i = \mathbf{R} + S^{-1}(\chi, \theta, \phi)S^{-1}(0, \beta, 0)[S_i^{-1}(\alpha, 0, 0)\mathbf{a}_i^0 - \mathbf{A}]. \quad (23)$$

The angle β is independent of α in this simple example. It is Eq. (23) that we will use to verify our (up to now tentative) transformation equations.

Before going on, it is helpful to review the five coordinate systems involved in Eq. (23). The vectors \mathbf{a}_i^0 are constants and describe the C_s equilibrium structure in a coordinate system with y perpendicular to the symmetry plane, xz in the molecular symmetry plane, and z along the methyl top axis. The vectors $[S_i^{-1}(\alpha, 0, 0)\mathbf{a}_i^0 - \mathbf{A}]$ describe an internally rotated molecule in a center-of-mass coordinate system with y perpendicular to the symmetry plane and z parallel to the methyl top axis. The vectors $S^{-1}(0, \beta, 0)[S_i^{-1}(\alpha, 0, 0)\mathbf{a}_i^0 - \mathbf{A}]$ describe an internally rotated molecule in a center-of-mass coordinate system with y perpendicular to the symmetry plane and z pointing in some chosen direction in the molecular symmetry plane. The vectors $S^{-1}(\chi, \theta, \phi)S^{-1}(0, \beta, 0)[S_i^{-1}(\alpha, 0, 0)\mathbf{a}_i^0 - \mathbf{A}]$ describe an internally rotated molecule in a center-of-mass coordinate system with X, Y and Z parallel to a set of laboratory-fixed axes. The vectors $\mathbf{R} + S^{-1}(\chi, \theta, \phi)S^{-1}(0, \beta, 0)[S_i^{-1}(\alpha, 0, 0)\mathbf{a}_i^0 - \mathbf{A}]$ describe an internally rotated molecule in the laboratory-fixed coordinate system.

By using Eq. (18a) it becomes relatively easy to verify that the equivalent rotation of the generator (123) is E and the transformation of α is $\alpha_{\text{new}} = \alpha_{\text{old}} + 2\pi/3$, in the sense of Eqs. (10)–(12). For $i = 1, 2$, or 3 :

$$\begin{aligned} (123)\mathbf{R}_i &= (123)\{\mathbf{R} + S^{-1}(\chi_{\text{old}}, \theta_{\text{old}}, \phi_{\text{old}})S^{-1}(0, \beta, 0) \\ &\quad \times [S_i^{-1}(\alpha_{\text{old}}, 0, 0)\mathbf{a}_i^0 - \mathbf{A}]\} \\ &= \mathbf{R} + S^{-1}(\chi_{\text{new}}, \theta_{\text{new}}, \phi_{\text{new}})S^{-1}(0, \beta, 0) \\ &\quad \times [S_i^{-1}(\alpha_{\text{new}}, 0, 0)\mathbf{a}_i^0 - \mathbf{A}] \\ &= \mathbf{R} + S^{-1}(\chi_{\text{old}}, \theta_{\text{old}}, \phi_{\text{old}})S^{-1}(0, \beta, 0) \\ &\quad \times [S_i^{-1}(\alpha_{\text{old}} + 2\pi/3, 0, 0)\mathbf{a}_i^0 - \mathbf{A}] \\ &= \mathbf{R} + S^{-1}(\chi_{\text{old}}, \theta_{\text{old}}, \phi_{\text{old}})S^{-1}(0, \beta, 0) \\ &\quad \times [S_i^{-1}(\alpha_{\text{old}}, 0, 0)\mathbf{a}_{i+1}^0 - \mathbf{A}] = \mathbf{R}_{i+1}. \end{aligned} \quad (24)$$

For brevity, an imprecise atom subscript labeling has been used in the last line of Eq. (24), i.e., $i = 4$ really means $i = 1$. This reflects permutation cycle notation, where the atom “after” 3 in the cycle (123) is 1. The reader can easily show, by setting $S_i^{-1}(\alpha, 0, 0) = E$ for $i \geq 5$ in Eq. (24), that (123) has no effect on the laboratory-fixed coordinates of all those atoms in the molecule.

Since (23)^{*} will be a point group operation for the equilibrium configuration if H_1 lies in the molecular symmetry plane, we can determine its equivalent rotation from Section 11 if we require \mathbf{a}_1^0 in Eq. (18a) to have no y component. In this case, $B = \sigma(xz)$ and the equivalent rotation is $i\sigma(xz) = C_2(y)$, with $\{\chi_{\text{new}}, \theta_{\text{new}}, \phi_{\text{new}}\} = \{\pi - \chi_{\text{old}}, \pi - \theta_{\text{old}}, \pi + \phi_{\text{old}}\}$, from Eq. (A.16). If we take $\alpha = 0$ at the equilibrium configuration with H_1 in the symmetry plane, we can guess that a small positive α will turn into a small negative α upon reflection in the symmetry plane of the equilibrium configuration, i.e., $\alpha_{\text{new}} = -\alpha_{\text{old}}$. Point-group considerations

for SAVs of the C_s equilibrium configuration indicate that the torsion is of species A'' , which is another way of guessing that $\alpha_{\text{new}} = -\alpha_{\text{old}}$ for (23)* (see Section 11). In any case, we are led to try

