Eckart vectors, Eckart frames, and polyatomic molecules*†

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The fundamental role of Eckart vectors and Eckart frames is demonstrated in the theory of the vibration–rotation Hamiltonian for a polyatomic molecule.

CONTENTS

I. INTRODUCTION AND SUMMARY

In his famous paper, "Some Studies Concerning Rotating Axes and Polyatomic Molecules," Carl Eckart (1935) introduced a set of conditions for defining a system of rotating axes in terms of the instantaneous position vectors of the nuclei in a polyatomic molecule. These conditions are now part of the standard theory of polyatomic molecules (Margeneau and Murphy, 1943; Herzburg, 1945; Nielson, 1951; Wilson, 1955; Landau and Lifschitz, 1958). In this same paper, Eckart also gave the explicit construction of the rotating frame in terms of three vectors $\vec{F}_1, \vec{F}_2, \vec{F}_3$. These three vectors—which we will call *Eckart vectors*—appear not to be well known, despite the fact that they play (as Eckart showed) a fundamental role in the definition of the rotating frame.

It is the purpose of the present paper to demonstrate that the Eckart vectors, and the corresponding *Eckart frame* defined by them, occupy a far more significant place in the theory of the vibration–rotation motions of polyatomic molecules than has previously been recognized. Textbooks and modern papers (Nielson, 1951; Longuet-Higgens, 1963; Hougen, 1962, 1975) devote only a few lines of discussion to the Eckart conditions. Yet, as we shall show, the Eckart vectors and the Eckart frame should be considered to be basic conceptual constructs on which the theory of the vibration–rotation spectra of molecules is erected (along, of course, with our usual notions of classical and quantum mechanics).

The development follows the traditional viewpoint (Wilson, 1955) in assuming the validity of the Born–Oppenheimer approximation in separating the electronic and nuclear motions. Thus, the motions of the electrons are regarded as defining the potential energy wells in which the nuclei move. This is the basic physical picture which motivates the introduction of the equilibrium or static molecular model which serves as the starting point for the discussion of the vibration–rotation motions of the nuclei in a polyatomic molecule.

It might be argued that the reconstruction of molecular theory along such lines is a mere academic exercise, of little practical value and offering no new results. In order to persuade the reader that this is not the case, we present here in the Introduction a summary of the contents of this paper, noting, when appropriate, the contribution of the concepts of Eckart vectors and Eckart frames to the developments, and pointing to new results and new approaches as they emerge.

The concept of a static molecular model is introduced in Sec. II. Since it is on this model that the notion of the point group of a molecule is built, it is important to distinguish it from the molecule in motion. The purpose of this section is to give the problem a general setting as well as to review the basic notions of rotations and permutations as abstract operators in order to establish notations.

It is appropriate to remark here that while our approach in this study is group theoretically oriented, no sophisticated group theoretical concepts are actually used. A good intuitive feeling for the meaning of rotations in ordinary 3-space (see, for example Wigner, 1959) and an elementary understanding of set theoretical concepts and notations (we recommend Simmons, 1963) should provide sufficient mathematical background. To this extent, this paper is largely self-contained.

After the brief excursion into geometry given in Sec.

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II, we come in Sec. III to the concept of a molecule in motion—the dynamical molecular model. Here we attempt to give a new perspective to Eckart's contribution to the subject: The dependence of the notion "moving frame" on the underlying static model and the particle positions is presented in the way we believe Eckart understood it.

With the notions of Eckart vectors and Eckart frames in hand, we move naturally into the investigation of what motions of the molecule define the same Eckart frame. This leads to the discovery of the manner in which the point group of the static molecular model makes its entry into the molecular motions problem. The principal new result is the discovery of a group of transformations which leave the Eckart frame invariant. Further properties of the Eckart frame are presented in anticipation of its subsequent role in the molecular problem. All of these results are new, although it might be argued that some of the structures are implicit in the work of Hougen (1975).

We are now led into a discussion of the internal motions problem in Sec. IV. Astonishingly, the properties of an obvious modification of the Eckart vectors—to what we call Eckart vectors of the second kind—reduces the determination of symmetry coordinates to almost trivial calculations, at least for molecules possessing a static model of high symmetry. We illustrate the rather abstruse general theory by three instructive examples.

While we believe that the structures presented in Sec. IV are new, we are confronted here with an enormously difficult problem of literature search. The significance of group theory and normal coordinates in the molecular problem was apparently recognized as early as 1923 and 1930 by Brester (1923) and Wigner (1930). But the number of subsequent papers determining normal coordinates for particular molecules must run into the hundreds. The variations of techniques are impossible to assess. We mention only a few general references, with apologies to those authors whose contributions we would like to acknowledge but which are unfamiliar to us: (Dennison, 1931; Rosenthal and Murphy, 1936; Wilson, 1939, 1941; Glocker, 1943; Vankataraykdu, 1943; Kilpatrick, 1948; Corben and Stehle, 1950; Crawford, 1953).

We now come to Sec. V, where we consider the induced action of the abstract operators, previously defined, on the coordinates of the molecular problem. At first glance, these results seem more general than required. However, they are later (Sec. VI) shown to be significant in perturbation theory. In Sec. V, we study the action of permutations on the molecular coordinates in rigorous fashion, the basic idea stemming from the more intuitive approach of Longuet-Higgins (1963) and Hougen (1962, 1963, 1975). The most significant concept to emerge from this study of permutations is a general definition of the group of feasible operators for the so-called rigid molecules. It is a clear understanding of the role of the Eckart frame which makes the definition possible and physically relevant. Applications of this concept to the determination of intensity ratios of high-resolution laser induced absorption spectra in SF_6 have already been made (Cantrell and Galbraith, 1975), in agreement with experiment (Aldridge *et al.*, 1975).

A second important and longstanding question is clarified in Sec. V.D. What is the group of the classical spherical rigid rotator? Is it $\mathcal{O}_3 \times \mathcal{O}_3 \sim \mathcal{O}_4$, where $\mathcal{O}_3$ is the group of rotation-inversions of 3-space, and $\mathcal{O}_4$ is the group of rotation-inversions of 4-space? The answer to this question is no. Instead, it is demonstrated that the group of the classical spherical rigid rotator is a group of transformations of two 3-spaces which are geometrically related. This group is designated by $\mathcal{O}_3 * \mathcal{O}_3$, the * designating that the product space $R^3 * R^3$ of the two underlying 3-spaces is not the usual Cartesian product space. It is the geometrical relation between the two R^3 spaces which accounts for the fact that the angular momentum is the same (generators of rotations of the two $\mathcal{O}_3$'s in $\mathcal{O}_3 * \mathcal{O}_3$ commute, but have the same J^2). This type of group structure generalizes to other spaces and has been known for some time (Louck, 1965, 1970, 1970a; Biedenharn, 1967, 1968).

In Sec. VI, we present the general invariance properties of the molecular Hamiltonian. While these results have been, more or less, intuitively known for years, they are given here the precise mathematical and global settings required for use in the further development of Hamiltonians which describe the level splittings of complicated spherical top molecules (Hecht, 1960, 1960a; Moret-Bailly, 1959, 1961, 1965; Michelot *et al.*, 1974, 1974a).

Let us remark that we have felt obliged for the sake of clarity to note what seems to us to be important differences of interpretation between our work, that of Longuet-Higgens (1963), and the very important work of Hougen (1962, 1964, 1975). We acknowledge the considerable influence of Hougen's work in clarifying our thinking.

Finally, it should be noted that this work is restricted to the so-called "rigid" molecules, although a few speculative remarks concerning "nonrigid" molecules are made in the concluding section.

II. THE STATIC MOLECULAR MODEL AND ITS SYMMETRY GROUPS

A. The static molecular model

We begin with a definition: *The static molecular model is a collection of N particles (nuclei) labeled* $1, 2, \ldots, N$ *which have point masses* $m_1, m_2, \ldots, m_N$, *located at points specified by the position vectors* $\vec{a}^1, \vec{a}^2, \ldots, \vec{a}^N$, *respectively, whose common origin is the center of mass, that is,*

$$\sum_\alpha m_\alpha \vec{a}^\alpha = \vec{0}\,. \tag{2.1}$$

Thus, the picture we have of the static molecular model is the naive one of a collection of mass points connected by rigid rods. We are allowed to place it on the table in front of us, examine it, and describe it in terms of our tastes.

There is one aspect of the model which we prefer to leave vague—namely, those intrinsic attributes of certain classes of particles which lead us to call them *identical*. It suffices here to remark that the equality of masses and equality of charges are implied by the phrase "identical particles."

We choose to describe the particle positions by first

locating a principal axis frame $\hat{e}_1, \hat{e}_2, \hat{e}_3$ (a right-handed triad of unit vectors satisfying $\hat{e}_i \cdot \hat{e}_j = \delta_{ij}$) and giving the particle positions in terms of this frame

$$\vec{a}^{\alpha} = a_1^{\alpha}\hat{e}_1 + a_2^{\alpha}\hat{e}_2 + a_3^{\alpha}\hat{e}_3 \,. \tag{2.2}$$

The frame $\hat{e}_1, \hat{e}_2, \hat{e}_3$ is tied, once and for all time, to the rigid configuration of particles, and the set of real numbers

$$\{a_i^{\alpha}: \ \alpha = 1, 2, \ldots, N, \ \ i = 1, 2, 3\} \tag{2.3}$$

is fixed, once and for all time, by the equilibrium configuration which one has assumed for the particular molecule under study.

We have dwelt overlong, perhaps, on the concept of the static molecular model in order to contrast it with the *dynamical molecular model* introduced later in Sec. III. This distinction of models, we believe, clarifies one's understanding of the role of the point group of covering operations in molecular theory. We now turn to the definition of the point group of the static molecular model, reviewing first the concepts of rotations as abstract operators.

B. The rotation-inversion group

We introduce the space R^3 which is defined to be the *set of all vectors* in Euclidean 3-space (directed arrows in the usual elementary sense with the customary geometric rules for equivalence, addition, multiplication by a scalar, and dot and cross products).

A rotation $\mathcal{R}$ is, by definition, a *linear operator* which maps R^3 into itself, leaving the dot product invariant and the sense of the cross product unchanged. These properties are transcribed into the mathematical statements which follow:

$$\mathcal{R}: R^3 \to R^3, \tag{2.4a}$$

that is, for each $\vec{x} \in R^3$, we have

$$\vec{x} \to \vec{x}' = \mathcal{R}\vec{x} \in R^3 \,. \tag{2.4b}$$

The dot and cross product properties read

$$\mathcal{R}\vec{x} \cdot \mathcal{R}\vec{y} = \vec{x} \cdot \vec{y} \,, \tag{2.4c}$$

$$\mathcal{R}\vec{x} \times \mathcal{R}\vec{y} = \mathcal{R}(\vec{x} \times \vec{y}) \tag{2.4d}$$

for each pair $\vec{x}, \vec{y} \in R^3$.

The set of all linear operators $\{\mathcal{R}\}$ which satisfy the rules (2.4) together with the multiplication rule

$$(\mathcal{R}'\mathcal{R})\vec{x} = \mathcal{R}'(\mathcal{R}\vec{x}) \tag{2.5}$$

defines a group—the group $\mathcal{SO}_3$ of rotations of the space R^3.

The inversion operator $\mathcal{I}$ is also defined to be the mapping $\mathcal{I}$: $R^3 \to R^3$ given by

$$\mathcal{I}\vec{x} = -\vec{x} \tag{2.6}$$

for each $\vec{x} \in R^3$. An inversion also has the property of preserving the dot product, but it changes the sense of the cross product:

$$\mathcal{I}\vec{x} \times \mathcal{I}\vec{y} = -\mathcal{I}(\vec{x} \times \vec{y}) \,. \tag{2.7}$$

The set of linear operators which map R^3 into itself and preserve the dot product defines the rotation–inversion group. It is the set of operators given by

$$\mathcal{O}_3 = \{\mathcal{R}, \mathcal{I}\mathcal{R}: \ \mathcal{R} \in \mathcal{SO}_3\} \,. \tag{2.8}$$

At the risk of some confusion, we will use the same notation $\mathcal{R}$ for a general element of $\mathcal{O}_3$ as used for a general element of $\mathcal{SO}_3$. Henceforth, if $\mathcal{R}$ is a rotation, it will always be so indicated explicitly; otherwise, $\mathcal{R} \in \mathcal{O}_3$.

It is sometimes convenient to parametrize the rotation operators $\mathcal{R}$. The most convenient parametrization for use with point groups is the characterization of a rotation by a unit vector $\hat{n}$ (which specifies the direction about which the rotation takes place in the right-handed sense) and the rotation angle θ, where $0 \leq \theta \leq \pi$. There is then a one-to-one correspondence between the points of the *solid sphere* of radius π and the set of rotations, when one identifies (as being the same) diametrically opposite points on the surface of the sphere. We denote such a parametrized rotation by $\mathcal{R}(\theta, \hat{n})$. The action of $\mathcal{R}(\theta, \hat{n})$ on an arbitrary vector $\vec{x} \in R^3$ is then given by (Corben and Stehle, 1950)

$$\mathcal{R}(\theta, n)\vec{x} = \cos\theta\vec{x} + (1 - \cos\theta)(\hat{n} \cdot \vec{x})\hat{n} + \sin\theta(\hat{n} \times \vec{x}) \,. \tag{2.9}$$

Note in particular that

$$\mathcal{R}(\pi, -\hat{n}) = \mathcal{R}(\pi, \hat{n}) \tag{2.10}$$

obtains automatically from Eq. (2.9).

After this brief review of rotation and inversion operators as abstract operations defined on R^3, let us now return to the discussion of the static model.

C. The mathematical model of the static molecule

We represent the static model mathematically by the set $\mathfrak{A}$ of vectors of R^3:

$$\mathfrak{A} = \{\vec{a}^1, \vec{a}^2, \ldots, \vec{a}^N\} \,. \tag{2.11a}$$

We now give the definition of the *equivalence under* $\mathcal{O}_3$ of two static model vectors: $\vec{a}^{\beta}$ *is equivalent to* $\vec{a}^{\alpha}$ *if* (a) *particle* β *is identical to particle* α; (b) *there exists at least one rotation–inversion operator* $\mathcal{R}_0 \in \mathcal{O}_3$ *such that* $\vec{a}^{\beta} = \mathcal{R}_0\vec{a}^{\alpha}$. Observe that this is a true equivalence relation (Simmons, 1963) in the strict mathematical sense. Accordingly, the set $\mathfrak{A}$ is partitioned into *disjoint subsets of equivalent vectors called equivalence classes of* $\mathfrak{A}$ (Simmons, 1963). Let us denote these equivalence classes by $\mathfrak{A}_a, \mathfrak{A}_b, \ldots, \mathfrak{A}_d$, where

$$\mathfrak{A}_a = \{\vec{a}^1, \vec{a}^2, \ldots, \vec{a}^{n_a}\} \,, \tag{2.11b}$$

$$\mathfrak{A}_b = \{\vec{b}^1, \vec{b}^2, \ldots, \vec{b}^{n_b}\} \,, \tag{2.11c}$$

$$\vdots$$

$$\mathfrak{A}_d = \{\vec{d}^1, \vec{d}^2, \ldots, \vec{d}^{n_d}\} \,. \tag{2.11d}$$

$$\mathfrak{A} = \{\mathfrak{A}_a, \mathfrak{A}_b, \ldots, \mathfrak{A}_d\} \,, \tag{2.12a}$$

$$N = n_a + n_b + \cdots + n_d \,. \tag{2.12b}$$

(Observe that by a relabeling of particles we can always take the first n_a of the $\vec{a}^1, \ldots, \vec{a}^N$ to be equivalent.)

D. The point group of the static model

We are now ready to define the point group of the static molecular model. Definition: *The point group* $G(\mathfrak{A})$ *is*

the subgroup of $\mathcal{O}_3$ *which maps each equivalence class of* $\mathfrak{A}$ *onto itself, that is* $\mathcal{G} \in G(\mathfrak{A})$ *if and only if*

$$\begin{aligned} &\mathcal{G}\colon \mathfrak{A}_a \to \mathfrak{A}_a\,,\\ &\mathcal{G}\colon \mathfrak{A}_b \to \mathfrak{A}_b\,,\\ &\cdot\\ &\cdot\\ &\cdot\\ &\mathcal{G}\colon \mathfrak{A}_d \to \mathfrak{A}_d\,. \end{aligned} \tag{2.13}$$

This definition becomes more tangible if we *order* the elements of the sets $\mathfrak{A}_a, \mathfrak{A}_b, \ldots, \mathfrak{A}_d$ and consider these ordered sets to be row matrices:

$$\begin{aligned} &[\vec{a}^{\,1}\,\vec{a}^{\,2}\cdots\vec{a}^{\,n_a}]\,,\\ &[\vec{b}^{\,1}\vec{b}^{\,2}\cdots\vec{b}^{\,n_b}]\,,\\ &\cdot\\ &\cdot\\ &\cdot\\ &[\vec{d}^{\,1}\vec{d}^{\,2}\cdots\vec{d}^{\,n_d}]. \end{aligned} \tag{2.14}$$

The action of $\mathcal{G}$ on the sets $\mathfrak{A}_a, \mathfrak{A}_b, \ldots, \mathfrak{A}_d$ may now be expressed concisely as

$$\begin{aligned} &\mathcal{G}\colon [\vec{a}^{\,1}\vec{a}^{\,2}\cdots\vec{a}^{\,n_a}] \to [\mathcal{G}\vec{a}^{\,1}\mathcal{G}\vec{a}^{\,2}\cdots\mathcal{G}\vec{a}^{\,n_a}]\\ &\qquad\qquad = [\vec{a}^{\,1}\vec{a}^{\,2}\cdots\vec{a}^{\,n_a}]S_a(\mathcal{G})\,,\\ &\mathcal{G}\colon [\vec{b}^{\,1}\vec{b}^{\,2}\cdots\vec{b}^{\,n_b}] \to [\mathcal{G}\vec{b}^{\,1}\mathcal{G}\vec{b}^{\,2}\cdots\mathcal{G}\vec{b}^{\,n_b}]\\ &\qquad\qquad = [\vec{b}^{\,1}\vec{b}^{\,2}\cdots\vec{b}^{\,n_b}]S_b(\mathcal{G})\,,\\ &\cdot\\ &\cdot\\ &\cdot\\ &\mathcal{G}\colon [\vec{d}^{\,1}\vec{d}^{\,2}\cdots\vec{d}^{\,n_d}] \to [\mathcal{G}\vec{d}^{\,1}\mathcal{G}\vec{d}^{\,2}\cdots\mathcal{G}\vec{d}^{\,n_d}]\\ &\qquad\qquad = [\vec{d}^{\,1}\vec{d}^{\,2}\cdots\vec{d}^{\,n_d}]S_d(\mathcal{G})\,, \end{aligned} \tag{2.15}$$

where $S_a(\mathcal{G}), S_b(\mathcal{G}), \ldots, S_d(\mathcal{G})$ are square matrices of dimensions $n_a, n_b, \ldots, n_d$, respectively, each of which may be obtained from the unit matrices I_a of dimension n_a, I_b of dimension n_b, etc., by some permutation of the columns (hence, the matrices are real, orthogonal and contain as elements only zeroes and ones).

It is convenient to define

$$\mathcal{G}[\vec{a}^{\,1}\vec{a}^{\,2}\cdots\vec{a}^{\,N}] = [\mathcal{G}\vec{a}^{\,1}\mathcal{G}\vec{a}^{\,2}\cdots\mathcal{G}\vec{a}^{\,N}]\,. \tag{2.16}$$

If we define the product of two elements of $G(\mathfrak{A})$ by the rule

$$\begin{aligned} (\mathcal{G}'\mathcal{G})[\vec{a}^{\,1}\vec{a}^{\,2}\cdots\vec{a}^{\,N}] &= \mathcal{G}'(\mathcal{G}[\vec{a}^{\,1}\vec{a}^{\,2}\cdots\vec{a}^{\,N}])\\ &= \mathcal{G}'[\mathcal{G}\vec{a}^{\,1}\mathcal{G}\vec{a}^{\,2}\cdots\mathcal{G}\vec{a}^{\,N}]\\ &= [\mathcal{G}'\mathcal{G}\vec{a}^{\,1}\mathcal{G}'\mathcal{G}\vec{a}^{\,2}\cdots\mathcal{G}'\mathcal{G}\vec{a}^{\,N}]\,, \end{aligned} \tag{2.17}$$

then the correspondence

$$\mathcal{G} \to S_a(\mathcal{G}) \tag{2.18}$$

is a representation of $G(\mathfrak{A})$ by $n_a \times n_a$ orthogonal matrices. Similarly, each of the correspondences $\mathcal{G} \to S_b(\mathcal{G}), \ldots, \mathcal{G} \to S_d(\mathcal{G})$ is a representation of $G(\mathfrak{A})$ by orthogonal matrices. We call these matrix representations of $G(\mathfrak{A})$ *static model representations*.