$$\begin{aligned}
 (23)^* \mathbf{R}_i &= (23)^* \{ \mathbf{R} + S^{-1}(\chi_{\text{old}}, \theta_{\text{old}}, \phi_{\text{old}}) S^{-1}(0, \beta, 0) \\
 &\quad \times [S_i^{-1}(\alpha_{\text{old}}, 0, 0) \mathbf{a}_i^0 - \mathbf{A}] \} \\
 &= -\mathbf{R} + S^{-1}(\chi_{\text{new}}, \theta_{\text{new}}, \phi_{\text{new}}) S^{-1}(0, \beta, 0) \\
 &\quad \times [S_i^{-1}(\alpha_{\text{new}}, 0, 0) \mathbf{a}_i^0 - \mathbf{A}] \\
 &= -\mathbf{R} + S^{-1}(\pi - \chi_{\text{old}}, \pi - \theta_{\text{old}}, \pi + \phi_{\text{old}}) S^{-1}(0, \beta, 0) \\
 &\quad \times [S_i^{-1}(-\alpha_{\text{old}}, 0, 0) \mathbf{a}_i^0 - \mathbf{A}] \\
 &= -\mathbf{R} + S^{-1}(\chi_{\text{old}}, \theta_{\text{old}}, \phi_{\text{old}}) C_2(y) S^{-1}(0, \beta, 0) \\
 &\quad \times [S_i^{-1}(-\alpha_{\text{old}}, 0, 0) \mathbf{a}_i^0 - \mathbf{A}] \\
 &= -\mathbf{R} + S^{-1}(\chi_{\text{old}}, \theta_{\text{old}}, \phi_{\text{old}}) S^{-1}(0, \beta, 0) \\
 &\quad \times [S_i^{-1}(\alpha_{\text{old}}, 0, 0) C_2(y) \mathbf{a}_i^0 - C_2(y) \mathbf{A}] \\
 &= -\mathbf{R} + S^{-1}(\chi_{\text{old}}, \theta_{\text{old}}, \phi_{\text{old}}) S^{-1}(0, \beta, 0) \\
 &\quad \times [S_i^{-1}(\alpha_{\text{old}}, 0, 0) C_2(y) \mathbf{a}_i^0 + \mathbf{A}], \quad (25)
 \end{aligned}$$

for hydrogens $i = 1, 2, 3$. In Eq. (25) we have used the fact that the center-of-mass position \mathbf{A} has no y component, since the xz plane was originally chosen to coincide with the molecular symmetry plane. We have also used some of the properties of the direction cosine matrix cataloged in Appendix C to move the $C_2(y)$ operator to the right. From Eq. (18a) we find

$$\begin{aligned}
 C_2(y) \mathbf{a}_i^0 &= C_2(y) S^{-1}[2\pi(i-1)/3, 0, 0] \mathbf{a}_1^0 \\
 &= S^{-1}[-2\pi(i-1)/3, 0, 0] C_2(y) \mathbf{a}_1^0 \\
 &= S^{-1}[2\pi(1-i)/3, 0, 0] \mathbf{a}_1^0 \\
 &= S^{-1}[2\pi(4-i)/3, 0, 0] \mathbf{a}_1^0, \quad (26)
 \end{aligned}$$

i.e., $C_2(y) \{\mathbf{a}_1^0, \mathbf{a}_2^0, \mathbf{a}_3^0\} = \{-\mathbf{a}_1^0, -\mathbf{a}_3^0, -\mathbf{a}_2^0\}$. When these results are substituted into the last of Eq. (25), we see that (23)* is indeed obtained. The reader can easily show that (23)* simply changes the sign of the laboratory-fixed coordinates of all other atoms in the molecule.

Some of the changes required in Eq. (23) when more than one internally rotating top is present in the molecule are mentioned in Appendix E.

13.3. $-NH_2$ or $>N-H$ inversions

These “inversion” motions can be modeled mathematically to a first approximation as straight-line motions which carry the hydrogen atom(s) from one side of the local symmetry plane of the “transition state” to the other. If the local symmetry plane happens to be xy , for example, we could try taking $\gamma = 0$ at the transition state and requiring for the hydrogen(s) involved in the LAM: $a_i(\gamma)_x = (a_i^0)_x = \text{constant}$, $a_i(\gamma)_y = (a_i^0)_y = \text{constant}$, and $a_i(-\gamma)_z = -a_i(\gamma)_z$, with the two pyramidal equilibrium configurations corresponding to $\gamma = \pm\gamma^0$. If the $-NH_2$ case preserves an additional plane of symmetry bisecting the H-N-H angle during the LAM, we should also require, if that plane is yz and the two hydrogens are labeled 1 and 2, for example, that $(a_2^0)_x = -(a_1^0)_x$, $(a_2^0)_y = +(a_1^0)_y$, and $a_2(\gamma)_z = +a_1(\gamma)_z$.

These “inversion” motions can also be modeled mathematically to a first approximation using direction cosine matrices, if they are considered to be “internal rotations” of the hydrogens that do not take place about a chemical bond. For example, if the $-NH_2$ or $>NH$ functional group preserves a local xz symmetry plane during its umbrella motion (so the internal rotation is about the y axis), and if i labels a hydrogen atom bonded to the nitrogen, then the

internal-rotation model leads to replacing the expression in square brackets in Eq. (21) by $[S^{-1}(0, \gamma, 0)(\mathbf{a}_i^0 - \mathbf{a}_N^0) + \mathbf{a}_N^0 - \mathbf{A}]$.

A question that must be decided when treating inversions is the choice of reference configuration, e.g., should we take the reference configuration for NH_3 to be its C_{3v} equilibrium configuration or should we take it to be its D_{3h} planar “transition state” configuration. For ammonia, one often uses the D_{3h} configuration because D_{3h} is isomorphic with the full PI group for inverting ammonia. From the author’s experience, the most convenient choice for reference configuration is the one with highest symmetry. Furthermore, it is convenient to put the zero of an inversion coordinate γ at the transition state, so that symmetry operations take the form $\gamma \rightarrow \pm\gamma$. This choice of zero is in fact convenient for any coordinate that describes a back-and-forth motion between only two molecular frameworks.

13.4. Generalized inversions

For lack of a better word, the term “inversion” is sometimes used in a generalized sense to mean any motion which takes the molecular structure back and forth along a single path connecting two (and only two) energetically equal end-points. Many umbrella motions, hydrogen transfer motions, ring-puckering motions, etc. are examples of this, and their LAMs can often be treated mathematically just as described for the amino inversions in Section 13.3 above.

14. Application of PI symmetry operations to rotational operators and basis functions

Task (iv) begins in this section, where we use equivalent rotation ideas to determine symmetry species for functions of the rotational variables (χ, θ, ϕ) . For the total angular momentum operator, we have by definition

$$\begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix} = S(\chi, \theta, \phi) \begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix}, \quad (27)$$

where J_x, J_y, J_z are molecule-fixed components and J_x, J_y, J_z are laboratory-fixed components of the total angular momentum operator. The laboratory-fixed components, e.g.,

$$J_x = -i\hbar \sum_i m_i [Y_i(\partial/\partial Z_i) - Z_i(\partial/\partial Y_i)], \quad (28)$$

are immediately seen to be invariant under any PI symmetry operation. Therefore, if we apply a given pure-permutation symmetry operation T to the molecule-fixed components on the left of Eq. (28), we have

$$T \begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix} = T S(\chi, \theta, \phi) \begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix} = C S(\chi, \theta, \phi) \begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix} = C \begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix}, \quad (29)$$

where C is a proper rotation. A similar equation, with C replaced by iB (which is again a proper rotation) is obtained for any PI operation with a π . The form of the matrices C and iB determine the characters for the basis set $\{J_x, J_y, J_z\}$ for each symmetry operation in the PI group, and thus determine also the symmetry species for J_x, J_y , and J_z in that group.

In general a procedure like that used for methane [18,19] (not discussed here) is required to determine the transformation properties of the symmetric top rotational functions, but for many molecules of interest, the matrices C and iB (see Section 11) take one of the simple forms $E, C_n(z), C_2(x)$ or $C_2(y)$, so that the new Eulerian angles can be written as explicit functions of the old. These explicit transformations can be used to determine transformations of the symmetric top rotational basis functions [17],

$$\begin{aligned}
C_n(z)|KJM\rangle &= \exp(2\pi i K/n)|KJM\rangle \\
C_2(x)|KJM\rangle &= (-1)^J | -KJM\rangle \\
C_2(y)|KJM\rangle &= (-1)^{J-K} | -KJM\rangle.
\end{aligned} \quad (30)$$

If the z, x, y axes correspond (approximately) to a, b, c , we can write for the asymmetric-rotor basis functions

$$\begin{aligned}
C_2(z)|JK_aK_c\rangle &= (-1)^{K_a} |JK_aK_c\rangle \\
C_2(x)|JK_aK_c\rangle &= (-1)^{K_a+K_c} |JK_aK_c\rangle \\
C_2(y)|JK_aK_c\rangle &= (-1)^{K_c} |JK_aK_c\rangle.
\end{aligned} \quad (31)$$

The symmetry species in the PI group for rotational functions can be determined from these equations and the PI group character table.

15. Application of PI symmetry operations to several LAM basis set functions

For internal rotation problems it is convenient to use torsional basis functions of the form $\exp(im\alpha)$, where m is a positive or negative integer. For n -fold barrier problems, it is sometimes more convenient to represent these as $\exp[i(nk + \sigma)\alpha]$, where k is a positive or negative integer and σ is an integer in the range $0 \leq \sigma \leq n/2$. The symmetry species of the torsional functions are then partially determined by the value of σ , where “partially” here means that the 1 and 2 subscripts on A and B species can be defined only after taking the linear combinations $\exp[i(nk + \sigma)\alpha] \pm \exp[-i(nk + \sigma)\alpha]$ when $\sigma = 0$ or $n/2$.

For multiple-top problems the basis functions are products of the individual top basis functions, e.g., for a three-top molecule [12] one has $\exp(im_1\alpha_1) \exp(im_2\alpha_2) \exp(im_3\alpha_3)$. If some or all of the tops are equivalent, exchange of the α_i variables must be considered when determining symmetry species (such exchanges may force one to expand one's original guess for a small basis set belonging to a given symmetry species).

Many LAMs, that are not strictly speaking internal rotations, but that involve passing through n symmetrically equivalent positions along a “circular” path which only allows the system point to go directly from position p to positions $p \pm 1$, can be described by an angular coordinate with symmetry transformations similar to those used above for internal rotation [22,23].

For large-amplitude motion between two symmetrically equivalent wells separated by a barrier, one can use a basis set of harmonic oscillator functions centered at the top of the barrier. In this case, even v functions are even and odd v functions are odd with respect to $\gamma \rightarrow -\gamma$. When using a tunneling approach, harmonic oscillator functions centered at the minimum of each well are often convenient. This complicates symmetry determinations a bit, because $\gamma \rightarrow -\gamma$ turns LAM functions in one well into those for the other well. For example, if the equilibrium values for an inversion coordinate are $\pm\gamma_o$, where $\gamma = 0$ at the top of the barrier, then we can take a basis set of harmonic oscillator vibrational functions in each well, of the form

$$\psi_1(\gamma) = \psi_v^{HO}(\gamma + \gamma_o) \quad (32a)$$

$$\psi_2(\gamma) = \psi_v^{HO}(\gamma - \gamma_o), \quad (32b)$$

where the functions in Eq. (32a) are centered at the minimum of well 1, i.e., at $\gamma = -\gamma_o$, while the functions in Eq. (32b) are centered at the minimum of well 2, i.e., at $\gamma = +\gamma_o$. Transformations under $\gamma \rightarrow -\gamma$ then become

$$\psi_1(-\gamma) = \psi_v^{HO}(-\gamma + \gamma_o) = (-1)^v \psi_v^{HO}(\gamma - \gamma_o) = (-1)^v \psi_2(\gamma) \quad (33a)$$

$$\psi_2(-\gamma) = \psi_v^{HO}(-\gamma - \gamma_o) = (-1)^v \psi_v^{HO}(\gamma + \gamma_o) = (-1)^v \psi_1(\gamma). \quad (33b)$$

Eq. (33) indicates that $\psi_1(\gamma) \pm \psi_2(\gamma)$ transforms into $\pm(-1)^v$ times itself under $\gamma \rightarrow -\gamma$.