It is somewhat awkward to enumerate repeatedly sets of equations such as Eqs. (2.11)–(2.15). In the subsequent discussion we will therefore write such equations as a single composite one:

$$\begin{aligned} \mathcal{G}\colon [\vec{a}^{\,1}\vec{a}^{\,2}\cdots\vec{a}^{\,N}] &\to \mathcal{G}[\vec{a}^{\,1}\vec{a}^{\,2}\cdots\vec{a}^{\,N}]\\ &= [\mathcal{G}\vec{a}^{\,1}\mathcal{G}\vec{a}^{\,2}\cdots\mathcal{G}\vec{a}^{\,N}] = [\vec{a}^{\,1}\vec{a}^{\,2}\cdots\vec{a}^{\,N}]S(\mathcal{G})\,, \end{aligned} \tag{2.19a}$$

where it is to be understood that

$$[\vec{a}^{\,1}\vec{a}^{\,2}\cdots\vec{a}^{\,N}] = [\vec{a}^{\,1}\vec{a}^{\,2}\cdots\vec{a}^{\,n_a}\vec{b}^{\,1}\vec{b}^{\,2}\cdots\vec{b}^{\,n_b}\cdots\vec{d}^{\,1}\vec{d}^{\,2}\cdots\vec{d}^{\,n_d}]\,, \tag{2.19b}$$

and that $S(\mathcal{G})$ has the block diagonal form

$$S(\mathcal{G}) = \begin{bmatrix} S_a(\mathcal{G}) & 0 & \cdots & 0\\ 0 & S_b(\mathcal{G}) & \cdots & 0\\ \cdot & & & \cdot\\ \cdot & & & \cdot\\ 0 & 0 & \cdots & S_d(\mathcal{G}) \end{bmatrix}. \tag{2.19c}$$

Observe that the mass matrix defined by

$$\begin{aligned} M &= \begin{bmatrix} m_1 & 0 & \cdots & 0\\ 0 & m_2 & \cdots & 0\\ \cdot & & & \cdot\\ \cdot & & & \cdot\\ \cdot & & & \cdot\\ 0 & 0 & \cdots & m_N \end{bmatrix}\\ &= \begin{bmatrix} m_a I_a & 0 & \cdots & 0\\ 0 & m_b I_b & \cdots & 0\\ \cdot & & & \cdot\\ \cdot & & & \cdot\\ \cdot & & & \cdot\\ 0 & 0 & \cdots & m_d I_d \end{bmatrix} \end{aligned} \tag{2.20}$$

commutes with $S(\mathcal{G})$:

$$S(\mathcal{G})M = MS(\mathcal{G}) \tag{2.21}$$

for each $\mathcal{G} \in G(\mathfrak{A})$.

E. The symmetric group of the static model

The belief that arbitrary labelings of identical particles should have no consequences for the predictions of a physical theory leads one to the study of the symmetric group.

We first consider the manner in which one defines the action of the symmetric group S_N on a quite general set of N objects which we can take without loss of generality to be the set $\mathfrak{A}$ of static model vectors.

A permutation P of the labels $1, 2, \ldots, N$ is defined by

$$P\colon 1 \to \alpha_1, 2 \to \alpha_2, \ldots, N \to \alpha_N\,, \tag{2.22}$$

where $\alpha_1, \alpha_2, \ldots, \alpha_N$ is a rearrangement of $1, 2, \ldots, N$. The product $P'P$ of two such permutations

$$P'\colon 1 \to \alpha'_1, 2 \to \alpha'_2, \ldots, N \to \alpha'_N$$

and

$$P\colon 1 \to \alpha_1, 2 \to \alpha_2, \ldots, N \to \alpha_N$$

is by definition the permutation of $1, 2, \ldots, N$ obtained by first applying P followed by applying P'. For example, for

$$P\colon 1\to 2, 2\to 3, 3\to 4, 4\to 1$$

and

$$P'\colon 1\to 4, 2\to 2, 3\to 1, 4\to 3,$$

we have

$$P'P\colon 1\to 2, 2\to 1, 3\to 3, 4\to 4.$$

S_N is the set of all permutations $\{P\}$ corresponding to all $N!$ rearrangements of $1, 2, \ldots, N$ with this rule of multiplication.

Each permutation $P\in S_N$ induces a transformation $\mathcal{P}$ of the set $\mathfrak{A}$ given by the following rule:

$$\mathcal{P}\colon \vec{a}^1\to\vec{a}^{\alpha_1}, \vec{a}^2\to\vec{a}^{\alpha_2}, \ldots, \vec{a}^N\to\vec{a}^{\alpha_N}. \tag{2.23}$$

The product $\mathcal{P}'\mathcal{P}$ of two such transformations is defined to be the rule of first transforming by $\mathcal{P}$ *followed by* transforming by $\mathcal{P}'$. The correspondence $P\to\mathcal{P}$ is a representation of S_N by a group of transformations of the static model vectors. We designate this group of transformations by $G(S_N)$.

For $\mathcal{P}$ given by Eq. (2.23), we write $\vec{a}^{\alpha_1}=\mathcal{P}\vec{a}^1, \vec{a}^{\alpha_2}=\mathcal{P}\vec{a}^2, \ldots, \vec{a}^{\alpha_N}=\mathcal{P}\vec{a}^N$. Defining

$$\mathcal{P}[\vec{a}^1\vec{a}^2\cdots\vec{a}^N]=[\mathcal{P}\vec{a}^1\mathcal{P}\vec{a}^2\cdots\mathcal{P}\vec{a}^N], \tag{2.24}$$

we obtain

$$\mathcal{P}[\vec{a}^1\vec{a}^2\cdots\vec{a}^N]=[\vec{a}^1\vec{a}^2\cdots\vec{a}^N]S(\mathcal{P}), \tag{2.25a}$$

where

$$S(\mathcal{P})=[e_{\alpha_1}e_{\alpha_2}\cdots e_{\alpha_N}], \tag{2.25b}$$

in which e_α is the column matrix of length N, $e_\alpha=\mathrm{col}[0\cdots010\cdots0]$, where the 1 appears in position α. The correspondence

$$\mathcal{P}\to S(\mathcal{P}) \tag{2.26}$$

is a matrix representation of $G(S_N)$, hence, of S_N, by orthogonal matrices of dimension N containing only zeroes and ones.

Let us now return to the question of identical particles by giving the definition of the *equivalence under particle identity* of two static model vectors: $\vec{a}^\beta$ *is equivalent to* $\vec{a}^\alpha$ *if particle* β *is identical to particle* α. Again this is an equivalence relation which partitions the set $\mathfrak{A}$ into disjoint sets of equivalence classes. The elements of one of these equivalence classes are, of course, the position vectors which point to particles which have been called identical. Observe that *each* such equivalence class may be further partitioned into disjoint equivalence classes with respect to $\mathfrak{G}_3$. *For simplicity of presentation, we will assume through the remainder of this paper that the equivalence classes of* $\mathfrak{A}$ *under particle identity are the same as the equivalence classes of* $\mathfrak{A}$ *under* $\mathfrak{G}_3$.

Under the above assumption, the group of permutation operators which interchange the position vectors pointing to identical particles is the direct product subgroup of $G(S_N)$ given by

$$\prod_\lambda G(S_{n_\lambda})=G(S_{n_a})\times G(S_{n_b})\times\cdots\times G(S_{n_d})\subset G(S_n), \tag{2.27}$$

where the $G(S_{n_\lambda})$, $\lambda=a, b, \ldots, d$, denote the groups of permutation operators defined, respectively, on the sets $\mathfrak{A}_a, \mathfrak{A}_b, \ldots, \mathfrak{A}_d$. Thus, each $\mathcal{P}_a\in G(S_{n_a})$ has the form

$$\mathcal{P}_a\colon \vec{a}^1\to\vec{a}^{\alpha_1}, \vec{a}^2\to\vec{a}^{\alpha_2}, \ldots, \vec{a}^{n_a}\to\vec{a}^{\alpha_{n_a}}, \tag{2.28a}$$

where $\alpha_1, \alpha_2, \ldots, \alpha_{n_a}$ is a rearrangement of $1, 2, \ldots, n_a$; each $\mathcal{P}_b\in G(S_{n_b})$ has the form

$$\mathcal{P}_b\colon \vec{b}^1\to\vec{b}^{\beta_1}, \vec{b}^2\to\vec{b}^{\beta_2}, \ldots, \vec{b}^{n_b}\to\vec{b}^{\beta_{n_b}}, \tag{2.28b}$$

where $\beta_1, \beta_2, \ldots, \beta_{n_b}$ is a rearrangement of $1, 2, \ldots, n_b$, etc. Each permutation operator $\mathcal{P}$ in the group

$$\prod_\lambda G(S_{n_\lambda}) \tag{2.29a}$$

has the form

$$\mathcal{P}=(\mathcal{P}_a, \mathcal{P}_b, \ldots, \mathcal{P}_d), \tag{2.29b}$$

and the order of the group is $n_a!n_b!\cdots n_d!$.

For each

$$\mathcal{P}\in\prod_\lambda G(S_{n_\lambda}) \tag{2.30a}$$

the matrix $S(\mathcal{P})$ appearing in Eq. (2.25a) takes the block diagonal form

$$S(\mathcal{P})=\begin{bmatrix} S(\mathcal{P}_a) & 0 & \cdots & 0 \\ 0 & S(\mathcal{P}_b) & \cdots & 0 \\ \vdots & & & \vdots \\ 0 & 0 & \cdots & S(\mathcal{P}_d) \end{bmatrix} \tag{2.30b}$$

in which each $S(\mathcal{P}_\lambda)$ is of the form (2.25b) (replace N by n_λ). Finally, the correspondence

$$\mathcal{P}_\lambda\to S(\mathcal{P}_\lambda) \tag{2.31}$$

is a matrix representation of S_{n_λ} by *permutation matrices* (matrices obtained from the unit matrix by permuting its columns).

We conclude this discussion of the static molecular model with a final observation: *The point group* $G(\mathfrak{A})$ *of the static molecular model is a subgroup of the permutation group* $\prod_\lambda G(S_{n_\lambda})$. The correspondence between the elements of this subgroup of permutation operators and the elements of the point group $G(\mathfrak{A})$ is given by the rule

$$\mathcal{P}\leftrightarrow\mathcal{G} \quad \text{if } S(\mathcal{P})=S(\mathcal{G}). \tag{2.32}$$

III. THE DYNAMICAL MOLECULAR MODEL

We now let the static molecular model translate and rotate about the center of mass, while at the same time allowing the particles to move away from their rigid body positions. It was just for the purpose of describing motions of this type that Eckart introduced a moving frame which has its instantaneous orientation determined by the instantaneous position vectors of the particles and the static molecular model. We will introduce Eckart's moving frame from the outset. Although this method of presentation is not so well motivated physically, it has the logical advantage of presenting a well-defined moving frame at the beginning of the discussion, thus obviating the need of imagining its existence (and resolving vectors along its axes) prior to having it defined.

A. Eckart vectors and Eckart frames

Let the N instantaneous position vectors of the particles $1, 2, \ldots, N$ be denoted by $\vec{r}^1, \vec{r}^2, \ldots, \vec{r}^N$ relative to some fixed point O. Following Eckart, we introduce three vectors which are defined completely by the set of numbers (equilibrium position vectors) $\{a_i^\alpha: \alpha = 1, 2, \ldots, N; i = 1, 2, 3\}$ given to us by the static molecular model, by the masses of the particles, and by the instantaneous position vectors $\vec{r}^1, \vec{r}^2, \ldots, \vec{r}^N$:

$$\vec{F}_i = \sum_\alpha m_\alpha a_i^\alpha \vec{r}^\alpha, \quad i = 1, 2, 3. \tag{3.1}$$

We emphasize that the numbers a_i^α appearing in this definition are considered to be fixed (and never to be transformed) by the static model. Observe that we can just as well write

$$\vec{F}_i = \sum_\alpha m_\alpha a_i^\alpha (\vec{r}^\alpha - \vec{R}), \tag{3.2}$$

where $\vec{R}$ is the center of mass vector defined by

$$\vec{R} = \sum_\alpha m_\alpha \vec{r}^\alpha \Big/ \sum_\alpha m_\alpha, \tag{3.3a}$$

since

$$\sum_\alpha m_\alpha a_i^\alpha = 0. \tag{3.3b}$$

We propose to call the three vectors $\vec{F}_1, \vec{F}_2, \vec{F}_3$ *Eckart vectors*. The purpose in introducing these vectors has been justified by Eckart, but it is useful to demonstrate again their role in the more familiar Eckart conditions, which we do below.

Still following Eckart, we next define a right-handed triad of unit vectors $\hat{f}_1, \hat{f}_2, \hat{f}_3$ in terms of the vectors $\vec{F}_1, \vec{F}_2, \vec{F}_3$. For nonlinear and nonplanar molecules, the definition is[1,2]

$$[\hat{f}_1 \hat{f}_2 \hat{f}_3] = [\vec{F}_1 \vec{F}_2 \vec{F}_3] F^{-1/2}, \tag{3.4a}$$

where F is the symmetric (Gram) matrix given by

$$F = \begin{bmatrix} \vec{F}_1 \cdot \vec{F}_1 & \vec{F}_1 \cdot \vec{F}_2 & \vec{F}_1 \cdot \vec{F}_3 \\ \vec{F}_2 \cdot \vec{F}_1 & \vec{F}_2 \cdot \vec{F}_2 & \vec{F}_2 \cdot \vec{F}_3 \\ \vec{F}_3 \cdot \vec{F}_1 & \vec{F}_3 \cdot \vec{F}_2 & \vec{F}_3 \cdot \vec{F}_3 \end{bmatrix}. \tag{3.4b}$$

For planar molecules, we always choose $\hat{e}_3$ perpendicular to the plane of the static model. Then $a_3^\alpha = 0$. In this case, the right-handed triad of unit vectors $\hat{f}_1, \hat{f}_2, \hat{f}_3$ is defined by

$$[\hat{f}_1 \hat{f}_2] = [\vec{F}_1 \vec{F}_2] F^{-1/2}, \tag{3.4c}$$

$$\hat{f}_3 = \hat{f}_1 \times \hat{f}_2, \tag{3.4d}$$

where F is the symmetric matrix given by

$$F = \begin{bmatrix} \vec{F}_1 \cdot \vec{F}_1 & \vec{F}_1 \cdot \vec{F}_2 \\ \vec{F}_2 \cdot \vec{F}_1 & \vec{F}_2 \cdot \vec{F}_2 \end{bmatrix}. \tag{3.4e}$$

For linear molecules, we do not define an Eckart frame (hence, linear molecules are excluded from this discussion).

A Gram matrix is always positive definite as long as the vectors entering into its definition are linearly independent. The requirement of the linear independence of the Eckart vectors then becomes conditions on the position vectors $\vec{r}^\alpha$ under which the unit vectors $\hat{f}_1, \hat{f}_2, \hat{f}_3$ are defined. (We will usually address the three-dimensional molecular model, it being obvious how to modify the results for the planar case.) We assume for molecular motions that F is positive definite. F^{-1} is then also positive definite, and $F^{-1/2}$ denotes the positive definite matrix—a unique matrix—such that $F^{-1/2}F^{-1/2} = F^{-1}$ (Perlis, 1952). We shall call the triplet of vectors $\hat{f}_1, \hat{f}_2, \hat{f}_3$ the *Eckart frame*.

The Eckart frame is located at the center of mass of the collection of particles [see the interpretation of Eq. (3.6) given in the remarks below], and its instantaneous orientation is determined solely by the instantaneous position vectors (and the underlying static molecular model). It happens, in practice, that one never actually constructs explicitly the Eckart frame vectors in terms of the instantaneous position vectors. What we do is quite different. We turn the problem around and ask what is the class of motions which define the *same* Eckart frame. These then become the motions which an observer in the Eckart frame can record. In this manner, the constraints have been placed on the motions of the particles, and we are free to consider that the Eckart frame has an arbitrary orientation in space. We must keep this dual perspective of the Eckart frame. One of the purposes of this paper is to make clear the content of the preceding remarks.[3]

To make the connection of the preceding results with the Eckart conditions, we note that the vectors $\hat{f}_1, \hat{f}_2, \hat{f}_3$ and $\vec{F}_1, \vec{F}_2, \vec{F}_3$ satisfy

$$\hat{f}_1 \times \vec{F}_1 + \hat{f}_2 \times \vec{F}_2 + \hat{f}_3 \times \vec{F}_3 = \vec{0}. \tag{3.5}$$

Substituting the $\vec{F}_i$ vectors of Eq. (3.1) into this result and defining

$$\vec{c}^\alpha = \sum_i a_i^\alpha \hat{f}_i, \tag{3.6}$$

we obtain the original conditions given by Eckart:

[1] Our procedure differs slightly from Eckart's since he uses reciprocal vectors, but this distinction is unimportant.

[2] This method generalizes directly to the construction of n perpendicular vectors $x_1, x_2, \ldots, x_n$ from n given linearly independent vectors $y_1, y_2, \ldots, y_n$. This method was brought to our attention by Dr. Robert D. Cowan of the Los Alamos Scientific Laboratory. Schweinler and Wigner (1970) attribute it to Landshoff (1936). It is interesting to observe that the standard Gram–Schmidt procedure is invariant under the group of triangular transformations

$$y_1 \to a_{11} y_1, \quad y_2 \to a_{21} y_1 + a_{22} y_2, \ldots,$$

$$y_n \to a_{n1} y_1 + a_{n2} y_2 + \cdots + a_{nn} y_n,$$

while the method above is invariant under the group of permutations in the sense that any rearrangement of order of vectors in the given set $y_1, y_2, \ldots, y_n$ followed by the orthonormalization procedure produces the same rearrangement of the perpendicular vectors (Schweinler and Wigner, 1970).

[3] It seems possible that this method of introducing a moving frame into a collection of N particles might have applications to other problems. Observe that the a_i^α in Eq. (3.1) can be taken to be the components of any set of N position vectors such as initial positions, average positions, expectation values of position operators, etc.

$$\sum_\alpha m_\alpha \vec{c}^\alpha \times (\vec{r}^\alpha - \vec{R}) = \vec{0}\,. \tag{3.7}$$

It is also useful to put

$$\vec{r}^\alpha - \vec{R} = \vec{c}^\alpha + \vec{\rho}^\alpha\,, \tag{3.8}$$

and then the Eckart conditions become

$$\sum_\alpha m_\alpha \vec{c}^\alpha \times \vec{\rho}^\alpha = \vec{0}\,. \tag{3.9}$$

Remarks. Some comments about the interpretation of the preceding equations are in order. Consider Eq. (3.6) first. By definition, *the vectors $\vec{c}^\alpha$ are constant vectors when referred to the Eckart frame.* It is just this requirement which leads us to the following picture: We imagine at each instant of time that the principal axes $\hat{e}_1, \hat{e}_2, \hat{e}_3$ of Sec. II.A are coincident with the Eckart frame $\hat{f}_1, \hat{f}_2, \hat{f}_3$, which is itself placed at the center of mass position vector $\vec{R}$. Then, indeed, the $\vec{c}^\alpha$ vectors are constant vectors with respect to $\hat{f}_1, \hat{f}_2, \hat{f}_3$ with components $a_1^\alpha, a_2^\alpha, a_3^\alpha$. The interpretation of the $\vec{\rho}^\alpha$ in Eq. (3.8) is then also clear—in the Eckart frame the $\vec{c}^\alpha$ are constant vectors so that the meaning of $\vec{\rho}^\alpha$ is that of a displacement of particle α away from its equilibrium position. Having established this significance of $\vec{\rho}^\alpha$ in one frame, it retains this significance in any reference frame. Indeed, it should be emphasized that all of the results, Eqs. (3.1)–(3.9), have been obtained without benefit of a laboratory frame—they are abstract vector relations, valid as geometrical relations between vectors.

Let us summarize the steps which have led us from our intuitive conception of a (classical) molecule to the mathematical description of it:

Step 1. In the static model, we label the particles $1, 2, \ldots, N$ and put in the corresponding vectors $\vec{a}^1, \vec{a}^2, \ldots, \vec{a}^N$.

Step 2. We introduce any principal axes system whatsoever and calculate the set of numbers $\{a_i^\alpha\}$.

Step 3. We introduce the Eckart vectors $\vec{F}_1, \vec{F}_2, \vec{F}_3$ and the Eckart frame $\hat{f}_1, \hat{f}_2, \hat{f}_3$, which is completely defined in terms of the static model and the instantaneous position vectors $\vec{r}^1, \vec{r}^2, \ldots, \vec{r}^N$ of the particles. (We ignore the possibility that the instantaneous vectors might define a straight line at some instant of time.)

Step 4. We place the Eckart frame at the instantaneous center of mass and take the static model of step 1 and step 2 and align the principal axes system we have chosen with the Eckart frame. In this Eckart frame, the constant vectors $\vec{c}^\alpha = \sum_i a_i^\alpha \hat{f}_i$ define what we call the equilibrium positions of the particles. Finally, we introduce the vectors $\vec{\rho}^\alpha = \vec{r}^\alpha - \vec{R} - \vec{c}^\alpha$, $\alpha = 1, 2, \ldots, N$, which we call displacement vectors of the particles.

We call the picture which emerges from steps 1–4 a *dynamical molecular model.* One will observe that there is nothing "intrinsically small" about the displacement vectors. One might, however, question the usefulness of the above model unless there is some reason to believe that each particle α stays in the vicinity of the point defined by $\vec{c}^\alpha$.

One will also observe that a dynamical molecular model is not unique. Its lack of uniqueness comes from steps 1 and 2: Different investigators will usually label the particles differently and choose different principal axes systems, thus obtaining various sets of numbers $\{a_i^\alpha\}$. Once one has made a definite choice of particle labeling and principal axes in steps 1 and 2, the dynamical model is unique. *Within this model, the numbers $\{a_i^\alpha\}$ are never to be altered.* The effect of choosing different particle labelings and different principal axes is discussed in Sec. III.D, after our understanding of a given dynamical model has been increased.

There is a second set of Eckart vectors which also plays an important role in the molecular problem. They are the same in form as Eqs. (3.1). We simply replace the position vectors $\vec{r}^\alpha$ by the displacement vectors $\vec{\rho}^\alpha$:

$$\vec{E}_i = \sum_\alpha m_\alpha a_i^\alpha \vec{\rho}^\alpha, \quad i = 1, 2, 3. \tag{3.10}$$

We may then write

$$\vec{F}_i = \vec{C}_i + \vec{E}_i\,, \tag{3.11a}$$

where

$$\vec{C}_i = \sum_\alpha m_\alpha a_i^\alpha \vec{c}^\alpha\,. \tag{3.11b}$$

Since

$$\hat{f}_1 \times \vec{C}_1 + \hat{f}_2 \times \vec{C}_2 + \hat{f}_3 \times \vec{C}_3 = \vec{0}\,, \tag{3.12}$$

the Eckart conditions in the form (3.9) become

$$\hat{f}_1 \times \vec{E}_1 + \hat{f}_2 \times \vec{E}_2 + \hat{f}_3 \times \vec{E}_3 = \vec{0}\,. \tag{3.13}$$

We will subsequently see that the Eckart vectors $\vec{E}_1, \vec{E}_2, \vec{E}_3$ have an important role in the normal coordinate problem. At the moment, we use Eq. (3.13) as the basis for making several definitions.

The term "displacement vector" for $\vec{\rho}^\alpha$ has been introduced because of its geometrical significance as describing the instantaneous position of a particle relative to an equilibrium position. Aside from having the form $\vec{\rho}^\alpha = \vec{r}^\alpha - \vec{c}^\alpha - \vec{R}$, $\alpha = 1, 2, \ldots, N$ (from which follows the center of mass condition $\sum_\alpha m_\alpha \vec{\rho}^\alpha = 0$), these displacement vectors are also required to have the property that their corresponding Eckart vectors satisfy the condition (3.13) with respect to the Eckart frame. We now take these properties as a formal definition: *A vector $\vec{\xi}^\alpha$ in the set $\{\vec{\xi}^1, \vec{\xi}^2, \ldots, \vec{\xi}^N\}$ is called a displacement vector compatible with the Eckart frame $\hat{f}_1, \hat{f}_2, \hat{f}_3$ defined by Eq. (3.4) if and only if* (a) *it has the form $\vec{\xi}^\alpha = \vec{r}^\alpha - \vec{c}^\alpha - \vec{R}$, where $\vec{c}^\alpha$ is given by Eq. (3.6);* (b) *the three Eckart vectors $\vec{E}_i = \sum_\alpha m_\alpha a_i^\alpha \vec{\xi}^\alpha$ satisfy $\hat{f}_1 \times \vec{E}_1 + \hat{f}_2 \times \vec{E}_2 + \hat{f}_3 \times \vec{E}_3 = \vec{0}$.* We call the set of vectors $\{\vec{\xi}^1, \ldots, \vec{\xi}^N\}$ a set of displacement vectors.

One of the most important problems in the kinematics of molecules is the following: Find the set

$$\{\{\vec{\xi}^1, \ldots, \vec{\xi}^N\}; \{\vec{\eta}^1, \ldots, \vec{\eta}^N\}; \ldots; \{\vec{\rho}^1, \ldots, \vec{\rho}^N\}, \ldots\} \tag{3.14}$$

of all displacement vectors compatible with a given Eckart frame. This problem is addressed in the following sections, the complete answer emerging only with the solution to the internal motions problem.

B. An invariance group of the Eckart frame

The purpose of this section is to determine certain sets of displacement vectors compatible with the Eckart

frame $\hat{f}_1, \hat{f}_2, \hat{f}_3$.

Let $\vec{r}^1, \vec{r}^2, \ldots, \vec{r}^N$ and $\vec{s}^1, \vec{s}^2, \ldots, \vec{s}^N$ denote sets of position vectors corresponding to two possible configurations of the particles—instantaneous position vectors which might have evolved, for example, from different initial conditions. The position vectors relative to the center of mass are given by

$$\vec{x}^\alpha = \vec{r}^\alpha - \vec{R}, \quad \alpha = 1, 2, \ldots, N, \tag{3.15a}$$

$$\vec{y}^\alpha = \vec{s}^\alpha - \vec{S}, \quad \alpha = 1, 2, \ldots, N. \tag{3.15b}$$

We seek *relationships* between the sets of vectors $\vec{y}^1, \vec{y}^2, \ldots, \vec{y}^N$ and $\vec{x}^1, \vec{x}^2, \ldots, \vec{x}^N$ which meet certain criteria, which we now discuss.

It is reasonable to consider only those relations between the $\vec{y}^\alpha$ and $\vec{x}^\alpha$ which leave form invariant the kinetic energy of the collection of particles relative to the center of mass. This is equivalent to requiring the equality of the quadratic forms

$$\sum_\alpha m_\alpha \vec{y}^\alpha \cdot \vec{y}^\alpha = \sum_\alpha m_\alpha \vec{x}^\alpha \cdot \vec{x}^\alpha, \tag{3.16}$$

where this relation is to hold *identically* in the vectors $\vec{x}^\alpha$ (when one is seeking to relate the $\vec{y}^\alpha$ to the $\vec{x}^\alpha$). Furthermore, since the Eckart vectors corresponding to the position vectors $\vec{s}^1, \vec{s}^2, \ldots, \vec{s}^N$ are given by

$$\vec{F}_i' = \sum_\alpha m_\alpha a_i^\alpha \vec{y}^\alpha, \tag{3.17}$$

we are led to consider solution vectors $\vec{y}^\alpha$ of Eq. (3.16) which relate to the $\vec{x}^1, \vec{x}^2, \ldots, \vec{x}^N$ either through real linear combinations[4] $\sum_\alpha a_\alpha \vec{x}^\alpha$ or rotation–inversions, or both.

Motivated by the preceding considerations, we introduce the class of solution vectors to Eq. (3.16) given by

$$\vec{y}^\alpha = \sum_\beta (\mathcal{R}\vec{x}^\beta) S_{\alpha\beta}, \tag{3.18}$$

where $\mathcal{R}$ is an arbitrary element of $\mathcal{O}_3$, and the $N \times N$ matrix S having elements $S_{\alpha\beta}$ is a real orthogonal matrix which commutes with the mass matrix M:

$$MS = SM. \tag{3.19}$$

This condition requires that S has the block diagonal form

$$S = \begin{bmatrix} S_a & 0 & \cdots & 0 \\ 0 & S_b & \cdots & 0 \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ 0 & 0 & \cdots & S_d \end{bmatrix}, \tag{3.20}$$

in which each S_λ is orthogonal. Thus, S is an element of the direct product group

$$\prod_\lambda O_\lambda = O_a \times O_b \times \cdots \times O_d, \tag{3.21a}$$

where O_λ denotes the set of all $n_\lambda \times n_\lambda$ orthogonal matrices:

$$O_\lambda = \{S_\lambda : \tilde{S}_\lambda S_\lambda = I_\lambda\}, \tag{3.21b}$$

where the tilde denotes matrix transposition.

An important point of interpretation enters into Eq. (3.18). A rotation–inversion operator $\mathcal{R}$, as generally understood, maps each vector in the set R^3 into a new vector in the set: $\vec{x} \to \mathcal{R}\vec{x}$, each $\vec{x} \in R^3$. However, in interpreting the meaning of the N vectors $\mathcal{R}\vec{x}^1, \mathcal{R}\vec{x}^2, \ldots, \mathcal{R}\vec{x}^N$ appearing in Eq. (3.18) we are not bound to regarding them as having originated geometrically from $\vec{x}^1, \vec{x}^2, \ldots, \vec{x}^N$ in consequence of a rotation–inversion $\mathcal{R}$ of each and every vector in R^3 (identified in this context as the set of all vectors with center of mass as origin). *A second more natural physical interpretation is to regard the vectors* $\mathcal{R}\vec{x}^1, \mathcal{R}\vec{x}^2, \ldots, \mathcal{R}\vec{x}^N$ *as new position vectors* (with respect to the center of mass) *which have evolved from some initial set by motions through the underlying space* R^3. It is this latter viewpoint which we adopt, extending it also to the $\vec{y}^1, \vec{y}^2, \ldots, \vec{y}^N$ of Eq. (3.18). Thus, for each $\mathcal{R} \in \mathcal{O}_3$, Eq. (3.18) is to be thought of as defining a new set of position vectors (they may need further restrictions before they qualify) of the N particles—*we attach no geometrical interpretation to this expression.*

It is probably best to be even more explicit on this point and define $\mathcal{R}\vec{x}^\alpha$ in the following manner. Calculate the matrix R representing $\mathcal{R}$ on the static model basis $\hat{e}_1, \hat{e}_2, \hat{e}_3$. We then have

$$R_{ij} = \hat{e}_i \cdot \mathcal{R}\hat{e}_j. \tag{3.22a}$$

Using the elements of this matrix, we *define* $\mathcal{R}\vec{x}^\alpha$ by

$$\mathcal{R}\vec{x}^\alpha = \sum_{i,j} R_{ij} (\vec{x}^\alpha \cdot \hat{f}_j) \hat{f}_i, \tag{3.22b}$$

where $\hat{f}_1, \hat{f}_2, \hat{f}_3$ are the Eckart frame vectors. Thus, each orthogonal matrix R defines a new set of vectors $\mathcal{R}\vec{x}^1, \mathcal{R}\vec{x}^2, \ldots, \mathcal{R}\vec{x}^N$ which stand in relation to $\vec{x}^1, \vec{x}^2, \ldots, \vec{x}^N$ *as though* we had rotated $\vec{x}^1, \vec{x}^2, \ldots, \vec{x}^N$ by $\mathcal{R}$, but we are not committed in interpretation to a rotation of the whole space.

The viewpoint expressed above accords with our earlier one of the meaning we attach to the position vectors $\vec{r}^\alpha$ and $\vec{s}^\alpha$. Note, in particular, that if the system has no translational motion, we have $\vec{s}^\alpha = \vec{y}^\alpha + \vec{R}$, where $\vec{y}^\alpha$ is given by Eq. (3.18), and $\vec{R}$ is the same center of mass vector as appears in Eq. (3.15a).

In light of the interpretation given above, it is clear that Eq. (3.18) does not represent the most general set of solution vectors which satisfy Eq. (3.16). We can replace the set of position vectors $\{\mathcal{R}\vec{x}^\beta : \beta = 1, 2, \ldots, N\}$ by the set of position vectors which follows:

$$\{\{\mathcal{R}_a \vec{x}^\alpha(a) : \alpha = 1, 2, \ldots, n_a\}, \{\mathcal{R}_b \vec{x}^\alpha(b) : \alpha = 1, 2, \ldots, n_b\}, \cdots \{\mathcal{R}_d \vec{x}^\alpha(d) : \alpha = 1, 2, \ldots, n_d\}\}, \tag{3.23}$$

where $\{\vec{x}^\alpha(\lambda) : \alpha = 1, 2, \ldots, n_\lambda\}$ denote the position vectors pointing to the identical particles of type $\lambda (\lambda = a, b, \ldots, d)$, and $\mathcal{R}_a, \mathcal{R}_b, \ldots, \mathcal{R}_d$ are rotation–inversion operators which may all be distinct. This generalization of Eq. (3.18) has a bearing on the theory of nonrigid molecules as discussed briefly in Sec. VII.

[4] Previous considerations of n particle motions in the work of Louck and Galbraith (1972) suggest this approach. We would like to take this opportunity to point out the Lemma 1 given by Louck and Galbraith (1972) is correct only for identical particles.

Throughout the entirety of Sec. II, unless indicated explicitly to the contrary, all symbols such as $\mathcal{R}\vec{x}^\alpha, \mathcal{R}\vec{\rho}^\alpha, \mathcal{R}\vec{F}_i$, *etc., are to be interpreted as new position vectors, new displacement vectors, new Eckart vectors, etc., in the same underlying space in the sense explained above.*

The solution (3.18)–(3.20) is far too general to meet the criteria: (a) $\vec{y}^1, \vec{y}^2, \ldots, \vec{y}^N$ are position vectors of the particles $1, 2, \ldots, N$ relative to the center of mass $\vec{S}$; (b) $\vec{y}^1, \vec{y}^2, \ldots, \vec{y}^N$ define the same Eckart frame as do the $\vec{x}^1, \vec{x}^2, \ldots, \vec{x}^N$. We seek now to impose conditions such that criteria (a) and (b) are true.

For condition (a) to be true, it is necessary that $\sum_\alpha m_\alpha \vec{y}^\alpha = \vec{0}$. Since it follows from Eq. (3.19) that $m_\alpha S_{\alpha\beta} = m_\beta S_{\alpha\beta}$, we find

$$\mathcal{R}\sum_\beta m_\beta \vec{x}^\beta \left(\sum_\alpha S_{\alpha\beta}\right) = \vec{0}, \tag{3.24a}$$

hence,

$$\sum_\beta m_\beta \vec{x}^\beta \left(\sum_\alpha S_{\alpha\beta}\right) = \vec{0}. \tag{3.24b}$$

Relation (3.24b) must hold for arbitrary $\vec{x}^\alpha$ which satisfy $\sum_\beta m_\beta \vec{x}^\beta = \vec{0}$, and this requires

$$\sum_\alpha S_{\alpha\beta} = 1, \quad \beta = 1, 2, \ldots, N.$$

Since S is orthogonal, each of the rows must also have the sum

$$\sum_\alpha S_{\beta\alpha} = 1, \quad \beta = 1, 2, \ldots, N.$$

It now follows that S is a permutation matrix of dimension N (a matrix which may be obtained from the $N \times N$ unit matrix by some permutation of the columns of the unit matrix). Furthermore, since S must also have the form (3.20), it follows that each S_λ in Eq. (3.20) is a permutation matrix of dimension n_λ.

Our first result may be summarized as follows: *A necessary condition that the* $\vec{y}^1, \vec{y}^2, \ldots, \vec{y}^N$ *defined by Eq. (3.18) be position vectors relative to the center of mass of particles* $1, 2, \ldots, N$ *is that the matrix* S *has the form*

$$S = \begin{pmatrix} S_a & 0 & \cdots & 0 \\ 0 & S_b & \cdots & 0 \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ 0 & 0 & \cdots & S_d \end{pmatrix}, \tag{3.25}$$

where each S_λ *is a permutation matrix of dimension* n_λ.

Consider next the conditions imposed by requirement (b)—the vectors $\vec{y}^1, \vec{y}^2, \ldots, \vec{y}^N$ are to define the same Eckart frame as the $\vec{x}^1, \vec{x}^2, \ldots, \vec{x}^N$. For this purpose, it is convenient to write Eq. (3.2) in the matrix form

$$[\vec{F}_1 \vec{F}_2 \vec{F}_3] = [\vec{x}^1 \vec{x}^2 \cdots \vec{x}^N] M\tilde{A}, \tag{3.26a}$$

where M is the mass matrix, and A is the $3 \times N$ matrix

$$A = \begin{pmatrix} a_1^1 & a_1^2 & \cdots & a_1^N \\ a_2^1 & a_2^2 & \cdots & a_2^N \\ a_3^1 & a_3^2 & \cdots & a_3^N \end{pmatrix}. \tag{3.26b}$$

Let us recall that the Eckart frame defined by the $\vec{x}^\alpha = \vec{r}^\alpha - \vec{R}$ is

$$[\hat{f}_1 \hat{f}_2 \hat{f}_3] = [\vec{F}_1 \vec{F}_2 \vec{F}_3] F^{-1/2}. \tag{3.27}$$

This frame is located at the center of mass point $\vec{R}$, and the vectors $\vec{c}^\alpha$ in $\vec{x}^\alpha = \vec{c}^\alpha + \vec{\rho}^\alpha$ are constant vectors $\vec{c}^\alpha = \sum_i a_i^\alpha \hat{f}_i$ relative to the Eckart frame. Correspondingly, any second set of displacement vectors $\vec{\eta}^1, \vec{\eta}^2, \ldots, \vec{\eta}^N$ of the particles $1, 2, \ldots, N$ which is compatible with the Eckart frame $\hat{f}_1, \hat{f}_2, \hat{f}_3$ must *necessarily* have position vectors relative to the center of mass given by

$$\vec{y}^\alpha = \vec{c}^\alpha + \vec{\eta}^\alpha, \tag{3.28}$$

where it is of no consequence whether we consider the center of mass to be at $\vec{R}$ or some new point $\vec{S}$ (the Eckart frame follows the center of mass point, but the location of the center of mass has no role in its determination). The important aspect of Eq. (3.28) is the fact that the $\vec{c}^\alpha$ is the same vector as appears in $\vec{x}^\alpha = \vec{c}^\alpha + \vec{\rho}^\alpha$. Substituting $\vec{x}^\alpha = \vec{c}^\alpha + \vec{\rho}^\alpha$ into Eq. (3.18) and comparing with Eq. (3.28), *we find that*

$$\sum_\beta (\mathcal{R}\vec{c}^\beta) S_{\alpha\beta} = \vec{c}^\alpha \tag{3.29}$$

is a necessary condition that the $\vec{y}^1, \ldots, \vec{y}^N$ *of Eq. (3.18) qualify as a set of position vectors which define the same Eckart frame* $\hat{f}_1, \hat{f}_2, \hat{f}_3$ [the frame (3.27)] *as do the* $\vec{x}^1, \vec{x}^2, \ldots, \vec{x}^N$.

Equations (3.25) and (3.29) express necessary conditions which must be satisfied by the $\vec{y}^1, \vec{y}^2, \ldots, \vec{y}^N$ of Eq. (3.18) in order that they are a set of position vectors relative to the center of mass which leaves invariant the Eckart frame $\hat{f}_1, \hat{f}_2, \hat{f}_3$ of the $\vec{x}^1, \vec{x}^2, \ldots, \vec{x}^N$. We will now prove these conditions are also sufficient.

Let us first rewrite Eq. (3.29) in the form

$$\mathcal{R}[\vec{c}^1 \vec{c}^2 \cdots \vec{c}^N] \tilde{S} = [\vec{c}^1 \vec{c}^2 \cdots \vec{c}^N], \tag{3.30}$$

and convert it into a matrix equation relative to the frame $\hat{f}_1, \hat{f}_2, \hat{f}_3$. We leave it to the reader to verify that the correct way to convert such a vector relation into a matrix relation is as follows: Replace each $\vec{c}^\alpha$ by its column matrix representation in the basis $\hat{f}_i$, i.e., $\vec{c}^\alpha \to \mathrm{col}(a_1^\alpha, a_2^\alpha, a_3^\alpha)$; replace $\mathcal{R}$ by its matrix representation R relative to the basis $\hat{f}_i$, i.e., by the matrix R whose element R_{ij} in row i and column j is

$$R_{ij} = \hat{f}_i \cdot \mathcal{R}\hat{f}_j. \tag{3.31}$$

Note that this is the same R as occurs in Eq. (3.22b). Thus, Eq. (3.30) becomes the matrix expression

$$RA\tilde{S} = A, \tag{3.32a}$$

or equivalently,

$$AS = RA. \tag{3.32b}$$

The Eckart vectors corresponding to the $\vec{y}^1, \vec{y}^2, \ldots, \vec{y}^N$ are

$$[\vec{F}_1' \vec{F}_2' \vec{F}_3'] = [\vec{y}^1 \vec{y}^2 \cdots \vec{y}^N] M\tilde{A}. \tag{3.33}$$

Equation (3.18) may be written

$$[\vec{y}^1 \vec{y}^2 \cdots \vec{y}^N] = \mathcal{R}[\vec{x}^1 \vec{x}^2 \cdots \vec{x}^N] \tilde{S}, \tag{3.34}$$

following again a convention of the type used in Eq. (2.16). Combining Eqs. (3.34), (3.33), (3.32b), and

(3.26a), we obtain

$$[\vec{F}_1'\vec{F}_2'\vec{F}_3'] = \mathfrak{R}[\vec{F}_1\vec{F}_2\vec{F}_3]\tilde{R} \ . \tag{3.35}$$

The Eckart frame corresponding to the Eckart vectors $\vec{F}_1', \vec{F}_2', \vec{F}_3'$ is given by

$$[\hat{f}_1'\hat{f}_2'\hat{f}_3'] = [\vec{F}_1'\vec{F}_2'\vec{F}_3']RF^{-1/2}\tilde{R}\,, \tag{3.36}$$

since the Gram matrix F' of $\vec{F}_1', \vec{F}_2', \vec{F}_3'$ is related to the Gram matrix of $\vec{F}_1, \vec{F}_2, \vec{F}_3$ by

$$F' = RF\tilde{R}\,. \tag{3.37}$$

This result follows from Eq. (3.35).

Using Eq. (3.35) in Eq. (3.36), we now obtain:

$$\begin{aligned}[\hat{f}_1'\hat{f}_2'\hat{f}_3'] &= \mathfrak{R}[\vec{F}_1\vec{F}_2\vec{F}_3]F^{-1/2}\tilde{R} \\ &= \mathfrak{R}[\hat{f}_1\hat{f}_2\hat{f}_3]\tilde{R} \\ &= [\hat{f}_1\hat{f}_2\hat{f}_3]\,,\end{aligned} \tag{3.38}$$

where the last step follows by using Eq. (3.31):

$$\begin{aligned}\hat{f}_i' &= \sum_j (\mathfrak{R}\hat{f}_j)R_{ij} = \sum_k \left(\sum_j R_{kj}R_{ij}\right)\hat{f}_k \\ &= \sum_k \delta_{ki}\hat{f}_k = \hat{f}_i\,.\end{aligned} \tag{3.39}$$

Thus, the Eckart frame is invariant under the transformations (3.18) for all $\mathfrak{R}$ and S which satisfy Eqs. (3.25) and (3.29).

Observe, in fact, that the Eckart frame is invariant under all the transformations for which there exists an S of the general form (3.20) satisfying Eq. (3.32b), i.e., there is nothing in the above proof which requires S to have the more restricted form (3.25). This latter condition comes in solely to assure that $\sum_\alpha m_\alpha \vec{y}^\alpha = \vec{0}$.