16. Application of PI symmetry operations to the electric dipole moment operator

To obtain electric-dipole selection rules on the rotational and LAM quantum numbers it is necessary to express one or more of the laboratory-fixed components of the dipole moment operator μ in terms of the molecule-fixed coordinates. For the purpose of determining symmetry species, the laboratory-fixed components μ_x, μ_y, μ_z of μ can be written symbolically as

$$\mu_L = \sum_i e_i R_i, \quad (34)$$

where either the subscript L or the upper-case subscripts X,Y,Z on μ indicate that its vector components are taken along the laboratory-fixed Cartesian axes. It is quickly seen that all components of μ_L transform into themselves under pure permutations and into their negatives under permutation-inversions, which makes $\Gamma(\mu_x) = \Gamma(\mu_y) = \Gamma(\mu_z)$ equal to one of the non-degenerate symmetry species in the character table for the molecular PI symmetry group. This PI-group symmetry species of μ_L can be used to determine electric-dipole selection rules on the rovibronic (i.e., rotation-LAM-SAV-electronic) symmetry species of the energy levels.

The symmetry species of the molecule-fixed components μ_x, μ_y, μ_z of the dipole moment operator (indicated by μ_M or lower-case x, y, z subscripts) can be found from the equation

$$\mu_M = S(\chi, \theta, \phi) \mu_L \quad (35)$$

together with the previously determined symmetry species for μ_L and the previously determined equivalent rotations for each PI operation in the molecular symmetry group, just as was done for J in Eqs. (27)–(29). Having determined the symmetry species of μ_M , we: (i) turn Eq. (35) around, (ii) keep only the laboratory-fixed Z component of the dipole moment operator, and (iii) indicate the dependence of the molecular-fixed components on the LAMs, leading us to write

$$\mu_Z = \mathbf{k} \cdot S^{-1}(\chi, \theta, \phi) \mu_M(\text{LAMs}). \quad (36)$$

The dipole moment operator $\mu_M(\text{LAMs})$ will only be useful if the LAM-dependence is expressed explicitly. It is normally convenient to use Fourier expansions for angular variables (i.e., variables with periodicity 2π) and Taylor expansions for other variables (e.g., inversion or hydrogen-transfer variables). If we consider the example of a molecule with one internal rotation LAM α and one hydrogen-transfer LAM γ [24], then we must determine the species of products of the type

$$\gamma^p \cos(q\alpha) \quad (37a)$$

$$\gamma^p \sin(q\alpha) \quad (37b)$$

for various values of the integers p and q . Only products in Eq. (37) with the same symmetry species as μ_x can be used in the expansion of $\mu_x(\text{LAMs})$, etc.

Eq. (36) then takes the more useful form

$$\begin{aligned}
\mu_Z = S^{-1}(\chi, \theta, \phi)_{Zx} \mu_x(\gamma, \alpha) + S^{-1}(\chi, \theta, \phi)_{Zy} \mu_y(\gamma, \alpha) \\
+ S^{-1}(\chi, \theta, \phi)_{Zz} \mu_z(\gamma, \alpha).
\end{aligned} \quad (38)$$

If we suppose that the molecule-fixed x, y, z axes correspond (or nearly correspond) to the principal axes b, c, a , then matrix elements of the direction cosine components $S^{-1}(\chi, \theta, \phi)_{Zx}$, $S^{-1}(\chi, \theta, \phi)_{Zy}$, and $S^{-1}(\chi, \theta, \phi)_{Zz}$ in the rotational basis set will correspond to traditional b -type, c -type and a -type transitions, respectively. If the symmetry species of any of the molecule-fixed dipole moment components is A_1 , then the first term in the expansion of this component can take a non-zero constant value (can correspond to a permanent dipole moment) and can give rise to a pure rotational transition in the LAM-rotational basis set. Components of other symmetry species

will have first terms in their expansions which vanish for some value(s) of γ and/or α . Nonvanishing matrix elements of these components will require a change in some quantum number(s) of the LAM basis set. In tunneling problems, for example, these components will often give rotational transitions across some tunneling splitting.

In discussing matrix elements of the dipole moment operator in the previous paragraph we focused on selection rules in the basis set, because basis sets are normally chosen to have “good” quantum numbers, which then obey well defined selection rules and often also obey selection rules that are familiar from spectroscopic experience with rigid molecules. When LAMs are present, however, LAM-rotation interactions are often large enough to cause the good quantum numbers of the basis set to be much less good in many of the heavily mixed final eigenfunctions of the Hamiltonian operator. One consequence of such a partial destruction of the rotational quantum numbers K_a and K_c is the extension by many authors of the rigid-molecule notation for rotational transitions, so that it includes *a*-type, *b*-type, *c*-type and *d*-type transitions, where *e*(ven) and *o*(dd) changes in the K_a, K_c quantum numbers are *eo*, *oo*, *oe*, and *ee*, respectively. In molecules with LAMs, traditional ideas associating changes in K_a and K_c with the direction of the dipole moment component causing the transition must often be abandoned (and must certainly be abandoned if *d*-type transitions are present).