We may now write our transformation of position vectors $\vec{s}^1, \vec{s}^2, \ldots, \vec{s}^N$ in the form

$$\vec{s}^\alpha - \vec{S} = \vec{c}^\alpha + \vec{\eta}^\alpha\,, \tag{3.40a}$$

where

$$\vec{\eta}^\alpha = \sum_\beta (\mathfrak{R}\vec{\rho}^\alpha)S_{\alpha\beta}\,, \tag{3.40b}$$

where we recall also that

$$\vec{r}^\alpha - \vec{R} = \vec{c}^\alpha + \vec{\rho}^\alpha\,. \tag{3.40c}$$

Since we have proved that $\vec{r}^\alpha$ and $\vec{s}^\alpha$ define one and the same Eckart frame, the dynamical molecular model corresponding to the new expression (3.40a) is clear: Our original dynamical molecular model corresponding to Eq. (3.40c) (the Eckart frame sits at the center of mass $\vec{R}$, the static molecular model is oriented in this frame by the constant vectors $\vec{c}^\alpha$, and the $\vec{\rho}^\alpha$ are the displacement of the nuclei away from these equilibrium position vectors) has been translated to the new center of mass point $\vec{S}$ *without change of orientation of the original Eckart frame,* and the nuclei $1, 2, \ldots, N$ have been assigned a new set of displacement vectors $\vec{\eta}^1$, $\vec{\eta}^2, \ldots, \vec{\eta}^N$.

Let us summarize the results thus far obtained in this subsection with a theorem:

Theorem 1. Let $\vec{x}^\alpha = \vec{c}^\alpha + \vec{\rho}^\alpha$, $\alpha = 1, 2, \ldots, N$, denote the position vectors relative to the center of mass of N particles in the dynamical molecular model. The most general transformation of the type

$$\vec{y}^\alpha = \sum_\beta (\mathfrak{R}\vec{x}^\beta)S_{\alpha\beta} \tag{3.41a}$$

which preserves the center of mass and the Eckart frame is given by

$$\vec{y}^\alpha = \vec{c}^\alpha + \vec{\eta}^\alpha\,, \tag{3.41b}$$

where

$$\vec{\eta}^\alpha = \sum_\beta (\mathfrak{R}\vec{\rho}^\alpha)S_{\alpha\beta}\,, \quad \alpha = 1, 2, \ldots, N, \tag{3.41c}$$

$$\mathfrak{R}\vec{\rho}^\alpha = \sum_{i,j} R_{ij}(\vec{\rho}^\alpha \cdot \hat{f}_j)\hat{f}_i\,, \tag{3.41d}$$

in which R is an orthogonal matrix, S is a matrix of the type (3.25), and R and S satisfy $RA = AS$.

We can now prove a second principal result.

Theorem 2. The set of displacements $\vec{\eta}^1, \vec{\eta}^2, \ldots, \vec{\eta}^N$ is compatible with the Eckart frame $\hat{f}_1, \hat{f}_2, \hat{f}_3$, provided the set $\vec{\rho}^1, \vec{\rho}^2, \ldots, \vec{\rho}^N$ is.

Proof. By assumption, $\vec{\rho}^1, \vec{\rho}^2, \ldots, \vec{\rho}^N$ is a set of displacement vectors compatible with $\hat{f}_1, \hat{f}_2, \hat{f}_3$. We may write Eq. (3.41c) in the form

$$[\vec{\eta}^1\vec{\eta}^2\cdots\vec{\eta}^N] = \mathfrak{R}[\vec{\rho}^1\vec{\rho}^2\cdots\vec{\rho}^N]\tilde{S}. \tag{3.42}$$

The Eckart vectors $\vec{E}_1', \vec{E}_2', \vec{E}_3'$ corresponding to the $\vec{\eta}^\alpha$ are thus related to the Eckart vectors $\vec{E}_1, \vec{E}_2, \vec{E}_3$ corresponding to the $\vec{\rho}^\alpha$ by an equation of the same form as (3.35):

$$[\vec{E}_1'\vec{E}_2'\vec{E}_3'] = \mathfrak{R}[\vec{E}_1\vec{E}_2\vec{E}_3]\tilde{R} \tag{3.43a}$$

from which one can now prove

$$\hat{f}_1 \times \vec{E}_1' + \hat{f}_2 \times \vec{E}_2' + \hat{f}_3 \times \vec{E}_3' = \vec{0}\,. \tag{3.43b}$$

Thus, substituting Eq. (3.43a) into Eq. (3.43b), we obtain:

$$\begin{aligned}\sum_{i,j}(\hat{f}_i \times \mathfrak{R}\vec{E}_j)R_{ij} &= \pm\mathfrak{R}\sum_{i,j}(\mathfrak{R}^{-1}\hat{f}_i \times \vec{E}_j)R_{ij} \\ &= \pm\mathfrak{R}\sum_{i,j,k}(\hat{f}_k \times \vec{E}_j)R_{ik}R_{ij} \\ &= \pm\mathfrak{R}\sum_j (\hat{f}_j \times \vec{E}_j) = \vec{0}\,,\end{aligned}$$

where the + sign is to be used for $\det R = 1$ and the − sign for $\det R = -1$.

It is natural now to consider the set of transformations between sets of displacement vectors compatible with a given Eckart frame.

Theorem 3. The set of transformations of Theorem 1 between sets of displacement vectors compatible with a given Eckart frame is a group.

Proof. Let $\mathfrak{L}_{(\mathfrak{R},S)}$ denote the transformation

$$\mathfrak{L}_{(\mathfrak{R},S)}\colon \vec{\rho}^\alpha - \sum_\beta (\mathfrak{R}\vec{\rho}^\beta)S_{\alpha\beta} = \vec{\eta}^\alpha\,, \tag{3.44a}$$

and let $\mathfrak{L}_{(\mathfrak{R}',S')}$ denote the transformation

$$\mathfrak{L}_{(\mathcal{R}',S')}\colon \vec{\eta}^{\alpha} \to \sum_{\beta} (\mathcal{R}'\vec{\eta}^{\beta}) S'_{\alpha\beta} = \vec{\xi}^{\alpha}. \tag{3.44b}$$

In Eqs. (3.44a) and (3.44b), S and S' are required also to satisfy the conditions of Theorem 1. The product transformation $\mathfrak{L}_{(\mathcal{R}',S')}\mathfrak{L}_{(\mathcal{R},S)}$ is, by definition, the result of first applying $\mathfrak{L}_{(\mathcal{R},S)}$ followed by $\mathfrak{L}_{(\mathcal{R}',S')}$. It is given by

$$\vec{\xi}^{\alpha} = \sum_{\beta} \mathcal{R}'\Big[\sum_{\gamma} (\mathcal{R}\vec{\rho}^{\gamma}) S_{\beta\gamma}\Big] S'_{\alpha\beta}$$

$$= \sum_{\gamma} [(\mathcal{R}'\mathcal{R})\vec{\rho}^{\gamma}](S'S)_{\alpha\gamma}. \tag{3.45}$$

We next observe that $AS = RA$ and $AS' = R'A$ imply $A(S'S) = (R'R)A$. Furthermore, $S'S$ is a permutation matrix of the required type of Theorem 1 if S and S' are. Thus, we indeed have from Eq. (3.45) that

$$\mathfrak{L}_{(\mathcal{R}',S')}\mathfrak{L}_{(\mathcal{R},S)} = \mathfrak{L}_{(\mathcal{R}'\mathcal{R},S'S)}, \tag{3.46}$$

which proves Theorem 3.

It is often convenient to write Eq. (3.40b) in the form

$$[\vec{\eta}^{1}\vec{\eta}^{2}\cdots\vec{\eta}^{N}] = \mathcal{R}[\vec{\rho}^{1}\vec{\rho}^{2}\cdots\vec{\rho}^{N}]\tilde{S}. \tag{3.47}$$

Writing $\vec{\eta}^{\alpha} = \mathfrak{L}_{(\mathcal{R},S)}\vec{\rho}^{\alpha}$ in Eq. (3.44a), we may then also write the transformation (3.44a) in the form

$$\mathfrak{L}_{(\mathcal{R},S)}[\vec{\rho}^{1}\vec{\rho}^{2}\cdots\vec{\rho}^{N}] = \mathcal{R}[\vec{\rho}^{1}\vec{\rho}^{2}\cdots\vec{\rho}^{N}]\tilde{S}, \tag{3.48}$$

where we are again employing a convention of type (2.16).

The next theorem reveals the true nature of the group of transformations of Theorem 1.

Theorem 4. The group of transformations of Theorem 1 is precisely the group of transformations

$$\mathfrak{L}_{\mathcal{G}}[\vec{\rho}^{1}\vec{\rho}^{2}\cdots\vec{\rho}^{N}] = \mathcal{G}[\vec{\rho}^{1}\vec{\rho}^{2}\cdots\vec{\rho}^{N}]\tilde{S}(\mathcal{G}), \tag{3.49}$$

where $\mathcal{G}$ is an element of the point group $G(\mathfrak{A})$, and $S(\mathcal{G})$ is the static molecular model representation of $\mathcal{G}$.

Remarks. The action of $\mathcal{G}$ on a displacement vector is defined according to the general rule (3.41d):

$$\mathcal{G}\vec{\rho}^{\alpha} = \sum_{i,j} G_{ij}(\vec{\rho}^{\alpha}\cdot\hat{f}_j)f_i, \tag{3.50}$$

where G is the matrix representing $\mathcal{G}$ on the static model basis $\hat{e}_1, \hat{e}_2, \hat{e}_3$. We have put $\mathfrak{L}_{\mathcal{G}} = \mathfrak{L}_{(\mathcal{G},S(\mathcal{G}))}$ in stating the result, Eq. (3.49).

Let us now give the proof of Theorem 4. The condition $RA = AS$, where S is a matrix of the type described in Eq. (3.25), is the key relation. From this matrix relation we can always reconstruct the static molecular model by defining $\vec{a}^{\alpha} = \sum_i a_i^{\alpha}\hat{e}_i$ and $\mathcal{R}\hat{e}_i = \sum_j R_{ji}\hat{e}_j$. Thus $RA = AS$ implies the existence of an element $\mathcal{R} \in \mathcal{O}_3$ such that

$$\mathcal{R}[\vec{a}^{1}\vec{a}^{2}\cdots\vec{a}^{N}] = [\vec{a}^{1}\vec{a}^{2}\cdots\vec{a}^{N}]S. \tag{3.51}$$

But since S is a matrix of the type described in Eq. (3.25), it follows that (a) $\mathcal{R}$ is a mapping of the static molecular model onto itself, and (b) S is the static model representation of $\mathcal{R}$. These two properties prove Theorem 4.

Since the class of all position vectors corresponding to the class of displacement vectors which are related by the group of transformations

$$\{\mathfrak{L}_{\mathcal{G}}\colon \mathcal{G} \in G(\mathfrak{A})\} \tag{3.52}$$

all define the same Eckart frame, we call this group *an invariance group of the Eckart frame.*

The next theorem is a consequence of the definitions.

Theorem 5. The correspondence

$$\mathcal{G} \to \mathfrak{L}_{\mathcal{G}}$$

is an isomorphism between the point group of the static molecular model and the invariance group of the Eckart frame.

The physical picture corresponding to the mathematical transformations (3.49) is quite clear: If an observer in the Eckart frame can observe the displacements $\vec{\rho}^{1}, \vec{\rho}^{2}, \ldots, \vec{\rho}^{N}$ of the N particles, then also he can observe the displacements $\mathfrak{L}_{\mathcal{G}}[\vec{\rho}^{1}\vec{\rho}^{2}\cdots\vec{\rho}^{N}]$, each $\mathcal{G} \in G(\mathfrak{A})$.

We have now partially solved the problem of finding all displacements compatible with a given Eckart frame. What remains is to assure that the $\vec{\rho}^{1}, \vec{\rho}^{2}, \ldots, \vec{\rho}^{N}$ with which we started are compatible with the Eckart frame, i.e., the Eckart $\vec{E}_i$ vectors satisfy Eq. (3.13). Let us restate these conditions in a form originally given also by Eckart: Let

$$E_j = \mathrm{col}(E_{1j}\, E_{2j}\, E_{3j}) \tag{3.53a}$$

denote the column matrix representing $\vec{E}_j$ on the frame $\hat{f}_1, \hat{f}_2, \hat{f}_3$, i.e.,

$$E_{ij} = \hat{f}_i \cdot \vec{E}_j. \tag{3.53b}$$

Then, conditions (3.13) are equivalent to the requirement that the matrix

$$[E_1\, E_2\, E_3] \tag{3.53c}$$

be symmetric.

The method of implementing the Eckart condition into the motions problem is the subject of Sec. IV, where the internal motions problem is discussed. Rather than entering into these detailed problems at this point, we turn now to some other general features of the dynamical molecular model.

C. The effect of rotations and permutations on the Eckart frame

We first consider the effect of an arbitrary rotation–inversion operator $\mathcal{R}$ on the Eckart frame.

Theorem 6. Let $\mathcal{R}$ denote a rotation–inversion of the entire space R_3, i.e., $\vec{x} \to \mathcal{R}\vec{x}$, each $\vec{x} \in R^3$, and consequently $\vec{r}^{\alpha} \to \mathcal{R}\vec{r}^{\alpha}$, $\alpha = 1, 2, \ldots, N$. Then

$$\mathcal{R}\colon\ [\hat{f}_1\hat{f}_2\hat{f}_3] \to \mathcal{R}[\hat{f}_1\hat{f}_2\hat{f}_3] = [\hat{f}_1\hat{f}_2\hat{f}_3]R, \tag{3.54}$$

where R is the matrix representing $\mathcal{R}$ on the Eckart frame, i.e., $R_{ij} = \hat{f}_i \cdot \mathcal{R}\hat{f}_j$.

Proof. This result follows easily from Eqs. (3.4), the property $\mathcal{R}$: $\vec{F}_i \to \mathcal{R}\vec{F}_i$, and the fact that dot products are invariant under $\mathcal{R}$.

A permutation $P \in S_N$ induces a transformation $\mathcal{P}$ of the position vectors $\vec{r}^{1}, \vec{r}^{2}, \ldots, \vec{r}^{N}$ given by the following rule:

$$\mathcal{P}\colon\ \vec{r}^{1} \to \vec{r}^{\alpha_1}, \vec{r}^{2} \to \vec{r}^{\alpha_2}, \ldots, \vec{r}^{N} \to \vec{r}^{\alpha_N} \tag{3.55a}$$

for each

$$P:\ 1\to\alpha_1, 2\to\alpha_2, \ldots, N\to\alpha_N . \tag{3.55b}$$

Since the permutations of the position vectors of identical particles leaves the center of mass vector invariant, the action of each such $\mathcal{P}$ on the sets of position vectors $\vec{x}^1, \vec{x}^2, \ldots, \vec{x}^N$ relative to the center of mass, the vectors $\vec{c}^1, \vec{c}^2, \ldots, \vec{c}^N$, and the displacement vectors $\vec{\rho}^1, \vec{\rho}^2, \ldots, \vec{\rho}^N$, where $\vec{r}^\alpha - \vec{R} = \vec{x}^\alpha = \vec{c}^\alpha + \vec{\rho}^\alpha$, is given, respectively, by

$$\mathcal{P}:\ \vec{x}^1\to\vec{x}^{\alpha_1}, \vec{x}^2\to\vec{x}^{\alpha_2}, \ldots, \vec{x}^N\to\vec{x}^{\alpha_N}, \tag{3.56a}$$

$$\mathcal{P}:\ \vec{c}^1\to\vec{c}^{\alpha_1}, \vec{c}^2\to\vec{c}^{\alpha_2}, \ldots, \vec{c}^N\to\vec{c}^{\alpha_N}, \tag{3.56b}$$

$$\mathcal{P}:\ \vec{\rho}^1\to\vec{\rho}^{\alpha_1}, \vec{\rho}^2\to\vec{\rho}^{\alpha_2}, \ldots, \vec{\rho}^N\to\vec{\rho}^{\alpha_N}, \tag{3.56c}$$

for each

$$\mathcal{P}\in\prod_\lambda G(S_{n_\lambda}). \tag{3.56d}$$

The first important result on permutations is stated in the next theorem.

Theorem 7. Each permutation operator $\mathcal{P}\in\prod_\lambda G(S_{n_\lambda})$ maps the Eckart frame $\hat{f}_1, \hat{f}_2, \hat{f}_3$ into a new Eckart frame $\hat{f}'_1, \hat{f}'_2, \hat{f}'_3$:

$$\mathcal{P}:\ [\hat{f}_1\hat{f}_2\hat{f}_3]\to[\hat{f}'_1\hat{f}'_2\hat{f}'_3], \tag{3.57}$$

where the identity permutation operator is the only one which maps the Eckart frame onto itself.

Proof: Each permutation operator induces the transformation

$$\mathcal{P}:\ [\vec{x}^1\vec{x}^2\cdots\vec{x}^N]\to[\vec{x}^1\vec{x}^2\cdots\vec{x}^N]S(\mathcal{P}). \tag{3.58}$$

This transformation has the form (3.18) in which $\mathfrak{R}$ is the identity. By Theorems 1–4, each such transformation of this type which preserves the Eckart frame has the form (3.49). This is possible if and only if $\mathcal{P}$ is the identity; all other permutations must therefore transform the Eckart frame.

The next theorem establishes the effect on the Eckart frame of a permutation operator corresponding to a point group operator.

Theorem 8. Let $\mathcal{G}\in G(\mathfrak{A})$ denote the operator in the point group of the static model which corresponds to $\mathcal{P}$ (as discussed in Sec. II.E). Then

$$\mathcal{P}:\ [\hat{f}_1\hat{f}_2\hat{f}_3]\to\mathcal{G}[\hat{f}_1\hat{f}_2\hat{f}_3]=[\hat{f}_1\hat{f}_2\hat{f}_3]G, \tag{3.59}$$

where $\mathcal{G}\in\mathcal{O}_3$ is a rotation-inversion of the whole space R^3.

The proof follows from the definitions and Theorem 6.

Longuet-Higgins (1963) and Hougen (1962, 1963, 1975) have put forth the thesis that the use of the symmetric group is a more powerful tool for the analysis of the molecular motions problem than is the use of the point group. They appear to base this viewpoint on the fact that one can express the action of a permutation operator $\mathcal{P}$ on the various sets of objects appearing in Eqs. (3.56) in the following manner[5]:

$$\mathcal{P}^{-1}[\vec{x}^1\vec{x}^2\cdots\vec{x}^N]=\mathcal{G}^{-1}\mathfrak{L}_\mathcal{G}[\vec{x}^1\vec{x}^2\cdots\vec{x}^N], \tag{3.60a}$$

$$\mathcal{P}^{-1}[\vec{c}^1\vec{c}^2\cdots\vec{c}^N]=\mathcal{G}^{-1}\mathfrak{L}_\mathcal{G}[\vec{c}^1\vec{c}^2\cdots\vec{c}^N], \tag{3.60b}$$

$$\mathcal{P}^{-1}[\vec{\rho}^1\vec{\rho}^2\cdots\vec{\rho}^N]=\mathcal{G}^{-1}\mathfrak{L}_\mathcal{G}[\vec{\rho}^1\vec{\rho}^2\cdots\vec{\rho}^N], \tag{3.60c}$$

for each $\mathcal{P}\in\prod_\lambda G(S_{n_\lambda})$. Note that the implication of Eq. (3.60b) is

$$\mathcal{P}[\vec{c}^1\vec{c}^2\cdots\vec{c}^N]=\mathcal{G}[\vec{c}^1\vec{c}^2\circ\circ\circ\vec{c}^N], \tag{3.61}$$

in consequence of

$$\mathfrak{L}_\mathcal{G}[\vec{c}^1\vec{c}^2\cdots\vec{c}^N]=[\vec{c}^1\vec{c}^2\circ\circ\circ\vec{c}^N]. \tag{3.62}$$

[cf. Eq. (3.30).] Thus, the $\mathcal{P}$ appearing in Eqs. (3.60) is the one corresponding to $\mathcal{G}$ in the static molecular model. We therefore may write

$$\mathcal{P}^{-1}=\mathcal{G}^{-1}\mathfrak{L}_\mathcal{G}, \tag{3.63}$$

where this is understood to be an operator identity when operating on the objects appearing in Eqs. (3.60). It is Eq. (3.63) which is the basis for Longuet-Higgens' and Hougen's conclusion that the symmetric group plays the more fundamental role. This conclusion appears tenable to us only if one is willing to accept the notion that Eq. (3.63) is in some sense to be regarded as the fundamental origin of the operators $\mathfrak{L}_\mathcal{G}=\mathcal{G}\mathcal{P}^{-1}$.

From our point of view, Longuet-Higgens and Hougen attribute an undeserved status to the role of the symmetric group in the *molecular motions problem* for reasons which we now enumerate:

(a) The group $G(\mathfrak{A})$ gets into the dynamical molecular model *quite on its own* because an invariance group of the Eckart frame is a *realization of the point group* by a set of transformations between sets of displacement vectors which are compatible with the Eckart frame.

(b) The group of permutations $\{\mathcal{P}:\mathcal{P}\in\prod_\lambda G(S_{n_\lambda})\}$ and the group of transformations $\{\mathfrak{L}_\mathcal{G}:\mathcal{G}\in G(\mathfrak{A})\}$ have but a single element in common—the identity. This implies that *only* the transformation group $\{\mathfrak{L}_\mathcal{G}\}$ can enter into the solution to the internal motions problem—the explicit construction of all motions compatible with the Eckart frame. To consider the $\{\mathfrak{L}_\mathcal{G}\}$ as a "piece" of a permutation operator is to deny the group $\{\mathfrak{L}_\mathcal{G}\}$ its true status in this construction—the group $\{\mathcal{P}\}$ cannot be used "on its own" to determine the internal motions.

We should explain that while we take the view that the transformations $\{\mathfrak{L}_\mathcal{G}:\mathcal{G}\in G(\mathfrak{A})\}$ relate certain displacements which an observer in the Eckart frame can record, and hence do not insist that one such set be obtained from another by geometrical operations on the molecule, it is nonetheless true that this latter viewpoint as implemented in Fig. 5–8 of Wilson (1955) does lead to precisely the same group of relations between displacement vectors as we have described.

D. Transformations between different dynamical models

In Sec. III.A, we pointed out that two different investigators will, in general, assign different labeling schemes and use different principal axes systems in setting up their dynamical models of a given molecule. The purpose of this section is to show quite generally how one investigator can take another's model and transcribe the mathematical symbols into agreement with his own.