17. Conclusion

In this short article it is not possible to cover all necessary details for advanced applications of PI group theory. A list of topics appropriate (and often necessary) for treatment of LAM-rotation problems, but omitted here (some of which were alluded to earlier) would include: (i) complex characters and the relation of time reversal to separable degeneracies; (ii) subtleties associated with different definitions of molecule-fixed coordinate systems, i.e., those that are fixed in one or another part of the floppy molecule versus those that try to maintain some “average position” between the moving parts; (iii) multiple-valued coordinate systems that arise when two chemically distinct LAMs (or one LAM and one overall rotation) connect the same pair of equilibrium frameworks, and the *n*-fold extended PI groups that they lead to; (iv) “axis-switching” effects on energy levels and intensities when one or more of the LAMs reorients the molecule-fixed principal axis system; (v) very loosely bound molecular complexes requiring a separate “molecule-fixed axis system” in each constituent molecule; (vi) derivation of the classical and quantum mechanical kinetic energy operator for molecule-fixed coordinates containing LAMs; and (vii) parameterization of multi-dimensional tunneling splittings in rotating molecules. There is also the whole set of questions associated with SAVs and molecular orbitals in floppy molecules, which were ignored here, e.g.: (i) what is the best way to determine what part of a floppy molecule the SAV displacements of each atom should be locked to, and how should the associated non-uniqueness of symmetry species for the SAVs be dealt with, (ii) under what circumstances do Berry phase effects become important for LAMs, (iii) what kind of large LAM-electronic interactions result from defining molecular orbitals as linear combinations of atomic orbitals, when the mixing coefficients vary rapidly during the LAMs, or (iv) how should the symmetry of molecular orbitals be treated when the positions of many atoms are quite delocalized and fixed-nucleus thinking is no longer a valid zeroth-order approximation.

As the reader can see, the present article discusses only a portion of the tools necessary to deal with the full range of spectroscopic problems arising in molecules with LAMs. Nevertheless, it

is hoped that the material covered will allow those readers with a relatively simple LAM problem, or with an LAM problem similar to one already treated in the literature, to deal with the situation by themselves. For readers with more complicated LAM problems, it is hoped that this material will take them one step further down the road, so they can ask for advice with more understanding than they had before of the “useful” questions and of the concepts involved in the possible answers.

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Appendix A. Recipe for rapid multiplication of permutation-inversion operations

Multiplication of an even number of $*$'s results in no $*$. Multiplication of an odd number of $*$'s results in a $*$. Multiplication of a sequence of permutations can be carried out by starting with the atom subscript 1 and seeing what it is ultimately replaced by when the permutation is read from the right to the left; then starting with that replacement subscript and seeing what it is replaced by; etc. Using \rightarrow 's as a shorthand notation for “is replaced by” we schematically represent in Eq. (A.1) the steps in computing the product of four permutations. Note that there are always four \rightarrow 's in this example, because we must keep track of what each of the four permutations does. Mechanically speaking, the four arrows after the first equal sign in Eq. (A.1) correspond to moving one's finger from right to left along (1236)(345)(12)(346), accompanied by the words: “1 is replaced by 1 by (346), 1 is replaced by 2 by (12), 2 is replaced by 2 by (345), 2 is replaced by 3 by (1236).” The final answer (13564)(2) is thus determined by only six right-to-left passes of the finger. Note that only the last equal sign represents a true equality with the first expression on the left, since the intermediate “equalities” are not complete.

$$\begin{aligned} (1236)(345)(12)(346) &= (1, 1 \rightarrow 1 \rightarrow 2 \rightarrow 2 \rightarrow 3 = (13, 3 \\ &\rightarrow 4 \rightarrow 4 \rightarrow 5 \rightarrow 5 = (135, 5 \rightarrow 5 \\ &\rightarrow 5 \rightarrow 3 \rightarrow 6 = (1356, 6 \rightarrow 3 \rightarrow 3 \\ &\rightarrow 4 \rightarrow 4 = (13564, 4 \rightarrow 6 \rightarrow 6 \rightarrow 6 \\ &\rightarrow 1 = (13564)(2, 2 \rightarrow 2 \rightarrow 1 \rightarrow 1 \\ &\rightarrow 2 = (13564)(2) \end{aligned} \quad (\text{A.1})$$

Cycles of length 1 are normally not written, so that (13564)(2) = (13564).

By successively applying the four operations on the left of Eq. (A.1) to the functions in Eq. (1a) or (1c), starting with the rightmost permutation, one can verify that the result obtained is the same as that obtained by applying (13564) to these functions directly.

Appendix B. Reducing the time required to find the class structure and character table for a PI group by considering only the generators of the group

B.1. Class structure

For each generator A, B, C, etc. there will be some exponent *n* such that

$$A^n = E, \quad (\text{A.2})$$

where E is the identity and *n* is called the order of A. A pure permutation cycle of length *n* is of order *n*, e.g., (123)³ = E and (12567)⁵ = E,

etc. This is not true when a^* is present on cycles of odd length, e.g., $[(123)^*]^3 = E^*$, but $[(123)^*]^6 = E$. For each pair of generating elements there will be some commutation relation of the form

$$BA = A^p B^q C^r \dots D^s \quad (\text{A.3})$$

Most commutation relations will only involve A and B on the right-hand side of Eq. (A.3). The author has occasionally had to consider commutation relations where a third element C was required [25], but has not yet had to deal with relations where a fourth element D was also required.

Chose a standard order for the generators (the standard order here is alphabetical) and represent each element of the PI group in the form (assuming four generators for this example)

$$A^p B^q C^r D^s, \quad (\text{A.4})$$

where the exponents p, q, r, s vary between 0 and the value n from Eq. (A.2) for that generator.

Eq. (3) for determining classes can then be written

$$P = (D^{-k} C^{-j} B^{-i} A^{-h}) (A^p B^q C^r D^s) (A^h B^i C^j D^k), \quad (\text{A.5})$$

where X and Q from Eq. (3) are given by $X = (A^h B^i C^j D^k)$ and $Q = (A^p B^q C^r D^s)$, and where A^{-h} is shorthand for A^{n-h} , with n given by Eq. (A.2), etc. One then makes repeated use of the set of generating equations analogous to Eq. (A.2) and (A.3) to bring the non-standard order of the generators in Eq. (A.5) into an expression like Eq. (A.4) with standard order.

To be more specific, consider CH_3F with a hypothetically chemically feasible inversion carried out by internally rotating an H_2 pair against the CHF group. One set of generators of the feasible PI group G_{12} is then $A = (123)$, $B = (12)$, and $C = E^*$ (but there are other possibilities as well). The generating equations are

$$\begin{aligned} A^3 &= B^2 = C^2 = E \\ BA &= A^2 B \\ CA &= AC \\ CB &= BC \end{aligned} \quad (\text{A.6})$$

A general element of G_{12} can be represented by $A^p B^q C^r$, where $0 \leq p \leq 2$ and $0 \leq q, r \leq 1$. This illustrates the fact that very often the number of elements of the group will be the product of the orders n of the various generating operations. Thus, for checking purposes, if the factors of the number of elements in one's PI group contain large prime numbers, one should be suspicious (e.g., 33, 34, 35, 37, 39 are suspicious values for the number of elements in a molecular symmetry group, while 32 and 36 are not.)

Now consider

$$P = (C^{2-j} B^{2-i} A^{3-h}) (A^p B^q C^r) (A^h B^i C^j) \quad (\text{A.7})$$

for given p, q, r and all allowed values of h, i, j . The generating equations show that C commutes with A and B, so we can immediately collect all C's at the far right and obtain

$$P = (B^{2-i} A^{3+p-h}) (B^q) (A^h B^i) C^r \quad (\text{A.8})$$

In this simple example, it would be relatively fast to just evaluate the 36 cases explicitly, since 13 of them ($i = q = 0$ with h, p arbitrary, and $h = p = 0$ with i, q arbitrary) lead immediately to $P = Q$. But for a more complicated group, it would save time to derive from Eq. (A.6) that $B^q A^p = A^{(2+q)p} B^q$ (using the notation $2+q = 2^q$ to avoid superscripts on superscripts), so that one can write

$$\begin{aligned} P &= (B^{2-i} A^{3+p-h}) (A^{h(2+q)} B^{i+q}) C^r = B^{2-i} A^{3+p-h+h(2+q)} B^{i+q} C^r \\ &= A^{[3+p-h+h(2+q)][2+q]} B^q C^r, \end{aligned} \quad (\text{A.9})$$

and then derive $A^{4p} = A^p$, so that for $i = q = 0$ and $h = p = 0$ we recover $P = Q$ as noted above, giving no new members for the class of Q,

while for the cases of $q = 0$ and $q = 1$ with h, i, p arbitrary, we find Eqs. (A.10a) and (A.10b), respectively:

$$P = A^{(p)[2+q(2-i)]} C^r \quad (\text{A.10a})$$

$$P = A^{(p+h)[2+q(2-i)]} B C^r. \quad (\text{A.10b})$$

Thus, from Eq. (A.10a) the class of A ($p = 1, q = r = 0$) contains A and A^2 . The class of AC ($p = 1, q = 0, r = 1$) contains AC and $A^2 C$. From Eq. (A.10b) The class of B ($p = 0, q = 1, r = 0$) contains B, AB and $A^2 B$, while the class of BC ($p = 0, q = r = 1$) contains BC, ABC and $A^2 BC$. Also from Eq. (A.10a) we find that the class of E ($p = q = r = 0$) contains only E, and that the class of $E^* \equiv C$ ($p = q = 0, r = 1$) contains only E^* . There are thus six classes in the PI group G_{12} for this example, which we choose (somewhat arbitrarily) to list in the order $\{E\}, \{A, A^2\}, \{B, AB, A^2 B\}, \{C\}, \{AC, A^2 C\}, \{BC, ABC, A^2 BC\}$.

A brute force method for finding the character table is given in Section 4. One can also use group theoretical knowledge to note that G_{12} above is the direct product of two groups, one of order 6 and one of order 2, i.e., $G_{12} = G_6 \times G_2$, where $G_6 = \{E, A, A^2, B, AB, A^2 B\}$ and $G_2 = \{E, E^*\}$. Then apply the procedures of Section 4 to the smaller groups separately, and use the rules for generating characters of direct-product groups from the characters of the individual groups [3–5].

Appendix C. Catalog of frequently used mathematical properties of the direction cosine matrix

The concept of a direction cosine matrix is not only used to define the rotational variables, but it is also often used to rotate from a temporary molecular-axis system to the principal-axis system, or to describe LAMs corresponding to internal rotation of some moiety about an atom-atom single bond (e.g., methyl top internal rotation and protein folding). It can even be used to describe other LAMs when large bond-length changes do not occur, e.g. an $-\text{NH}_2$ inversion (rotation of the N–H bonds about an axis passing through the N and lying in the NH_2 plane) or conversion of trans bent acetylene to cis bent (rotation of one C–H bond about an axis passing through the C and perpendicular to the bent acetylene plane). Thus, to help in relating transformations of the molecule-fixed coordinates to the various PI operations, we summarize a number of useful properties of the direction cosine matrix, which can be proved by direct calculation using Eq. (6).