[5]The $\mathcal{G}^{-1}$ occurring in Eqs. (3.60)–(3.63) is a rotation of the space R^3; the $\mathcal{G}$ appearing in the definition of $\mathfrak{L}_\mathcal{G}$ defines new vectors in the manner explained at the beginning of this section. Nonetheless, when a $\mathcal{G}^{-1}$ meets a $\mathcal{G}$ from $\mathfrak{L}_\mathcal{G}$, it does give the identity.

In the A model (our model theory), the static model is described by vectors $\vec{a}^1, \vec{a}^2, \ldots, \vec{a}^N$, and the principal axes system is $\hat{a}_1, \hat{a}_2, \hat{a}_3$. In the B model (another investigator's model), the static model is described by vectors $\vec{b}^1, \vec{b}^2, \ldots, \vec{b}^N$, and the principal axes system is $\hat{b}_1, \hat{b}_2, \hat{b}_3$.

To bring the B model into agreement with the A model, we perform the following actions. We first take the B static model and bring it into coincidence with ours—any matching up of identical particles with identical particles. This establishes a one-to-one mapping between the two sets of position vectors:

$$\vec{b}^\alpha = \vec{a}^{\nu_\alpha}, \quad \alpha = 1, 2, \ldots, N, \tag{3.64}$$

where $\nu_1, \nu_2, \ldots, \nu_N$ is some rearrangement of $1, 2, \ldots, N$. In general, the preceding action will not align the principal axes system $\hat{b}_1, \hat{b}_2, \hat{b}_3$ with $\hat{a}_1, \hat{a}_2, \hat{a}_3$. In the second step, we determine the rotation–inversion operator $\mathcal{R}$ such that

$$\hat{b}_i = \mathcal{R}\hat{a}_i, \quad i = 1, 2, 3. \tag{3.65}$$

Thus, $\mathcal{R}$ is the operator whose matrix representation on the basis $\hat{a}_1, \hat{a}_2, \hat{a}_3$ is given by

$$R_{ij} = \hat{a}_i \cdot \mathcal{R}\hat{a}_j = \hat{a}_i \cdot \hat{b}_j . \tag{3.66}$$

The two relations (3.64) and (3.65) may now be used to relate the matrix B to the matrix A:

$$\begin{aligned} b_i^\alpha &= \vec{b}^\alpha \cdot \hat{b}_i = \vec{a}^{\nu_\alpha} \cdot \mathcal{R}\hat{a}_i \\ &= \sum_j (\hat{a}_j \cdot \mathcal{R}\hat{a}_i)\, \vec{a}^{\nu_\alpha} \cdot \hat{a}_j \\ &= \sum_j R_{ji}\, a_j^{\nu_\alpha}. \end{aligned} \tag{3.67a}$$

In matrix form this result becomes

$$B = \tilde{R}AS , \tag{3.67b}$$

where S is the permutation matrix

$$S = [e_{\nu_1} e_{\nu_2} \cdots e_{\nu_N}], \tag{3.67c}$$

where $e_\nu = \mathrm{col}[0 \cdots 010 \cdots 0]$ with the 1 in position ν.

We now examine dynamical model B (constructed according to steps 3 and 4 of the rules given in Sec. III.A). We see that our perspective of model B will be the same as that of our model A if

$$\hat{g}_i = \mathcal{R}\hat{f}_i , \tag{3.68}$$

where $\hat{f}_1, \hat{f}_2, \hat{f}_3$ denote the Eckart frame of our model, $\hat{g}_1, \hat{g}_2, \hat{g}_3$ denote the Eckart frame of model B, and $\mathcal{R}$ is the rotation–inversion operator appearing in Eq. (3.65).

Equations (3.65)–(3.68) are the basic equations which allow us to transform the variables of any B theory into those of the A theory. The explicit transformations may be obtained either geometrically or by using the Eckart vectors of the two theories. We follow the latter course.

The Eckart vectors in the A model are given by

$$\vec{F}_i = \sum_\alpha m_\alpha a_i^\alpha \vec{x}^\alpha , \tag{3.69a}$$

where $\vec{x}^1, \vec{x}^2, \ldots, \vec{x}^N$ denote position vectors relative to the center of mass. The Eckart vectors in the B model are given by

$$\vec{G}_i = \sum_\alpha m_\alpha b_i^\alpha \vec{y}^\alpha , \tag{3.69b}$$

where $\vec{y}^1, \vec{y}^2, \ldots, \vec{y}^N$ denote position vectors relative to the center of mass. We seek the relation between $\vec{y}^1, \vec{y}^2, \ldots, \vec{y}^N$ and $\vec{x}^1, \vec{x}^2, \ldots, \vec{x}^N$. Noting that Eq. (3.68) implies

$$[\vec{G}_1 \vec{G}_2 \vec{G}_3] = [\vec{F}_1 \vec{F}_2 \vec{F}_3] R, \tag{3.70a}$$

we obtain from Eqs. (3.69) the relation

$$[\vec{y}^1 \vec{y}^2 \cdots \vec{y}^N] M\tilde{B} = [\vec{x}^1 \vec{x}^2 \circ \cdots \vec{x}^N] M\tilde{A}R . \tag{3.70b}$$

Using Eq. (3.67b) in this result and noting that S commutes with M (because of the way it is constructed), we obtain the desired result:

$$[\vec{y}^1 \vec{y}^2 \cdots \vec{y}^N] = [\vec{x}^1 \vec{x}^2 \cdots \vec{x}^N] S . \tag{3.71a}$$

To complete the transformation, we also observe that the equilibrium position vectors $\vec{d}^1, \vec{d}^2, \ldots, \vec{d}^N$ of the B model are given by

$$\begin{aligned} \vec{d}^\alpha &= \sum_i b_i^\alpha \hat{g}_i = \sum_j a_j^{\nu_\alpha} \mathcal{R}\Big(\sum_i R_{ji}\hat{f}_i\Big) \\ &= \sum_j a_j^{\nu_\alpha} \hat{f}_j = \vec{c}^{\,\nu_\alpha}, \end{aligned}$$

that is,

$$[\vec{d}^1 \vec{d}^2 \cdots \vec{d}^N] = [\vec{c}^{\,1} \vec{c}^{\,2} \cdots \vec{c}^{\,N}] S. \tag{3.71b}$$

Thus, the displacement vectors $\vec{\xi}^1, \vec{\xi}^2, \ldots, \vec{\xi}^N$ in the B model, $\vec{\xi}^\alpha = \vec{y}^\alpha - \vec{d}^\alpha$, also undergo the same transformation S:

$$[\vec{\xi}^1 \vec{\xi}^2 \cdots \vec{\xi}^N] = [\vec{\rho}^{\,1} \vec{\rho}^{\,2} \cdots \vec{\rho}^{\,N}] S. \tag{3.71c}$$

Summary: With the permutation matrix S determined by Eq. (3.64) and the orthogonal matrix R determined by Eq. (3.66), we may transform any B model theory into our A model theory by replacing the matrix B by $\tilde{R}AS$; the Eckart frame $[\hat{g}_1 \hat{g}_2 \hat{g}_3]$ by $[\hat{f}_1 \hat{f}_2 \hat{f}_3]R$; and the position vectors, equilibrium vectors, and displacement vectors by $\vec{y}^\alpha = \vec{x}^{\nu_\alpha}, \vec{d}^\alpha = \vec{c}^{\,\nu_\alpha}, \vec{\xi}^\alpha = \vec{\rho}^{\,\nu_\alpha}$, $\alpha = 1, 2, \ldots, N$, respectively.

Included as a special case of the preceding transformation rules is the case of a single investigator who wishes to consider the effect on his dynamical model due to a relabeling of the identical particles in his static model. In this case, he keeps the same principal axes system throughout. This corresponds to putting $\mathcal{R}$ = identity in Eqs. (3.65)–(3.70). The content of the transformation rules then has the following interpretation:

Theorem 9. There exists a one-to-one correspondence between the set of all dynamical models corresponding to the permutations of the position vectors among $\vec{a}^1, \ldots, \vec{a}^N$ which point to identical particles in the static model and the set of theories in which A is fixed and the permutations are applied to the position vectors among the $\vec{r}^1, \ldots, \vec{r}^N$ which point to identical particles in the dynamical A model.

It is interesting to note that Theorem 9 may be considered to be a direct consequence of *an invariance property of the Eckart vectors:*

Theorem 10. The Eckart vectors

$$\vec{F}_i = \sum_\alpha m_\alpha a_i^\alpha \vec{r}^\alpha \tag{3.72a}$$

are invariant under the simultaneous transformations

$$a_i^\alpha \to \sum_\beta a_i^\beta S_{\beta\alpha}, \tag{3.72b}$$

$$\vec{r}^\alpha \to \sum_\beta \vec{r}^\beta S_{\beta\alpha}, \tag{3.72c}$$

where S is an arbitrary orthogonal matrix which commutes with the mass matrix M.

Proof. By direct substitution of Eqs. (3.72b) and (3.72c) into Eq. (3.72a).

IV. THE INTERNAL COORDINATE PROBLEM

One could hardly justify another discussion of the normal coordinate problem were it not for the fact that the role of the Eckart vectors of the second kind

$$\vec{E}_i = \sum_\alpha m_\alpha a_i^\alpha \vec{\rho}^\alpha \tag{4.1}$$

seems to have gone unnoticed. Furthermore, most discussions appear not to have recognized the intrinsic direct product structure of the problem. In this section, we consider the normal coordinate problem from this point of view.

A. Reduction of the static model representation

Let us recall from Sec. II, Eqs. (2.15), that the static model representation of the point group has already been split [by the mass matrix property, Eq. (2.21)] into the study of the transformations between vectors associated with identical particles. We now make a corresponding split of the Eckart vectors (4.1). Let

$$\begin{aligned} &\vec{\rho}^\alpha(a), \quad \alpha = 1, 2, \ldots, n_a \\ &\vec{\rho}^\beta(b), \quad \beta = 1, 2, \ldots, n_b \\ &\cdot \\ &\cdot \\ &\cdot \\ &\vec{\rho}^\delta(d), \quad \delta = 1, 2, \ldots, n_d \end{aligned} \tag{4.2}$$

denote the displacement vectors of the identical particles of the a type, of the b type, ..., of the d type, i.e., the displacement vectors corresponding to the labeling in the static model given by Eq. (2.19b). Equation (4.1) becomes

$$\vec{E}_i = m_a \vec{\mathcal{E}}_i(a) + m_b \vec{\mathcal{E}}_i(b) + \cdots + m_d \vec{\mathcal{E}}_i(d), \tag{4.3}$$

where we have defined

$$\begin{aligned} &\vec{\mathcal{E}}_i(a) = \sum_\alpha a_i^\alpha \vec{\rho}^\alpha(a), \\ &\vec{\mathcal{E}}_i(b) = \sum_\beta b_i^\beta \vec{\rho}^\beta(b), \\ &\cdot \\ &\cdot \\ &\cdot \\ &\vec{\mathcal{E}}_i(d) = \sum_\delta d_i^\delta \vec{\rho}^\delta(d). \end{aligned} \tag{4.4}$$

The action of an operator $\mathcal{L}_\mathcal{G}$ of the group of transformations between displacement vectors compatible with the Eckart frame may also be written in the split form [cf. Eq. (3.49)]:

$$\mathcal{L}_\mathcal{G}[\vec{\rho}^1(\lambda)\cdots\vec{\rho}^{n_\lambda}(\lambda)] = \mathcal{G}[\vec{\rho}^1(\lambda)\cdots\vec{\rho}^{n_\lambda}(\lambda)]\tilde{S}_\lambda(\mathcal{G}) \tag{4.5}$$

for $\lambda = a, b, \ldots, d$.

The relation $RA = AS$ of Theorem 1 also takes a split form. We note that the $3\times N$ matrix A may be written

$$A = [AB\cdots D], \tag{4.6}$$

where the new A in the right-hand side is $3\times n_a$, B is $3\times n_b, \ldots, D$ is $3\times n_d$. Thus, $RA = AS$ for S of the form (2.19c) now becomes the set of relations

$$\begin{aligned} &GA = AS_a(\mathcal{G}), \\ &GB = BS_b(\mathcal{G}), \\ &\cdot \\ &\cdot \\ &\cdot \\ &GD = DS_d(\mathcal{G}), \end{aligned} \tag{4.7}$$

where G is the matrix representing $\mathcal{G}$ on the frame $\hat{e}_1, \hat{e}_2, \hat{e}_3$ of the static model, or, equivalently, G is the orthogonal matrix representing $\mathcal{G}$ on the Eckart frame $\hat{f}_1, \hat{f}_2, \hat{f}_3$:

$$\mathcal{G}\hat{f}_i = \sum_j G_{ji}\hat{f}_j. \tag{4.8}$$

The important transformation property, Eq. (3.43a), of the Eckart vectors now becomes

$$\mathcal{L}_\mathcal{G}[\vec{\mathcal{E}}_1(\lambda)\vec{\mathcal{E}}_2(\lambda)\vec{\mathcal{E}}_3(\lambda)] = \mathcal{G}[\vec{\mathcal{E}}_1(\lambda)\vec{\mathcal{E}}_2(\lambda)\vec{\mathcal{E}}_3(\lambda)]\tilde{G} \tag{4.9}$$

for each $\lambda = a, b, \ldots, d$.

For notational convenience, we now drop the index λ in the subsequent discussion, and write

$$\mathcal{L}_\mathcal{G}[\vec{\rho}^1\cdots\vec{\rho}^n] = \mathcal{G}[\vec{\rho}^1\cdots\vec{\rho}^n]\tilde{S}(\mathcal{G}), \tag{4.10a}$$

$$G\Lambda = \Lambda S(\mathcal{G}), \tag{4.10b}$$

$$\vec{\mathcal{E}}_i = \sum_\alpha \lambda_i^\alpha \vec{\rho}^\alpha, \tag{4.10c}$$

$$\mathcal{L}_\mathcal{G}[\vec{\mathcal{E}}_1\vec{\mathcal{E}}_2\vec{\mathcal{E}}_3] = \mathcal{G}[\vec{\mathcal{E}}_1\vec{\mathcal{E}}_2\vec{\mathcal{E}}_3]\tilde{G}. \tag{4.10d}$$

In these equations, $\vec{\rho}^1, \ldots, \vec{\rho}^n$ denote any of the sets of displacement vectors $\vec{\rho}^1(\lambda), \ldots, \vec{\rho}^{n_\lambda}(\lambda)$; Λ denotes the corresponding $3\times n_\lambda$ matrix $A, B, \ldots,$ or D; $S(\mathcal{G})$ denotes the corresponding $S_\lambda(\mathcal{G})$; and $\vec{\mathcal{E}}_1, \vec{\mathcal{E}}_2, \vec{\mathcal{E}}_3$ denote the corresponding $\vec{\mathcal{E}}_1(\lambda), \vec{\mathcal{E}}_2(\lambda), \vec{\mathcal{E}}_3(\lambda)$. Note, however, that it is the same G which occurs for any λ.

Let us now construct a real, orthogonal matrix which effects a partial reduction of the static model representation. Equation (4.10b) is the key relation, which we also require in its transposed form:

$$\tilde{S}(\mathcal{G})\tilde{\Lambda} = \tilde{\Lambda}\tilde{G}. \tag{4.11}$$

Multiplying Eq. (4.10b) from the left by $\tilde{S}(\mathcal{G})\tilde{\Lambda}G = \tilde{\Lambda}$ gives

$$S(\mathcal{G})K = KS(\mathcal{G}), \tag{4.12a}$$

where

$$K = \tilde{\Lambda}\Lambda. \tag{4.12b}$$

Since K is a real, symmetric matrix, there exists a real, orthogonal matrix W which brings K to diagonal form. The form of the diagonal matrix depends on the rank of the

matrix Λ. The rank of Λ may be 0, 1, 2, or 3, depending on the static configuration of the identical particles of type λ. If $\text{rank}\Lambda = 0$, then Λ itself is the zero matrix. This can happen only if a particle is located at the center of mass. Thus, K is the 1×1 zero matrix, and we choose $W = 1$. For all other cases, we have

$$\tilde{W}KW = \begin{bmatrix} k & 0 \\ 0 & 0 \end{bmatrix}, \tag{4.13a}$$

where k is a diagonal matrix having nonzero elements and having dimension given by

$$i_0 = \dim k = \text{rank}\Lambda\ . \tag{4.13b}$$

The 0's in the block matrix (4.13a) denote zero matrices of the appropriate dimensions as required to "fill out" the $n\times n$ matrix.

We will need an additional property of W which follows from Eq. (4.13a). Writing the left-hand side in the form $(\tilde{W}\tilde{\Lambda})(\Lambda W)$ and selecting the diagonal element of this product, we easily prove

$$\sum_{k=1}^{n} W_{ki}\Lambda_{jk} = 0 \tag{4.14}$$

for $i \geq 1 + \dim k$ and $j = 1, 2, 3$. The content of Eq. (4.14) may be summarized by the statement: *The space spanned by the rows of Λ is perpendicular to the space spanned by the columns W_i, $1 + \dim k \leq i \leq n$, of W.*

The next step is to multiply Eq. (4.12a) from the left by $\tilde{W}$ and from the right by W. This gives

$$\tilde{W}S(\mathcal{G})W\begin{bmatrix} k & 0 \\ 0 & 0 \end{bmatrix} = \begin{bmatrix} k & 0 \\ 0 & 0 \end{bmatrix}\tilde{W}S(\mathcal{G})W.$$

It is straightforward to show from this result that

$$\tilde{W}S(\mathcal{G})W = \begin{bmatrix} S_1(\mathcal{G}) & 0 \\ 0 & S_2(\mathcal{G}) \end{bmatrix}, \tag{4.15a}$$

where $S_1(\mathcal{G})$ is a real, orthogonal matrix (of dimension equal to $\text{rank}\Lambda$) which commutes with k,

$$S_1(\mathcal{G})k = kS_1(\mathcal{G}), \tag{4.15b}$$

and $S_2(\mathcal{G})$ is a real, orthogonal matrix. Thus, we have proved: *Any orthogonal matrix which diagonalizes $K = \tilde{\Lambda}\Lambda$ reduces the static model representation $S(\mathcal{G})$.*

The reason for reducing the static model representation first can now be made clear. If we define the vectors $\vec{\eta}^{\alpha}$ by

$$[\vec{\eta}^1\vec{\eta}^2\cdots\vec{\eta}^n] = [\vec{\rho}^1\vec{\rho}^2\cdots\vec{\rho}^n]W, \tag{4.16}$$

then combining Eq. (4.10a) and Eq. (4.15a) shows that we have also split the space of displacement vectors with respect to the operators $\mathfrak{L}_{\mathcal{G}}$:

$$\mathfrak{L}_{\mathcal{G}}[\vec{\eta}^1\cdots\vec{\eta}^{i_0}] = \mathcal{G}[\vec{\eta}^1\cdots\vec{\eta}^{i_0}]\tilde{S}_1(\mathcal{G}), \tag{4.17a}$$

$$\mathfrak{L}_{\mathcal{G}}[\vec{\eta}^{i_0+1}\cdots\vec{\eta}^{n}] = \mathcal{G}[\vec{\eta}^{i_0+1}\cdots\vec{\eta}^{n}]\tilde{S}_2(\mathcal{G}). \tag{4.17b}$$

The next result establishes the role of the Eckart vectors $\vec{\mathcal{E}}_1, \vec{\mathcal{E}}_2, \vec{\mathcal{E}}_3$ of Eq. (4.10c) in the preceding reduction. *The linearly independent vectors among $\vec{\mathcal{E}}_1, \vec{\mathcal{E}}_2, \vec{\mathcal{E}}_3$ span the carrier space of the representation $\mathfrak{L}_{\mathcal{G}}$ of $G(\mathfrak{A})$ occurring in Eq. (4.17a).* The proof of this statement is given as follows: Equation (4.14) implies that the rows of Λ span the same space as do the columns $W_1, W_2, \ldots, W_{i_0}$ ($i_0 = \text{rank}\Lambda$) of W. This result and the relation

$$[\vec{\mathcal{E}}_1\vec{\mathcal{E}}_2\vec{\mathcal{E}}_3] = [\vec{\rho}^1\vec{\rho}^2\cdots\vec{\rho}^n]\tilde{\Lambda} \tag{4.18}$$

now yield the desired proof.

Generally, the linearly independent rows of Λ will not be perpendicular (see, however, the examples presented in this section). This situation is easily remedied by the Gram–Schmidt procedure. If we denote the rows of Λ by the notation

$$\Lambda_i = \text{row}(\lambda_i^1\,\lambda_i^2\cdots\lambda_i^n), \tag{4.19}$$

then the first i_0 columns of W may be constructed by the following procedure: Let $\Lambda_1', \Lambda_2', \Lambda_3'$ denote any rearrangement of $\Lambda_1, \Lambda_2, \Lambda_3$ such that $\Lambda_1', \ldots, \Lambda_{i_0}'$ are linearly independent. Then the first i_0 columns of W may be taken to be

$$W_i = \det\begin{bmatrix} \Lambda_1'\tilde{\Lambda}_1' & \cdots & \Lambda_1'\tilde{\Lambda}_i' \\ \vdots & & \\ \Lambda_{i-1}'\tilde{\Lambda}_1' & \cdots & \Lambda_{i-1}'\tilde{\Lambda}_1' \\ \tilde{\Lambda}_1' & \cdots & \tilde{\Lambda}_i' \end{bmatrix}(G_{i-1}G_i)^{-1/2}, \tag{4.20a}$$

$i = 1, \ldots, i_0 = \text{rank}\Lambda$, where G_i is the Gram determinant

$$G_i = \det\begin{bmatrix} \Lambda_1'\tilde{\Lambda}_1' & \cdots & \Lambda_1'\tilde{\Lambda}_i' \\ \vdots & & \\ \Lambda_i'\tilde{\Lambda}_1' & \cdots & \Lambda_i'\tilde{\Lambda}_i' \end{bmatrix}, \tag{4.20b}$$

G_0 is defined to be 1, and W_1 is defined to be $\tilde{\Lambda}_1'/G_1^{1/2}$.

The preceding construction also determines a set of new Eckart vectors $\vec{\mathcal{E}}_1'', \ldots, \vec{\mathcal{E}}_{i_0}''$ which now carry the representation $\mathfrak{L}_{\mathcal{G}}$ of $G(\mathfrak{A})$ occurring in Eq. (4.17a), i.e., they are given by $\vec{\eta}^i = \vec{\mathcal{E}}_i''$:

$$\vec{\mathcal{E}}_i'' = \sum_{\alpha=1}^{n} w_{\alpha i}\vec{\rho}^{\alpha}, \quad i = 1, \ldots, i_0 \tag{4.21a}$$

$$[\vec{\mathcal{E}}_1''\cdots\vec{\mathcal{E}}_{i_0}''] = [\vec{\rho}^1\vec{\rho}^2\cdots\vec{\rho}^n][W_1\cdots W_{i_0}], \tag{4.21b}$$

where $w_{\alpha i}$ is the element in row α and column i of W. We call the vectors (4.21) new Eckart vectors (of the second kind) because they are linear combinations of the old Eckart vectors $\vec{\mathcal{E}}_1, \vec{\mathcal{E}}_2, \vec{\mathcal{E}}_3$.

The details of the relation between $\vec{\mathcal{E}}_1'', \ldots, \vec{\mathcal{E}}_{i_0}''$ and $\vec{\mathcal{E}}_1, \vec{\mathcal{E}}_2, \vec{\mathcal{E}}_3$ may be constructed. We first observe that Eq. (4.18) may be rewritten in the form

$$[\vec{\mathcal{E}}_1'\vec{\mathcal{E}}_2'\vec{\mathcal{E}}_3'] = [\vec{\rho}^1\vec{\rho}^2\cdots\vec{\rho}^n]\tilde{\Lambda}', \tag{4.22}$$

where $\vec{\mathcal{E}}_1', \vec{\mathcal{E}}_2', \vec{\mathcal{E}}_3'$ denotes the same rearrangement of $\vec{\mathcal{E}}_1, \vec{\mathcal{E}}_2, \vec{\mathcal{E}}_3$ as does $\Lambda_1', \Lambda_2', \Lambda_3'$ of $\Lambda_1, \Lambda_2, \Lambda_3$. Here Λ' denotes the $3\times n$ matrix having rows $\Lambda_1', \Lambda_2', \Lambda_3'$. The relationship between $W_1, \ldots, W_{i_0}$ and $\Lambda_1', \ldots, \Lambda_{i_0}'$ is of the form

$$[W_1\cdots W_{i_0}] = [\Lambda_1'\cdots\Lambda_{i_0}']\Delta, \tag{4.23}$$

where Δ is an upper triangular matrix having elements which are easily identified from Eq. (4.20a), but which we will not note explicitly. Deleting the redundant columns from Eq. (4.22) and multiplying the resulting equa-

tion from the right by Δ yields the desired relation:

$$[\vec{\mathcal{E}}_1'' \cdots \vec{\mathcal{E}}_{i_0}''] = [\vec{\mathcal{E}}_1' \cdots \vec{\mathcal{E}}_{i_0}']\Delta . \tag{4.24}$$

Finally, we can also determine the matrix $S_1(\mathcal{G})$ in terms of the G occurring in Eq. (4.10d). This is accomplished in the following manner. The Eckart vectors $\vec{\mathcal{E}}_i$ are uniquely expressible in terms of the $\vec{\mathcal{E}}_1'', \ldots, \vec{\mathcal{E}}_{i_0}''$ by the relation

$$[\vec{\mathcal{E}}_1\vec{\mathcal{E}}_2\vec{\mathcal{E}}_3] = [\vec{\mathcal{E}}_1'' \cdots \vec{\mathcal{E}}_{i_0}'']\tilde{V}, \tag{4.25a}$$

where V is the $3 \times i_0$ matrix of rank i_0 given by

$$V = \Lambda[W_1 \cdots W_{i_0}]. \tag{4.25b}$$

Using

$$\begin{aligned}\mathcal{L}_{\mathcal{G}}[\vec{\mathcal{E}}_1\vec{\mathcal{E}}_2\vec{\mathcal{E}}_3] &= \mathcal{G}[\vec{\mathcal{E}}_1\vec{\mathcal{E}}_2\vec{\mathcal{E}}_3]\tilde{G} \\ &= \mathcal{G}[\vec{\mathcal{E}}_1'' \cdots \vec{\mathcal{E}}_{i_0}'']\tilde{V}\tilde{G} \\ &= \mathcal{L}_{\mathcal{G}}[\vec{\mathcal{E}}_1'' \cdots \vec{\mathcal{E}}_{i_0}'']S_1(\mathcal{G})\tilde{V}\tilde{G},\end{aligned}$$

we obtain

$$[\vec{\mathcal{E}}_1\vec{\mathcal{E}}_2\vec{\mathcal{E}}_3] = [\vec{\mathcal{E}}_1'' \cdots \vec{\mathcal{E}}_{i_0}'']S_1(\mathcal{G})\tilde{V}\tilde{G}.$$

Comparing this result with Eq. (4.25a) yields $\tilde{V} = S_1(\mathcal{G})\tilde{V}\tilde{G}$, that is,

$$\tilde{V}G = S_1(\mathcal{G})\tilde{V}, \tag{4.26}$$

where we note again that V is $3 \times i_0$, $S_1(\mathcal{G})$ is $i_0 \times i_0$, and G is 3×3. Since the rank of V is i_0, Eq. (4.26) possesses a unique solution expressing the elements of $S_1(\mathcal{G})$ in terms of the known elements of G and the known elements of V.

For consistency, we must also prove that the $S_1(\mathcal{G})$ obtained by solving Eq. (4.26) commutes with the diagonal matrix k appearing in Eq. (4.15b). One easily verifies from Eqs. (4.13a) and (4.25b) that $\tilde{V}V = k$. Furthermore, upon multiplying the transpose of Eq. (4.26) with the original equation, we also verify $S_1(\mathcal{G})k = kS_1(\mathcal{G})$.

Let us summarize the results we have obtained for the reduction of the static model representation. First we have proved the existence of a real orthogonal matrix which reduces the representation (*not necessarily into irreducibles*). Second, we have given an explicit construction of that part of the orthogonal matrix which splits off the representation $S_1(\mathcal{G})$. Third, we have shown that this split is a consequence of the fact that the Eckart vectors already span the invariant subspace which carries $S_1(\mathcal{G})$. Finally, we have obtained the relation of the representation $S_1(\mathcal{G})$ to the representation G. Thus, we have given all the details for splitting off the invariant subspace

$$\vec{\eta}^1 = \vec{\mathcal{E}}_1'', \ldots, \vec{\eta}^{i_0} = \vec{\mathcal{E}}_{i_0}'' \text{ [cf. Eq. (4.17a)]}.$$

Up to this point we have said nothing about the reducibility or irreducibility of the representations $\mathcal{G} \to S_1(\mathcal{G})$ and $\mathcal{G} \to S_2(\mathcal{G})$. A number of interesting results which have a bearing on the properties of $S_1(\mathcal{G})$ are easily proved, and we state some of these without proof. *If $\mathcal{G} \to G$ is an irreducible representation of $G(\mathfrak{A})$, then*

(a) The matrix $\Lambda\tilde{\Lambda}$ is a multiple of the 3×3 unit matrix

$$\Lambda\tilde{\Lambda} = \alpha I_3,$$

where $\alpha \neq 0$ for $\Lambda \neq 0$.

(b) The matrix $K = \tilde{\Lambda}\Lambda$ satisfies $K^2 = \alpha K$. Hence $K/\alpha\ (\alpha \neq 0)$ is idempotent.

(c) The rank of Λ is 3 for each $\Lambda = A, B, \ldots, D\ (\Lambda \neq 0)$. Therefore, we have

$$S_1(\mathcal{G}) = \tilde{V}^{-1}G\tilde{V},$$

and $S_1(\mathcal{G})$ is irreducible and equivalent to G. Furthermore, V must be orthogonal, and k must be the 3×3 unit matrix.

(d) The cases rank $\Lambda = 1$ or rank $\Lambda = 2$ can never occur. *If $\mathcal{G} \to G$ is a reducible representation of $G(\mathfrak{A})$, then*

(e) $S_1(\mathcal{G})$ is irreducible for the case rank $\Lambda = 1$ [$S_1(\mathcal{G})$ is then 1×1].

(f) $S_1(\mathcal{G})$ may be reducible or irreducible in the cases rank $\Lambda = 2$ or rank $\Lambda = 3$. It depends on the diagonal matrix k—if the elements of k are not equal, the $S_1(\mathcal{G})$ is necessarily reducible.

Concerning the reduction of $S_2(\mathcal{G})$, one can say very little in a general way which would differ from the standard projection operator techniques. We wish, however, to make the following remarks: (a) Often this piece of the problem is so small, it can be solved by inspection; (b) if it happens that

$$\sum_{\alpha} \lambda_i^{\alpha} = 0 \quad (i = 1, 2, 3),$$

then the one-dimensional invariant subspace spanned by

$$\vec{\eta} = \sum_{\alpha=1}^{n} \vec{\rho}^{\alpha}/\sqrt{n} \tag{4.27}$$

always splits off; and (c) sufficient conditions that the representation $\mathcal{G} \to S_2(\mathcal{G})$ be completely reducible by a real orthogonal similarity transformation are that $S_2(\mathcal{G})$ contains no irreducible representation more than once and that the ones it does contain have real characters [this statement applies equally well to the representation $\mathcal{G} \to S_1(\mathcal{G})$].

No doubt, one could refine considerably upon our observations concerning the reduction of static model representations of $G(\mathfrak{A})$. (We have, for example, made no use of the fact that the matrices in these representations are permutation matrices.) However, since our principal purpose was to demonstrate the role of the Eckart vectors, we will not pursue these details further.

Let us suppose, then, that we have found a unitary matrix[6] U which completely reduces the static model representation:

$$U^{\dagger}S(\mathcal{G})U = \begin{bmatrix} \Gamma_1(\mathcal{G}) & 0 & \cdots \\ 0 & \Gamma_2(\mathcal{G}) & \cdots \\ \cdot & & \\ \cdot & & \\ \cdot & & \end{bmatrix}, \tag{4.28}$$

where the dagger designates Hermitian conjugation. Defining vectors $\vec{\eta}^{\alpha}$ by

$$[\vec{\eta}^1\vec{\eta}^2 \cdots \vec{\eta}^n] = [\vec{\rho}^1\vec{\rho}^2 \cdots \vec{\rho}^n]\tilde{U}^{\dagger}, \tag{4.29}$$

[6] Lacking a general proof that the static model representation is always reducible by an orthogonal matrix (which we suspect to be true), we only assume the known result that the matrix U is unitary.

we see that Eq. (4.10a) splits into a number of relations:

$$\mathcal{L}_{\mathcal{G}}[\vec{\eta}^1 \cdots \vec{\eta}^{m_1}] = \mathcal{G}[\vec{\eta}^1 \cdots \vec{\eta}^{m_1}]\,\tilde{\Gamma}_1(\mathcal{G}), \tag{4.30a}$$

$$\mathcal{L}_{\mathcal{G}}[\vec{\eta}^{m_1+1} \cdots \vec{\eta}^{m_1+m_2}] = \mathcal{G}[\vec{\eta}^{m_1+1} \cdots \vec{\eta}^{m_1+m_2}]\,\tilde{\Gamma}_2(\mathcal{G}), \tag{4.30b}$$

$$\vdots$$

where m_ν is the dimension of the irreducible representation $\mathcal{G} \to \Gamma_\nu(\mathcal{G})$.

Let us denote a typical one of the relations (4.30) by

$$\mathcal{L}_{\mathcal{G}}[\vec{\xi}^1 \cdots \vec{\xi}^m] = \mathcal{G}[\vec{\xi}^1 \cdots \vec{\xi}^m]\,\tilde{\Gamma}(\mathcal{G}). \tag{4.31}$$

This is the stage to which the complete reduction of the static model representation brings us.

B. The direct product structure and symmetry coordinates

To progress further with the internal coordinate problem, we must now go to the component version of Eq. (4.31) We must do this carefully. Equation (4.31) means

$$\mathcal{L}_{\mathcal{G}}\vec{\xi}^\alpha = \sum_\beta (\mathcal{G}\vec{\xi}^\beta)\Gamma_{\alpha\beta}(\mathcal{G}). \tag{4.32}$$

In terms of components with respect to the Eckart frame, it becomes

$$(\mathcal{L}_{\mathcal{G}}\vec{\xi}^\alpha)\cdot\hat{f}_i = \sum_j \sum_\beta G_{ij}(\hat{f}_j \cdot \vec{\xi}^\beta)\Gamma_{\alpha\beta}(\mathcal{G}) = \{G[\xi^1 \cdots \xi^m]\,\tilde{\Gamma}(\mathcal{G})\}_i^\alpha, \tag{4.33}$$

where G is the matrix representation of $\mathcal{G}$ on the Eckart frame and $\xi^\beta = \mathrm{col}(\xi_1^\beta \xi_2^\beta \xi_3^\beta)$, $\xi_j^\beta = \hat{f}_j \cdot \vec{\xi}^\beta$. We can restore Eq. (4.33) to a matrix relation by making the *definitions*

$$L_{\mathcal{G}}\xi_i^\alpha = (\mathcal{L}_{\mathcal{G}}\vec{\xi}^\alpha)\cdot\hat{f}_i, \tag{4.34a}$$

$$L_{\mathcal{G}}\xi^\alpha = \mathrm{col}(L_{\mathcal{G}}\xi_1^\alpha L_{\mathcal{G}}\xi_2^\alpha L_{\mathcal{G}}\xi_3^\alpha), \tag{4.34b}$$

$$L_{\mathcal{G}}[\xi^1 \cdots \xi^m] = [L_{\mathcal{G}}\xi^1 \cdots L_{\mathcal{G}}\xi^m]. \tag{4.34c}$$

The relation expressed by Eq. (4.33) may now be written

$$L_{\mathcal{G}}[\xi^1 \cdots \xi^m] = G[\xi^1 \cdots \xi^m]\,\tilde{\Gamma}(\mathcal{G}). \tag{4.35}$$

We may write the transformation (4.35) in a more conventional form by arranging the columns of the $3 \times m$ matrix $[\xi^1 \cdots \xi^m]$ in a single $(3m)\times 1$ column matrix in which ξ^1 occupies positions 1–3, ξ^2 positions 4–7, etc. It is a straightforward exercise in matrix algebra to verify that the transformation (4.35) then takes on the following appearance:

$$L_{\mathcal{G}}\begin{bmatrix}\xi^1\\ \xi^2\\ \vdots\\ \xi^m\end{bmatrix} = [\Gamma(\mathcal{G})\otimes G]\begin{bmatrix}\xi^1\\ \xi^2\\ \vdots\\ \xi^m\end{bmatrix}, \tag{4.36}$$

where the notation $A \otimes B$ denotes the direct product of two matrices. The notation on the left-hand side is a column matrix version of the convention (4.34c).

Equation (4.36) displays the "intrinsic direct product" structure alluded to at the beginning of this section. Observe that if the representation $\mathcal{G} \to G$ is not already irreducible, we can go one step further (it is only 3×3) and reduce it:

$$U_0^\dagger G U_0 = \begin{bmatrix} G_1 & \cdots & 0 \\ \vdots & & \vdots \\ 0 & \cdots & G_{k_0}\end{bmatrix}, \tag{4.37}$$

where $k_0 (k_0 \leq 3)$ is the number of irreducibles contained in G. Upon defining

$$\zeta^\alpha = U_0^\dagger \xi^\alpha, \quad \alpha = 1, 2, \ldots, m \tag{4.38}$$

the split of Eq. (4.36) corresponding to Eq. (4.37) is given by

$$L_{\mathcal{G}}\begin{bmatrix}\tau^1(k)\\ \tau^2(k)\\ \vdots\\ \tau^{r_k}(k)\end{bmatrix} = [\Gamma(\mathcal{G})\otimes G_k]\begin{bmatrix}\tau^1(k)\\ \tau^2(k)\\ \vdots\\ \tau^{r_k}(k)\end{bmatrix}, \tag{4.39a}$$

$k = 1, \ldots, k_0$. The number r_k is the dimension of G_k $(r_1 + \cdots + r_{k_0} = 3)$; each $\tau^\alpha(k)$ is a column matrix of length r_k; and the identification of the $\tau^\alpha(k)$ with the components of ζ^α is given by

$$\begin{bmatrix}\tau^\alpha(1)\\ \vdots\\ \tau^\alpha(k_0)\end{bmatrix} = \begin{bmatrix}\zeta_1^\alpha\\ \zeta_2^\alpha\\ \zeta_{k_0}^\alpha\end{bmatrix}. \tag{4.39b}$$

Observe now that the final step in the determination of symmetry coordinates [*coordinates transforming according to the irreducible representations of* $G(\mathfrak{A})$] *involves only the reduction of the direct product of two irreducible representations. This reduction may now be effected by the Wigner coefficients* (Griffith, 1962) *of the point group* $G(\mathfrak{A})$.

We may summarize our method of obtaining symmetry coordinates in three basic steps: (a) Reduce the static model representation, utilizing the Eckart vectors to accomplish part of this; (b) reduce G if it is not already irreducible; (c) use the Wigner coefficients of the point group $G(\mathfrak{A})$ to complete the reduction.

Recall that these three basic steps are to be applied to *each* of the $\Lambda = A, B, \ldots, D$ pieces of the problem.

The result of carrying out the preceding steps will be a number of sets of coordinates

$$\{Z_i^\mu(\lambda):\ \mu = 1, 2, \ldots, h_\lambda;\ i = 1, 2, \ldots, h_{\mu\lambda} \leq 3;\ \lambda = a, b, \ldots, d\}. \tag{4.40}$$

The integer $h_{\mu\lambda}$ is the number of partners transforming irreducibly:

$$L_{\mathcal{G}}\begin{bmatrix}Z_1^\mu(\lambda)\\ \vdots\\ Z_{h_{\mu\lambda}}^\mu(\lambda)\end{bmatrix} = \Gamma(\mathcal{G})\begin{bmatrix}Z_1^\mu(\lambda)\\ \vdots\\ Z_{h_{\mu\lambda}}^\mu(\lambda)\end{bmatrix}, \tag{4.41}$$

where $\Gamma(\mathcal{G})$ is a real, orthogonal irreducible representation of $G(\mathfrak{A})$ of dimension $h_{\mu\lambda}$. The integer h_λ is the number of irreducible representations obtained from the

reduction of the λth piece of the problem, and, as used consistently, λ enumerates the pieces $a, b, \ldots, d$ of the problem. Consequently, it must be true that

$$\sum_{\mu=1}^{h_\lambda} \mu h_{\mu\lambda} = 3n_\lambda \,, \tag{4.42a}$$

$$\sum_{\lambda} n_\lambda = N. \tag{4.42b}$$

The general form of each $Z_i^\mu(\lambda)$ is

$$Z_i^\mu(\lambda) = \sum_{\alpha=1}^{n_\lambda} \sum_{j=1}^{3} C_{ij}^{\mu\alpha}(\lambda) \vec{\rho}^{\alpha}(\lambda) \cdot \hat{f}_j \,, \tag{4.43}$$

where the $\vec{\rho}^{\alpha}(\lambda)$, $\alpha = 1, 2, \ldots, n_\lambda$, are the original displacements occurring in Eqs. (4.4) and (4.5). Furthermore, the coefficients $C_{ij}^{\mu\alpha}(\lambda)$ are the elements of a real, orthogonal matrix (rows are enumerated by the index pairs μi; columns by αj).

C. Alternative method of obtaining symmetry coordinates from the Eckart vectors

In Sec. IV.B, we have taken the route of reducing completely the static model representation before proceeding to the reduction of the direct product. This procedure obscures somewhat several interesting properties of the Eckart vectors. For many problems the reduction of the "Eckart vector part" of the problem constitutes a large piece of the symmetry coordinate problem. We therefore present an alternative procedure for dealing with the Eckart vectors.

In matrix form, Eq. (4.10d) may be written in either of the following ways:

$$L_{\mathcal{G}}[\mathcal{E}_1 \mathcal{E}_2 \mathcal{E}_3] = G[\mathcal{E}_1 \mathcal{E}_2 \mathcal{E}_3]\tilde{G} \,, \tag{4.44a}$$

$$L_{\mathcal{G}} \begin{pmatrix} \mathcal{E}_1 \\ \mathcal{E}_2 \\ \mathcal{E}_3 \end{pmatrix} = [G \otimes G] \begin{pmatrix} \mathcal{E}_1 \\ \mathcal{E}_2 \\ \mathcal{E}_3 \end{pmatrix} \,, \tag{4.44b}$$

where

$$\mathcal{E}_j = \mathrm{col}(\mathcal{E}_{1j} \mathcal{E}_{2j} \mathcal{E}_{3j}), \tag{4.44c}$$

$$\mathcal{E}_{ij} = \hat{f}_i \cdot \vec{\mathcal{E}}_j \,. \tag{4.44d}$$

These equations are valid despite the fact that the $\vec{\mathcal{E}}_i$ may not be linearly independent.