$$S^{-1}(\chi, \theta, \phi) = S^{\text{tr}}(\chi, \theta, \phi) \quad (\text{A.11a})$$

$$S^{-1}(\chi, \theta, \phi) = S^{-1}(0, 0, \phi) S^{-1}(0, \theta, 0) S^{-1}(\chi, 0, 0) \quad (\text{A.11b})$$

$$S^{-1}(\chi, 0, 0) = S^{-1}(0, 0, \chi) \quad (\text{A.11c})$$

$$|S^{-1}(\chi, \theta, \phi)| = +1 \quad (\text{A.11d})$$

Note that both $S^{-1}(0, 0, \phi)$ and $S^{-1}(\chi, 0, 0)$ represent right-handed rotations about the z axis through an angle of ϕ and χ , respectively, in the sense that a point originally on the positive x axis will move in the positive y direction for small positive ϕ or χ . Similarly, $S^{-1}(0, \theta, 0)$ represents a right-handed rotation about the y axis, in the sense that a point originally on the positive z axis will move in the positive x direction for small positive θ . Finally, $S^{-1}(+\pi/2, \theta, -\pi/2)$ represents a right-handed rotation about the x axis, in the sense that a point originally on the positive y axis will move in the positive z direction for small positive θ .

The implications of Eqs. (A.11a) and (A.11d) can be rewritten in terms of components of the $S^{-1}(\chi, \theta, \phi)$ matrix, or for simplicity in terms of its transpose $S(\chi, \theta, \phi)$, as follows.

$$\begin{aligned} S_{ik}(\chi, \theta, \phi) S_{jk}(\chi, \theta, \phi) &= S_{ki}(\chi, \theta, \phi) S_{kj}(\chi, \theta, \phi) = \delta_{ij} \\ e_{ijk} S_{im}(\chi, \theta, \phi) S_{jn}(\chi, \theta, \phi) &= e_{mnp} S_{kp}(\chi, \theta, \phi) \\ e_{ijk} S_{mi}(\chi, \theta, \phi) S_{nj}(\chi, \theta, \phi) &= e_{mnp} S_{pk}(\chi, \theta, \phi), \end{aligned} \quad (\text{A.12})$$

where the repeated-index summation convention and the symbols δ_{ij} and ϵ_{ijk} (where $\epsilon_{xyz} = 0$, $\epsilon_{xyx} = +1$, $\epsilon_{xzy} = -1$, etc.) have been used. Eq. (A.12) simply states that rows 1, 2, 3 of S form a right-handed orthonormal triple of vectors, and that columns 1, 2, 3 of S do also.

Consider next the three diagonal matrices corresponding to a two-fold rotation about each of the Cartesian axes

$$\begin{aligned} C_2(x) &= \begin{bmatrix} +1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \\ C_2(y) &= \begin{bmatrix} -1 & 0 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \\ C_2(z) &= \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & +1 \end{bmatrix}, \end{aligned} \quad (\text{A.13})$$

which also obey $C_2(x)C_2(y) = C_2(y)C_2(x) = C_2(z)$ and cyclic permutations thereof. These matrices obey the following commutation relations with parts of the S matrix

$$\begin{aligned} C_2(x)S(\chi, 0, 0) &= S(-\chi, 0, 0)C_2(x) \\ C_2(y)S(\chi, 0, 0) &= S(-\chi, 0, 0)C_2(y) \\ C_2(z)S(\chi, 0, 0) &= S(\chi, 0, 0)C_2(z) \\ C_2(x)S(0, \theta, 0) &= S(0, -\theta, 0)C_2(x) \\ C_2(y)S(0, \theta, 0) &= S(0, \theta, 0)C_2(y) \\ C_2(z)S(0, \theta, 0) &= S(0, -\theta, 0)C_2(z) \end{aligned} \quad (\text{A.14})$$

It can be seen by taking the transposes of Eq. (A.14) that they also hold if S is replaced by S^{-1} . It is convenient to introduce two more definitions

$$\begin{aligned} C_n(z) &\equiv S(+2\pi/n, 0, 0) \\ i &\equiv -E \end{aligned} \quad (\text{A.15})$$

where E is the 3×3 identity matrix. It can be shown by direct calculation using various equations above that

$$\begin{aligned} S^{-1}(\chi + 2\pi/n, \theta, \phi) &= S^{-1}(\chi, \theta, \phi)C_n^{-1}(z) \\ S^{-1}(\pi - \chi, \pi - \theta, \pi + \phi) &= S^{-1}(\chi, \theta, \phi)C_2(y) \\ S^{-1}(-\chi, \pi - \theta, \pi + \phi) &= S^{-1}(\chi, \theta, \phi)C_2(x) \end{aligned} \quad (\text{A.16})$$

Derivatives of the S matrices with respect to each of the three Eulerian angles can be expressed using equations similar to those above, but they are needed only for derivations of the kinetic energy operator and not for symmetry considerations, so we do not reproduce those results here.

Appendix D. Constraint equations needed to begin a consideration of SAVs

It is well known that a molecule with N atoms requires $3N$ Cartesian coordinates to specify the positions of all the atoms in a laboratory-fixed axis system. These coordinates also represent $3N$ degrees of freedom on the left side of Eq. (8) or $3N$ variables in the quantum mechanical problem. The infinitesimal vibrational displacement vectors \mathbf{d}_i likewise represent $3N$ Cartesian coordinates, so the total number of degrees of freedom on the right side of Eq. (8) is $3N$ displacement components plus 3 center-of-mass coordinates plus 3 rotational angles plus n LAMs. Constraint equations are essentially schemes to reduce the number of independent \mathbf{d}_i vector components (or equivalently the number of SAVs) to $3N - 6 - n$, so that the number of degrees of freedom on the left of Eq. (8) matches the number on the right. These constraint equations often take the forms:

$$\sum_i m_i \mathbf{d}_i = \mathbf{0} \quad (\text{A.17a})$$

$$\sum_i m_i \mathbf{a}_i(\gamma_j) \times \mathbf{d}_i = \mathbf{0} \quad (\text{A.17b})$$