Equation (4.44b) is interesting because we know how to reduce it partially by standard angular momentum techniques: Since G is an $l=1$ representation of the orthogonal group, $G \otimes G$ contains $l=0$, $l=1$, and $l=2$ irreducible representations. These representations are carried by a scalar (the trace of the matrix $[\mathcal{E}_1 \mathcal{E}_2 \mathcal{E}_3]$), a vector (three components), and a second-rank tensor (five components). Explicitly, these invariant subspaces are spanned by the following symmetry coordinates:

$$\eta_1 = \mathcal{E}_{11} + \mathcal{E}_{22} + \mathcal{E}_{33} \,, \tag{4.45a}$$

$$(\xi_1 \xi_2 \xi_3) = (\mathcal{E}_{23} - \mathcal{E}_{32}, \mathcal{E}_{31} - \mathcal{E}_{13}, \mathcal{E}_{12} - \mathcal{E}_{21}), \tag{4.45b}$$

$$(\zeta_1 \zeta_2 \zeta_3 \zeta_4 \zeta_5) = (\mathcal{E}_{11} + \mathcal{E}_{22}, \mathcal{E}_{31} + \mathcal{E}_{13}, \mathcal{E}_{33} - \mathcal{E}_{11} - \mathcal{E}_{22}, + \mathcal{E}_{32}, \mathcal{E}_{12} + \mathcal{E}_{21}). \tag{4.45c}$$

In general, of course, the second two of these invariant subspaces may be reducible with respect to the operators $L_{\mathcal{G}}$. Thus, in this second approach, one must account not only for the possible linear dependence of the vectors $\vec{\mathcal{E}}_1, \vec{\mathcal{E}}_2, \vec{\mathcal{E}}_3$, but also continue with the reduction process. This can, of course, be done in a general way, but it is perhaps better to carry this out for the particular cases.

One can also apply the preceding analysis to the full Eckart vectors of Eq. (4.1). For nonplanar molecules, the Eckart vectors $\vec{E}_1, \vec{E}_2, \vec{E}_3$ are always linearly independent. The invariant subspaces are spanned by the symmetry coordinates

$$\eta_1 = E_{11} + E_{22} + E_{33} \,, \tag{4.46a}$$

$$(\xi_1 \xi_2 \xi_3) = (E_{23} - E_{32}, E_{31} - E_{13}, E_{12} - E_{21}), \tag{4.46b}$$

$$(\zeta_1 \zeta_2 \zeta_3 \zeta_4 \zeta_5) = (E_{11} + E_{22}, E_{31} + E_{13}, E_{33} - E_{11} - E_{22}, E_{23} + E_{32}, E_{12} + E_{21}) \,. \tag{4.46c}$$

Quite remarkably the vector

$$\vec{\xi} = \xi_1 \hat{f}_1 + \xi_2 \hat{f}_2 + \xi_3 \hat{f}_3 \tag{4.47a}$$

which appears in this reduction is just

$$\vec{\xi} = \hat{f}_1 \times \vec{E}_1 + \hat{f}_2 \times \vec{E}_2 + \hat{f}_3 \times \vec{E}_3 \tag{4.47b}$$

which, by the Eckart conditions, is required to be the zero vector. The natural occurrence of $\vec{\xi}$ as a symmetry coordinate gives yet added insight into the ingenuity of Carl Eckart's choice of conditions for fixing the molecular frame.[7]

The results given by Eqs. (4.46) are related to those of Eqs. (4.45): When the suppressed index λ is restored to Eqs. (4.45), this relation is expressed by Eq. (4.3).

The procedure given in this section may be used to replace part of the general procedure of Sec. IV B. The part which it replaces is described as follows: Partition the matrix on the right-hand side of Eq. (4.28) into two parts—the irreducibles originating from $S_1(\mathcal{G})$ and the irreducibles originating from $S_2(\mathcal{G})$ [cf. Eq. (4.15a)]. Then the content of Eqs. (4.45) (after accounting for any linear dependence of the $\vec{\mathcal{E}}_i$) must agree with the results one obtains from the sets of the type of Eq. (4.36) corresponding to $\Gamma_1(\mathcal{G}) \otimes G, \Gamma_2(\mathcal{G}) \otimes G, \ldots$, where $\Gamma_1(\mathcal{G}), \Gamma_2(\mathcal{G}), \ldots$ are the irreducibles contained in $S_1(\mathcal{G})$.

D. Normal coordinates

Whether we use the method of Sec. IV.B, Sec. IV.C, or a combination, the results of the group theoretical analysis are expressed by Eq. (4.43). We still must impose the center of mass conditions

$$\sum_{\lambda} \sum_{\alpha=1}^{n_\lambda} m_\lambda \vec{\rho}^{\alpha}(\lambda) \cdot \hat{f}_i = 0 \,, \tag{4.48a}$$

for $i = 1, 2, 3$, and the Eckart conditions

$$\sum_{\lambda} m_\lambda \mathcal{E}_{ij}(\lambda) = \sum_{\lambda} m_\lambda \mathcal{E}_{ji}(\lambda) \tag{4.48b}$$

for $i < j$.

The method of imposing conditions (4.48) may be out-

[7] Note also then the requirement $E_{ij} = E_{ji}$ places the preceding analysis of the Eckart vectors $\vec{E}_1, \vec{E}_2, \vec{E}_3$ in one-to-one correspondence with the analysis of the polarizability tensor (Wilson, 1955).

lined in the following manner: We first invert Eq. (4.43) to obtain

$$\vec{\rho}^{\alpha}(\lambda)\cdot\hat{f}_j=\sum_{\mu=1}^{h_\lambda}\sum_{i=1}^{h_{\mu\lambda}}C_{ij}^{\mu\alpha}(\lambda)Z_i^{\mu}(\lambda). \tag{4.49}$$

The idea now is to impose the six conditions to obtain six relations among the $3N$ quantities $Z_i^{\mu}(\lambda)$. One then introduces $3N-6$ independent internal symmetry coordinates S_i^{γ}, $\gamma=1,2,\ldots,h$, $i=1,2,\ldots,h_\gamma\leq 3$. Relation (4.49) takes the form

$$\vec{\rho}^{\alpha}\cdot\hat{f}_j=\sum_{\gamma=1}^{h}\sum_{i=1}^{h_\gamma}C_{ij}^{\gamma\alpha}S_i^{\gamma}, \tag{4.50}$$

where now $\alpha=1,2,\ldots,N$. The index γ enumerates the number of irreducible representations h (repetitions counted) which are carried by the internal symmetry coordinates, and the index i enumerates the number of partners h_γ participating in a particular irreducible transformation. The method of going from Eq. (4.49) to Eq. (4.50) is best illustrated by our examples given in Secs. IV.E, IV.F, and IV.G.

If two (or more) internal symmetry coordinates $(S_1^{\gamma},\ldots,S_{h_\gamma}^{\gamma})$ and $(S_1^{\gamma'},\ldots,S_{h_{\gamma'}}^{\gamma'})$ carry the same irreducible representation of $G(\mathfrak{A})$, and if the direct product of this irreducible representation contains the identity representation, then these internal symmetry coordinates are still not *normal coordinates*. To split such a representation, one must proceed by the well known method of diagonalizing the appropriate quadratic form (a portion of the quadratic part of the potential energy). The end result of such calculations is a set of normal coordinates

$$\{q_i^{\gamma}:\ \gamma=1,2,\ldots,h;\ i=1,2,\ldots,h_\gamma\leq 3\}. \tag{4.51a}$$

The normal coordinates are transformed under the action of $L_{\mathcal{G}}$ in the following manner:

$$L_{\mathcal{G}}\begin{bmatrix}q_1^{\gamma}\\ \cdot\\ \cdot\\ \cdot\\ q_{h_\gamma}^{\gamma}\end{bmatrix}=\Gamma^{\gamma}(\mathcal{G})\begin{bmatrix}q_1^{\gamma}\\ \cdot\\ \cdot\\ \cdot\\ q_{h_\gamma}^{\gamma}\end{bmatrix}, \tag{4.51b}$$

where $\mathcal{G}\to\Gamma^{\gamma}(\mathcal{G})$ is a real, orthogonal irreducible representation of $G(\mathfrak{A})$. Finally, the displacement components are given in terms of the normal coordinates by an expression of the form:

$$\vec{\rho}^{\alpha}\cdot\hat{f}_j=\sum_{\gamma=1}^{h}\sum_{i=1}^{h_\gamma}l_{ij}^{\gamma\alpha}q_i^{\gamma}. \tag{4.52}$$

This relationship alone is, of course, not invertible since $3N$ components are defined by the left-hand side and $3N-6$ components occur in the right-hand side.

The results presented in this section are, of course, well known and have been included only for completeness of the presentation of the symmetry coordinate methods of Secs. IV.B and IV.C.

The presentation of Secs. IV.B and IV.C gets quite intricate because of its generality and the corresponding need to keep track of the large number of pieces into which the problem splits. We therefore invite the reader to work through the nontrivial examples given in the next three sections to convince himself of the simplicity and power of these techniques.

E. Static model XY_4 with symmetry group T_d

With respect to a principal axis system $\hat{e}_1,\hat{e}_2,\hat{e}_3$, the static model matrix A is given by

$$A=[AB], \tag{4.53a}$$

where

$$A=\begin{pmatrix}0\\0\\0\end{pmatrix},\quad B=\begin{bmatrix}1&-1&1&-1\\-1&1&1&-1\\1&1&-1&-1\end{bmatrix}. \tag{4.53b}$$

The X nucleus is labeled 0, and its equilibrium position is given by the column A; the four Y nuclei are labeled 1, 2, 3, 4 and their equilibrium positions are given up to a single constant by the columns 1, 2, 3, 4 of B, respectively. The point group of the static model, $G(\mathfrak{A})$, is well known to be tetrahedral T_d, of order 24.

Any operator of T_d can be written as a product formed from the two generators (Biedenharn *et al.*, 1968):

$$\mathcal{G}(1)=\mathcal{G}\mathcal{R}(\pi/2,\hat{e}_1), \tag{4.54a}$$

$$\mathcal{G}(2)=\mathcal{G}\mathcal{R}(\pi,(\hat{e}_1+\hat{e}_3)/\sqrt{2}). \tag{4.54b}$$

Thus, whenever the matrices representing these two operators are reduced, we are assured that the matrices representing the remaining elements of the group are also reduced.

We begin with the static model representation matrices corresponding to the group elements (4.54). These matrices are written down directly by the geometrical rules described in Sec. II.D: $S_a(k)=1$,

$$S_b(1)=\begin{bmatrix}0&1&0&0\\0&0&1&0\\0&0&0&1\\1&0&0&0\end{bmatrix},\quad S_b(2)=\begin{bmatrix}0&0&0&1\\0&1&0&0\\0&0&1&0\\1&0&0&0\end{bmatrix}. \tag{4.55}$$

Our first problem is to reduce the representation generated by the matrices (4.55). The representation $S_a(k)$ is already reduced. To reduce the representation generated by $S_b(1)$ and $S_b(2)$, we follow the procedure of Eqs. (4.16)–(4.27), noting, however, that the rows of B are already orthogonal so that it is unnecessary to use the Gram–Schmidt procedure.

The matrix W corresponding to the reduction of the a part of the problem is $W=1$.

For the reduction of the b part of the problem, we introduce the corresponding normalized Eckart vectors [cf. Eq. (4.10c)]:

$$\begin{aligned}\vec{\mathcal{E}}_1&=(\vec{\rho}^{\,1}-\vec{\rho}^{\,2}+\vec{\rho}^{\,3}-\vec{\rho}^{\,4})/2,\\ \vec{\mathcal{E}}_2&=(-\vec{\rho}^{\,1}+\vec{\rho}^{\,2}+\vec{\rho}^{\,3}-\vec{\rho}^{\,4})/2,\\ \vec{\mathcal{E}}_3&=(\vec{\rho}^{\,1}+\vec{\rho}^{\,2}-\vec{\rho}^{\,3}-\vec{\rho}^{\,4})/2.\end{aligned} \tag{4.56}$$

Furthermore, upon noting that $\sum_\alpha b_i^{\alpha}=0$, $i=1,2,3$ [cf. Eq. (4.27)], we also introduce

$$\vec{\eta}=\frac{1}{2}\sum_{\alpha=1}^{4}\vec{\rho}^{\alpha}, \tag{4.57}$$

which is a vector proportional to the center of mass of the four identical Y nuclei.

The matrix W which reduces the b part of the problem

is now read off directly from the coefficients of Eqs. (4.56) and (4.57):

$$W=\tfrac{1}{2}\begin{bmatrix}1&-1&1&1\\-1&1&1&1\\1&1&-1&1\\-1&-1&-1&1\end{bmatrix}. \tag{4.58}$$

One may now verify directly that [cf. Eq. (4.15a)]

$$\tilde{W}S_b(k)W=\begin{bmatrix}S_1(k)&0\\0&S_2(k)\end{bmatrix}, \tag{4.59}$$

where

$$S_2(k)=1, \tag{4.60a}$$

and $S_1(k)=G(k)$ [cf. Eq. (4.26)]; $G(k)$ is the matrix representing $\mathcal{G}(k)$ on the basis $\hat{e}_1,\hat{e}_2,\hat{e}_3$:

$$G(1)=\begin{bmatrix}-1&0&0\\0&0&1\\0&-1&0\end{bmatrix},\quad G(2)=\begin{bmatrix}0&0&-1\\0&1&0\\-1&0&0\end{bmatrix}. \tag{4.60b}$$

Remarkably, knowledge of the Eckart vectors and the center of mass vector (4.57) of the Y nuclei completely determines the reduction of the static model representation (4.55).

The irreducible representations of T_d generated by (4.60a) and (4.60b), respectively, are the ones designated by A_1 and F_2.

We may now proceed in our development to Eq. (4.31), noting now that the only nontrivial part of this problem is the b part corresponding to the normalized Eckart vectors themselves:

$$L_{(k)}[\vec{\mathcal{E}}_1\vec{\mathcal{E}}_2\vec{\mathcal{E}}_3]=\mathcal{G}(k)[\vec{\mathcal{E}}_1\vec{\mathcal{E}}_2\vec{\mathcal{E}}_3]\tilde{G}(k). \tag{4.61}$$

In terms of matrices, this relation may be expressed in either of the forms given by Eqs. (4.35) or (4.36):

$$L_{(k)}\begin{pmatrix}\mathcal{E}_1\\\mathcal{E}_2\\\mathcal{E}_3\end{pmatrix}=G(k)\otimes G(k)\begin{pmatrix}\mathcal{E}_1\\\mathcal{E}_2\\\mathcal{E}_3\end{pmatrix}. \tag{4.62}$$

The direct product of two F_2 representations is reducible as follows:

$$F_2\times F_2=A_1+E+F_1+\boldsymbol{F}_2. \tag{4.63}$$

Thus, the reduction of the representation of T_d generated by $G(k)\otimes G(k)$ $(k=1,2)$ can be carried out fully by using the Wigner coefficients (Griffith, 1962) for the group T_d (see also the general results given in Sec. IV.C). For example, to obtain the A_1 component, we write

$$\eta=\sum_{\alpha,i}\langle F_2\boldsymbol{F}_2\alpha i|F_2\boldsymbol{F}_2A_1\rangle\,\mathcal{E}_{\alpha i}, \tag{4.64a}$$

where $\mathcal{E}_{\alpha i}=\vec{\mathcal{E}}_\alpha\cdot\hat{f}_i$. The reduction coefficients are given by $\delta_{\alpha i}/\sqrt{3}$, thus giving

$$\eta=\frac{1}{\sqrt{3}}\sum_{\alpha=1}^{3}\mathcal{E}_{\alpha\alpha}. \tag{4.64b}$$

Continuing in this manner, we reduce $G(k)\otimes G(k)$, obtaining the linear combination of the $\mathcal{E}_{\alpha i}$ which transform irreducibly amongst themselves under the action of the $L_{\mathcal{G}}$.

We have now found all invariant spaces which can be constructed from the components of the displacement vectors such that the operators $L_{\mathcal{G}}$, $\mathcal{G}\in T_d$, are irreducible. We summarize the results below:

(a) The A_1 representation occurs once, originating from the reduction of $F_2\times F_2$ in the b part of the problem. The basis is

$$\eta=\sum_{\alpha=1}^{3}\mathcal{E}_{\alpha\alpha}/\sqrt{3}. \tag{4.65a}$$

(b) The E representation occurs once, originating from the reduction of $F_2\times F_2$ in the b part of the problem. The basis pair is

$$(\mathcal{E}_{11}-\mathcal{E}_{22})/\sqrt{2},\quad(\mathcal{E}_{11}+\mathcal{E}_{22}-2\mathcal{E}_{33})/\sqrt{3}. \tag{4.65b}$$

(c) The F_1 representation occurs once, originating from the reduction of $F_2\times F_2$ in the b part of the problem. The basis triplet is

$$(\mathcal{E}_{23}-\mathcal{E}_{32})/\sqrt{2},\quad(\mathcal{E}_{31}-\mathcal{E}_{13})/\sqrt{2},\quad(\mathcal{E}_{12}-\mathcal{E}_{21})/\sqrt{2}. \tag{4.65c}$$

(d) The F_2 representation occurs three times, originating once from the $1\otimes G(k)$ of the a part of the problem, once from the reduction of $G(k)\otimes G(k)$ in the b part of the problem, and once from the reduction of $1\otimes G(k)$ in the b part of the problem. The respective bases triplets are

$$\begin{aligned}&\text{components of }\vec{\rho}^{\,0}\text{: }\rho_1^0,\rho_2^0,\rho_3^0;\\&\text{components of }\vec{\eta}\text{: }\eta_1,\eta_2,\eta_3;\\&\zeta_1=(\mathcal{E}_{23}+\mathcal{E}_{32})/\sqrt{2},\ \zeta_2=(\mathcal{E}_{31}+\mathcal{E}_{13})/\sqrt{2},\ \zeta_3=(\mathcal{E}_{12}+\mathcal{E}_{21})/\sqrt{2}.\end{aligned} \tag{4.65d}$$

It is worth noting that F_2 occurs with multiplicity three, yet the structure of the reduction process is such that no difficulties with this multiplicity arise.

The transformation properties of the coordinates (4.65) are examples of the general result expressed by Eq. (4.41). They are summarized as follows:

(a) A_1 representation

$$L_{(k)}\eta=\eta. \tag{4.66a}$$

(b) E representation. Denote the pair (4.65b) by ζ_a,ζ_b. Then

$$\begin{aligned}L_{(1)}\begin{pmatrix}\zeta_a\\\zeta_b\end{pmatrix}&=\begin{pmatrix}1/2&\sqrt{3}/2\\\sqrt{3}/2&-1/2\end{pmatrix}\begin{pmatrix}\zeta_a\\\zeta_b\end{pmatrix},\\L_{(2)}\begin{pmatrix}\zeta_a\\\zeta_b\end{pmatrix}&=\begin{pmatrix}1/2&-\sqrt{3}/2\\-\sqrt{3}/2&-1/2\end{pmatrix}\begin{pmatrix}\zeta_a\\\zeta_b\end{pmatrix}.\end{aligned} \tag{4.66b}$$

(c) F_1 representation. Denote the triple (4.65c) by y_1,y_2,y_3. Then

$$L_{(k)}\begin{pmatrix}y_1\\y_2\\y_3\end{pmatrix}=-G(k)\begin{pmatrix}y_1\\y_2\\y_3\end{pmatrix}. \tag{4.66c}$$

(d) F_2 representation. Denote any one of the triples (4.65d) by x_1,x_2,x_3. Then

$$L_{(k)}\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = G(k)\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} . \tag{4.66d}$$

The center of mass condition imposes the relation

$$M\vec{\rho}^{\,0} + 2m\vec{\eta} = \vec{0} , \tag{4.67a}$$

where M and m are the masses of X and Y particles, respectively. Hence, we replace $\vec{\rho}^{\,0}$ and $\vec{\eta}$ by the single vector

$$\vec{\eta}^{\,0} = \vec{\rho}^{\,0} - (M/2m)\vec{\eta} . \tag{4.67b}$$

The Eckart conditions, Eq. (4.48b), are satisfied by specifying

$$y_i = 0, \quad i = 1, 2, 3. \tag{4.68}$$

We are thus left with the following set of internal symmetry coordinates:

$$\{\vec{\eta}^{\,0}, (\zeta_1\zeta_2\zeta_3), (\zeta_a\zeta_b), \eta_1\} . \tag{4.69}$$

Since $\vec{\eta}^{\,0}$ and $(\zeta_1\zeta_2\zeta_3)$ each belongs to the F_2 irreducible representation, they may enter the potential energy function coupled as $\sum_i \eta_i^0 \zeta_i$. The F_2 normal coordinates must therefore be obtained by the diagonalization of a simple quadratic form. [See Moret-Bailly (1961) and Shaffer (1939) for the normal coordinates.]

F. Static model XY_5 with symmetry group D_{3h}

The case of trigonal bipryamidal XY_5 is perhaps more illustrative of our general methods. Here we have three sets of inequivalent particles, in the sense of equivalence under $\mathcal{O}_3$ of the static model vectors [cf. Eqs. (2.11)]: the first set consists of the single X particle whose equilibrium position is at the origin of the principal axis frame $\hat{e}_1, \hat{e}_2, \hat{e}_3$; the second set consists of the three Y nuclei, sitting at the vertices of an equilateral triangle in the $\hat{e}_1\hat{e}_2$ plane; and the third set consists of the two remaining Y nuclei having equilibrium positions on the $\hat{e}_3$ axis at distances c to either side of the $\hat{e}_1\hat{e}_2$ plane: Specifically, the static model matrix A is given by

$$A = [ABC] , \tag{4.70a}$$

where

$$A = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad B = \begin{bmatrix} \sqrt{3}/2 & -\sqrt{3}/2 & 0 \\ 1/2 & 1/2 & -1 \\ 0 & 0 & 0 \end{bmatrix},$$
$$C = \begin{bmatrix} 0 & 0 \\ 0 & 0 \\ c & -c \end{bmatrix} . \tag{4.70b}$$

The X nucleus is labeled 0, and its equilibrium position is given by the column A; three of the Y nuclei are labeled 1, 2, 3 and their equilibrium positions are given up to a single constant by columns 1, 2, 3 of B, respectively; and the remaining two Y nuclei are labeled 4, 5 and their equilibrium positions are given by columns 1 and 2 of matrix C.