$$\sum_i m_i [\partial \mathbf{a}_i(\gamma_j) / \partial \gamma_j] \cdot \mathbf{d}_i = 0, \quad (\text{A.17c})$$

where i runs over all the atoms in the molecule. Eq. (A.17a) is called the center-of-mass constraint. It forces the mass-weighted infinitesimal displacement vectors $m_i \mathbf{d}_i$ to be orthogonal to a translation of the molecule, and thus removes translation from the SAVs. Eq. (A.17b) is called the Eckart condition [13] when the \mathbf{a}_i are all constant. It forces the mass-weighted displacement vectors to be orthogonal to an overall rotation of the molecule, and thus removes overall rotation from the SAVs. Eq. (A.17c), one for each LAM γ_j , are called the Sayvetz conditions [14]. They force the mass-weighted displacement vectors to be orthogonal to all the LAMs, and thus remove the LAMs from the SAVs.

By ignoring the SAVs we avoid a lengthy discussion of all the physical and mathematical implications of Eq. (A.17).

Appendix E. Changes to Eq. (23) required for multi-top molecules

When more than one top is present in a molecule with a plane of symmetry (again chosen as the xz plane, and again under the simplifying assumption that all top axes lie in this plane), it will in general not be possible to start from an equilibrium configuration \mathbf{a}^0 with all top axes simultaneously lying along the z axis. But it is still possible to start from an (often highly) artificial non-equilibrium configuration \mathbf{a}_i^0 that satisfies this criterion [10,12], and perform the internal rotation of each top j through an angle α_j about z . After that, each of the $\text{CH}_3\text{-X}$ moieties can be rotated by a constant matrix about an axis parallel to y and passing through X , to bring it to its true orientation in the molecule. Symbolically, we start with $|\text{top}_1\rangle_0 + |\text{top}_2\rangle_0 + |\text{frame}\rangle_0$, then perform the internal rotations of the tops to obtain $R(\alpha_1)|\text{top}_1\rangle_0 + R(\alpha_2)|\text{top}_2\rangle_0 + |\text{frame}\rangle_0$, then orient each top correctly in the molecule using constant matrices T_i to obtain $T_1 R(\alpha_1)|\text{top}_1\rangle_0 + T_2 R(\alpha_2)|\text{top}_2\rangle_0 + |\text{frame}\rangle_0$, and finally rotate the whole molecule to its correct orientation in our chosen molecule-fixed axis stem to obtain $Q[T_1 R(\alpha_1)|\text{top}_1\rangle_0 + T_2 R(\alpha_2)|\text{top}_2\rangle_0 + |\text{frame}\rangle_0]$.

This procedure can be expressed in mathematically more precise algebra by replacing $S_i^{-1}(\alpha, 0, 0)\mathbf{a}_i^0$ in Eq. (23) by a more complicated expression to obtain

$$\begin{aligned} \mathbf{R}_i &= \mathbf{R} + S^{-1}(\chi, \theta, \phi)S^{-1}(0, \beta_{j(i)}, 0)[S^{-1}(\alpha_{j(i)}, 0, 0) \\ &\quad \times (\mathbf{a}_i^0 - \mathbf{a}_{Xj}^0) + \mathbf{a}_{Xj}^0 - \mathbf{A}]. \end{aligned} \quad (\text{A.18})$$

The subscript notation here is awkward, but is meant to indicate that $\alpha_{j(i)} = \beta_{j(i)} \equiv 0$ for all atoms i not in some methyl top j , while $\beta_{j(i)} = \beta_j^0 = \text{constant}$ and $\alpha_{j(i)} = \alpha_j$ is the internal rotation angular variable for top j when i denotes one of the CH_3 atoms in top j . Consider the internal rotation operations (123), (456), (789) for the hydrogen atoms in a three-top molecule ($j = 1, 2, 3$). It can be shown rather quickly, using the same techniques as for the one-top molecule in Section 13, that (456), for example, corresponds to transformations of the internal rotation angles given by $\alpha_{j,\text{new}} = \alpha_{j,\text{old}} + 2\pi/3$ for $j = 2$ and by $\alpha_{j,\text{new}} = \alpha_{j,\text{old}}$ for $j \neq 2$, with the equivalent rotation E , while (23)(56)(89)^{*} corresponds to $\alpha_{j,\text{new}} = -\alpha_{j,\text{old}}$ for all j , with the equivalent rotation $C_2(y)$, just as for the one-top example.

If some of the tops are equivalent, it will be necessary to consider exchanging the angles α_j to achieve some of the PI operations [12,26,27].

Just as in Section 13, an alternative approach to that outlined above would be to start from constant reference positions $\mathbf{a}_i^{\text{OTQ}}$ that already describe the molecule in its equilibrium structure and

correctly oriented in our chosen molecule-fixed axis system, i.e., to start symbolically with $|\text{top}_1\rangle_{OTQ} + |\text{top}_2\rangle_{OTQ} + |\text{frame}\rangle_{OQ}$. It is then fairly obvious that we need to apply the rotation matrix $QT_1R(\alpha_1)T_1^{-1}Q^{-1}$ to $|\text{top}_1\rangle_{OTQ}$ and $QT_2R(\alpha_2)T_2^{-1}Q^{-1}$ to $|\text{top}_2\rangle_{OTQ}$ to arrive at our internally rotated and correctly oriented structure $QT_1R(\alpha_1)T_1^{-1}Q^{-1}|\text{top}_1\rangle_{OTQ} + QT_2R(\alpha_2)T_2^{-1}Q^{-1}|\text{top}_2\rangle_{OTQ} + |\text{frame}\rangle_{OQ}$.

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