The point group $G(\mathfrak{A})$ is D_{3h} of order 12. D_{3h} is a direct product group generated by three operations:

$$\mathcal{G}(1) = \mathfrak{R}(\pi, \hat{e}_2), \ \mathcal{G}(2) = \mathfrak{R}(\tfrac{2}{3}\pi, \hat{e}_3), \ \mathcal{G}(3) = \mathcal{G}\mathfrak{R}(\pi, \hat{e}_3) . \tag{4.71}$$

$\mathcal{G}(1)$ and $\mathcal{G}(2)$ alone generate the group D_3, while $\mathcal{G}(3)$ generates a commuting group of order two. $\mathcal{G}(3)$ has been written as a proper rotation times the inversion, which is easily seen to be a reflection through the $\hat{e}_1\hat{e}_2$ plane. The irreducible representations of D_3 are denoted by A_1', A_2', E' and A_1'', A_2'', E'', corresponding, respectively, to even and odd properties under reflection.

The geometrical method of Sec. II.D yields the following static model representation of the generator elements $\mathcal{G}(k)$, $k = 1, 2, 3$:

$$S_a(k) = 1, \tag{4.72a}$$

$$S_b(1) = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad S_b(2) = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix},$$

$$S_b(3) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{4.72b}$$

$$S_c(1) = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad S_c(2) = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad S_c(3) = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} . \tag{4.72c}$$

Again our first problem is to reduce the representations (4.72). To accomplish this, we write out the Eckart vectors for the "b particles" and the "c particles." We first consider the b particles. Since the rank of B is two and its rows are already perpendicular, we have two linearly independent Eckart vectors [cf. (4.21b)]:

$$\vec{\mathcal{E}}_1(b) = (\vec{\rho}^{\,1} - \vec{\rho}^{\,2})/\sqrt{2} ,$$
$$\vec{\mathcal{E}}_2(b) = (\vec{\rho}^{\,1} + \vec{\rho}^{\,2} - 2\vec{\rho}^{\,3})/\sqrt{6} . \tag{4.73}$$

Furthermore, since $\sum_\alpha b_i^\alpha = 0$ [cf. Eq. (4.27)], we know that

$$\vec{\eta}(b) = \frac{1}{\sqrt{3}} \sum_{\alpha=1}^{3} \vec{\rho}^{\,\alpha} \tag{4.74}$$

spans a one-dimensional invariant subspace in the reduction of the b representation (4.72b). The matrix $W(b)$ which effects this reduction is obtained from the coefficients of the vectors (4.73) and (4.74):

$$W(b) = \begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{6} & 1/\sqrt{3} \\ -1/\sqrt{2} & 1/\sqrt{6} & 1/\sqrt{3} \\ 0 & -2/\sqrt{6} & 1/\sqrt{3} \end{bmatrix} . \tag{4.75}$$

It may now be verified directly that

$$\tilde{W}(b)S_b(k)W(b) = \left[\begin{array}{cc:c} & & 0 \\ & E'(k) & 0 \\ \hdashline 0 & 0 & A_1'(k) \end{array}\right] , \tag{4.76a}$$

where

$$E'(1) = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}, \quad E'(2) = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix},$$

$$E'(3)=\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}, \tag{4.76b}$$

$$A_1'(k)=1, \quad k=1,2,3. \tag{4.76c}$$

Thus, the representation generated by $S_b(k)$ $(k=1,2,3)$ has been reduced into $E'+A_1'$.

We now carry out the same procedure for the c particles. Since the rank of C is one, there is only one Eckart vector:

$$\vec{\mathcal{E}}_3(c)=(\vec{\rho}^{\,4}-\vec{\rho}^{\,5})/\sqrt{2}\,. \tag{4.77a}$$

Again the vector [cf. Eq. (4.27)]

$$\vec{\eta}(c)=(\vec{\rho}^{\,4}+\vec{\rho}^{\,5})/\sqrt{2} \tag{4.77b}$$

spans an invariant subspace for the reduction of the c representation.

The matrix W is given by

$$W(c)=\begin{bmatrix}1/\sqrt{2} & 1/\sqrt{2}\\ -1/\sqrt{2} & 1/\sqrt{2}\end{bmatrix}, \tag{4.78a}$$

and one may verify directly that

$$\tilde{W}(c)S_c(k)W(c)=\begin{bmatrix}A_2''(k) & 0\\ 0 & A_1'(k)\end{bmatrix}, \tag{4.78b}$$

where $A_1'(k)=1$, $A_2''(1)=A_2''(3)=-1$, and $A_2''(2)=1$. Thus, the representation generated by the $S_c(k)$ has been reduced into $A_2''+A_1'$.

Again, knowledge of the Eckart vectors and the three "center of mass" vectors, $\sum_{\alpha=1}^{6}\vec{\rho}^{\,\alpha}$, $\sum_{\alpha=1}^{3}\vec{\rho}^{\,\alpha}$, $\sum_{\alpha=4}^{5}\vec{\rho}^{\,\alpha}$ completely determines the reduction of the static model representation of D_{3h}.

We now proceed to the second part of the problem: the reduction of $G(k)$, $k=1,2,3$. The matrices representing $\mathcal{G}(k)$ on the basis $\hat{e}_1,\hat{e}_2,\hat{e}_3$ are

$$G(1)=\left[\begin{array}{cc|c}-1 & 0 & 0\\ 0 & 1 & 0\\ \hline 0 & 0 & -1\end{array}\right], \quad G(2)=\left[\begin{array}{cc|c}-1/2 & -\sqrt{3}/2 & 0\\ \sqrt{3}/2 & -1/2 & 0\\ \hline 0 & 0 & 1\end{array}\right],$$

$$G(3)=\left[\begin{array}{cc|c}1 & 0 & 0\\ 0 & 1 & 0\\ \hline 0 & 0 & -1\end{array}\right]. \tag{4.79}$$

The representation already appears in reduced form and is just $E'+A_2''$.

We now proceed to the last step of the reduction process as given generally by Eqs. (4.39a). The only nontrivial part of this reduction comes from the b part of the problem and involves

$$E'\times E'=A_1'+A_2'+E''. \tag{4.80}$$

According to Sec. IV.C, the A_1' part of this reduction must be carried by $\mathcal{E}_{11}(b)+\mathcal{E}_{22}(b)$. We may systematically carry out the reduction using the Wigner coefficients for D_3. The results are as follows:

A_1' is carried by $[\mathcal{E}_{11}(b)+\mathcal{E}_{22}(b)]/\sqrt{2}$,

A_2' is carried by $[\mathcal{E}_{12}(b)-\mathcal{E}_{21}(b)]/\sqrt{2}$,

E' is carried by the pair

$[\mathcal{E}_{11}(b)-\mathcal{E}_{22}(b)]/\sqrt{2}$,

$[\mathcal{E}_{12}(b)+\mathcal{E}_{21}(b)]/\sqrt{2}$.

We have now found all the invariant spaces which can be constructed from the components of the displacement vectors such that the operators $L_{\mathcal{G}}$, $\mathcal{G}\in D_{3h}$, are irreducible. The results are summarized below:

(a) The A_1' representation occurs twice, originating once in the reduction of $E'\times E'$ in the b part of the problem, and originating once in the reduction of $A_2''\times A_2''=A_1'$ in the c part of the problem. The corresponding bases are

$$\zeta_0=[\mathcal{E}_{11}(b)+\mathcal{E}_{22}(b)]/\sqrt{2}\,, \quad \mathcal{E}_{33}(c)\,. \tag{4.81a}$$

(b) The A_2' representation occurs once, originating from the reduction of $E'\times E'$ in the b part of the problem. The basis is

$$[\mathcal{E}_{12}(b)-\mathcal{E}_{21}(b)]/\sqrt{2}\,. \tag{4.81b}$$

(c) The E' representation occurs three times, once from the reduction of $G(k)$ in the a part of the problem, once from the reduction of $E'\times E'$ in the b part of the problem, and once from the reduction of $E'\times A_1'=E'$ in the c part of the problem. The corresponding bases pairs are

$$\rho_1^0,\ \rho_2^0;$$
$$\xi=[\mathcal{E}_{11}(b)-\mathcal{E}_{22}(b)]/\sqrt{2}\,, \quad \xi'=[\mathcal{E}_{12}(b)+\mathcal{E}_{21}(b)]/\sqrt{2}\,;$$
$$\eta_1(c),\ \eta_2(c). \tag{4.81c}$$

(d) The A_1'' representation does not occur.

(e) The A_2'' representation occurs three times, once in the reduction of $G(k)$ in the a part of the problem, once in the reduction of $A_2''\times A_1'=A_2''$ in the b part of the problem, and once in the reduction of $A_2''\times A_1'=A_2''$ in the c part of the problem. The respective bases are

$$\rho_3^0,\ \eta_3(b),\ \eta_3(c)\,. \tag{4.81e}$$

(f) The E'' representation occurs twice, once in the reduction of $E'\times E'$ in the b part of the problem, and once in the reduction of $E'\times A_2''=E''$ in the c part of the problem. The respective bases pairs are

$$\mathcal{E}_{13}(b),\ \mathcal{E}_{23}(b);$$
$$\mathcal{E}_{31}(c),\ \mathcal{E}_{32}(c). \tag{4.81f}$$

The transformation properties of the coordinates (4.81) are summarized below:

(a) A_1' representation. Let ζ denote either of the bases of Eq. (4.81a). Then

$$L_{(k)}\zeta=\zeta, \quad k=1,2,3. \tag{4.82a}$$

(b) A_2' representation. Let y denote the basis coordinate (4.81b). Then

$$L_{(1)}y=-y, \quad L_{(2)}y=y, \quad L_{(3)}y=y\,. \tag{4.82b}$$

(c) E' representation. Let ξ, ξ' denote any of the basis pairs of Eq. (4.81c). Then

$$L_{(1)}\begin{pmatrix}\xi\\ \xi'\end{pmatrix}=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}\xi\\ \xi'\end{pmatrix},$$
$$L_{(2)}\begin{pmatrix}\xi\\ \xi'\end{pmatrix}=\begin{pmatrix}-1/2 & \sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix}\begin{pmatrix}\xi\\ \xi'\end{pmatrix}, \qquad (4.82c)$$
$$L_{(3)}\begin{pmatrix}\xi\\ \xi'\end{pmatrix}=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}\xi\\ \xi'\end{pmatrix}.$$

(e) A_2'' representation. Let z denote any one of the bases coordinates of Eq. (4.81e). Then

$$L_{(1)}z=-z,\quad L_{(2)}z=z,\quad L_{(3)}z=-z\ . \qquad (4.82e)$$

(f) E'' representation. Let ζ_a,ζ_b denote either of the basis pairs of Eq. (4.81f). Then

$$L_{(1)}\begin{pmatrix}\zeta_a\\ \zeta_b\end{pmatrix}=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}\zeta_a\\ \zeta_b\end{pmatrix},$$
$$L_{(2)}\begin{pmatrix}\zeta_a\\ \zeta_b\end{pmatrix}=\begin{pmatrix}-1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix}\begin{pmatrix}\zeta_a\\ \zeta_b\end{pmatrix}, \qquad (4.82f)$$
$$L_{(3)}\begin{pmatrix}\zeta_a\\ \zeta_b\end{pmatrix}=\begin{pmatrix}-1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}\zeta_a\\ \zeta_b\end{pmatrix}.$$

The center of mass of the system is proportional to $(\sqrt{3}\vec{\eta}(b)+\sqrt{2}\vec{\eta}(c))+(M/m)\vec{\rho}^{\,0}$, where m is the Y mass, M is the X mass, and $\vec{\rho}^{\,0}$ the displacement of the X particle. Two linearly independent vectors which are orthogonally related to the center of mass vector are

$$\vec{x}^{\,1}=\sqrt{2}\vec{\eta}(b)-\sqrt{3}\vec{\eta}(c), \qquad (4.83a)$$
$$\vec{x}^{\,2}=\sqrt{3}\vec{\eta}(b)+\sqrt{2}\vec{\eta}(c)-(5m/M)\vec{\rho}^{\,0}. \qquad (4.83b)$$

We may satisfy the center of mass condition by using the vectors $\vec{x}^{\,1}$ and $\vec{x}^{\,2}$ in place of $\vec{\eta}(b)$, $\vec{\eta}(c)$, and $\vec{\rho}^{\,0}$.

The Eckart conditions of Eq. (4.48b) are more complicated for this molecule. The full Eckart vectors of Eq. (4.1) are

$$[\vec{E}_1\vec{E}_2\vec{E}_3]=[\vec{\mathcal{E}}_1(b)\vec{\mathcal{E}}_2(b)\vec{\mathcal{E}}_3(c)]. \qquad (4.84a)$$

The requirement that the components form a symmetric matrix implies

$$\mathcal{E}_{12}(b)=\mathcal{E}_{21}(b),$$
$$\mathcal{E}_{13}(b)=\mathcal{E}_{31}(c), \qquad (4.84b)$$
$$\mathcal{E}_{23}(b)=\mathcal{E}_{32}(c).$$

This means that the A_2' coordinate vanishes and the two E'' bases coincide.

A final set of internal symmetry coordinates for trigonal bipyramidal XY_5 is

$$\zeta,\ \mathcal{E}_{33}(c),\ (\xi,\xi'),\ (x_1^1,x_2^1),\ (x_1^2,x_2^2),\ x_3^1,x_3^2 \qquad (4.85)$$

transforming, respectively, according to A_1', A_1', E', E', E', A_2'', and A_2''.

The construction of normal coordinates requires the diagonalization of three quadratic forms: a 2X2 on coordinates ζ and $\mathcal{E}_{33}(c)$; a 3X3 on coordinates (ξ,ξ'), (x_1^1,x_2^1), (x_1^2,x_2^2); and finally a 2X2 on coordinates x_3^1 and x_3^2, since the usual mixed scalar product of these coordinates contains the A_1' representation of D_{3h}.

G. Static model XY_6 with symmetry group O_h

The static model is described in a principal axis system $\hat{e}_1,\hat{e}_2,\hat{e}_3$ by the static model matrix

$$A=[AB], \qquad (4.86)$$

where

$$A=\begin{pmatrix}0\\ 0\\ 0\end{pmatrix},\quad B=\begin{bmatrix}1 & 0 & 0 & -1 & 0 & 0\\ 0 & 1 & 0 & 0 & -1 & 0\\ 0 & 0 & 1 & 0 & 0 & -1\end{bmatrix}. \qquad (4.87)$$

Again the X nucleus is labeled by 0 and has equilibrium position at the origin; and the Y nuclei are labeled by 1 through 6, and their equilibrium positions are given up to a single constant by columns 1 through 6 of B, respectively.

The point group $G(\mathfrak{A})$ is octahedral O_h of order 48. It is a direct product group consisting of O and the group of order 2 containing the inversion $\mathcal{I}$ and the identity. The generators of O_h may be chosen to be

$$\mathcal{I}(1)=\mathcal{R}(\pi/2,\hat{e}_1),\quad \mathcal{I}(2)=\mathcal{R}(\pi,(\hat{e}_1+\hat{e}_2)/\sqrt{2}),\quad \mathcal{I}(3)=\mathcal{I}, \qquad (4.88)$$

where for easy enumeration of results we write the inversion as $\mathcal{I}(3)$.

The static model representation matrices are once more constructed from the geometrical procedure of Sec. II.D:

$$S_a(k)=1, \qquad (4.89a)$$

$$S_b(1)=\begin{bmatrix}1&0&0&0&0&0\\0&0&0&0&0&1\\0&1&0&0&0&0\\0&0&0&1&0&0\\0&0&1&0&0&0\\0&0&0&0&1&0\end{bmatrix},\quad S_b(2)=\begin{bmatrix}0&0&1&0&0&0\\0&0&0&0&1&0\\1&0&0&0&0&0\\0&0&0&0&0&1\\0&1&0&0&0&0\\0&0&0&1&0&0\end{bmatrix},$$
$$S_b(3)=\begin{bmatrix}0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\\1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&1&0&0&0\end{bmatrix}. \qquad (4.89b)$$

The Eckart vectors corresponding to the b part of the problem are the full Eckart vectors of Eq. (4.1) (normalized):

$$\vec{E}_1=(\vec{\rho}^{\,1}-\vec{\rho}^{\,4})/\sqrt{2},$$
$$\vec{E}_2=(\vec{\rho}^{\,2}-\vec{\rho}^{\,5})/\sqrt{2}, \qquad (4.90)$$
$$\vec{E}_3=(\vec{\rho}^{\,3}-\vec{\rho}^{\,6})/\sqrt{2},$$

where we note that the rows of B are already perpendicular. Again, since $\sum_\alpha b_i^\alpha=0$ $(i=1,2,3)$, the Y-atom cen-

ter of mass vector

$$\vec{\eta} = \sum_{\alpha=1}^{6} \frac{\vec{\rho}^{\alpha}}{\sqrt{6}} \tag{4.91}$$

is a one-dimensional invariant subspace with respect to reduction of the representation generated by $S_b(k)$, $k = 1, 2, 3$.

By inspection, we observe that the symmetric combination of vectors given by

$$\begin{aligned} \vec{\eta}^{\,1} &= (\vec{\rho}^{\,1} + \vec{\rho}^{\,4})/\sqrt{2}\,, \\ \vec{\eta}^{\,2} &= (\vec{\rho}^{\,2} + \vec{\rho}^{\,5})/\sqrt{2}\,, \\ \vec{\eta}^{\,3} &= (\vec{\rho}^{\,3} + \vec{\rho}^{\,6})/\sqrt{2} \end{aligned} \tag{4.92}$$

span an invariant subspace perpendicular to that spanned by the Eckart vectors of Eq. (4.90). Since this space must contain the vector (4.91), we see that the appropriate basis to choose is not that of Eq. (4.92), but

$$\begin{aligned} \vec{\eta} &= \sum_{\alpha=1}^{6} \frac{\vec{\rho}^{\alpha}}{\sqrt{6}}\,, \\ \vec{\xi}^{\,1} &= (\vec{\eta}^{\,1} - \vec{\eta}^{\,2})/\sqrt{2}\,, \\ \vec{\xi}^{\,2} &= (\vec{\eta}^{\,1} + \vec{\eta}^{\,2} - 2\vec{\eta}^{\,3})/\sqrt{6}\,. \end{aligned} \tag{4.93}$$

The matrix W which reduces the b part of the problem is now read off directly from the coefficients of Eqs. (4.90)–(4.93):

$$W = \begin{bmatrix} 1/\sqrt{2} & 0 & 0 & 1/\sqrt{6} & 1/2 & 1/2\sqrt{3} \\ 0 & 1/\sqrt{2} & 0 & 1/\sqrt{6} & -1/2 & 1/2\sqrt{3} \\ 0 & 0 & 1/\sqrt{2} & 1/\sqrt{6} & 0 & -1/\sqrt{3} \\ -1/\sqrt{2} & 0 & 0 & 1/\sqrt{6} & 1/2 & 1/2\sqrt{3} \\ 0 & -1/\sqrt{2} & 0 & 1/\sqrt{6} & -1/2 & 1/2\sqrt{3} \\ 0 & 0 & -1/\sqrt{2} & 1/\sqrt{6} & 0 & -1/\sqrt{3} \end{bmatrix}. \tag{4.94}$$

One may now verify directly that

$$\tilde{W} S_b(k) W = \begin{bmatrix} G(k) & 0 & 0 \\ 0 & A_{1g}(k) & 0 \\ 0 & 0 & E_g(k) \end{bmatrix}. \tag{4.95}$$

In this result $G(1), G(2), G(3)$ generate the F_{1u} representation and are the matrices representing $\mathcal{G}(1), \mathcal{G}(2), \mathcal{G}(3)$:

$$G(1) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}, \quad G(2) = \begin{bmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{bmatrix},$$

$$G(3) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}; \tag{4.96}$$

the $A_{1g}(k) = 1$ generate the identity representation A_{1g}; and $E_g(1), E_g(2), E_g(3)$ generate the representation E_g:

$$E_g(1) = \begin{bmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}, \quad E_g(2) = \begin{bmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix},$$

$$E_g(3) = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \tag{4.97}$$

Thus, we have obtained the complete reduction of the static model representation ($W = 1$ for the a part of the problem).

We may now proceed in our development to the result given generally by Eq. (4.36) [cf. also Sec. IV.C]. We now carry out the reduction of the following direct product (b part): $G(k) \otimes G(k)$, that is,

$$F_{1u} \times F_{1u} = A_{1g} + E_g + F_{1g} + F_{2g}\,; \tag{4.98a}$$

$$A_{1g}(k) \otimes G(k) = G(k)\,; \tag{4.98b}$$

and $E_g(k) \otimes G(k)$, that is,

$$E_g \times F_{1u} = F_{1u} + F_{2u}\,. \tag{4.98c}$$

These reductions are carried out using the known Wigner coefficients for O_h. The results are summarized below:

(a) The A_{1g} representation occurs once, originating from the reduction of $F_{1u} \times F_{1u}$ [cf. Sec. IV.C]. The basis coordinate is

$$\zeta_0 = (E_{11} + E_{22} + E_{33})/\sqrt{3}\,. \tag{4.99a}$$

(b) The E_g representation occurs once, originating from the reduction of $F_{1u} \times F_{1u}$ [cf. Sec. IV.C]. The basis pair is

$$\xi_a = (E_{11} - E_{22})/\sqrt{2}\,, \quad \xi_b = (E_{11} + E_{22} - 2E_{33})/\sqrt{6}\,. \tag{4.99b}$$

(c) The F_{1g} representation occurs once, originating from the reduction of $F_{1u} \times F_{1u}$ [cf. Sec. IV.C]. The basis triplet is

$$\zeta_1 = (E_{23} - E_{32})/\sqrt{2}\,, \quad \zeta_2 = (E_{31} - E_{13})/\sqrt{2}\,,$$
$$\zeta_3 = (E_{12} - E_{21})/\sqrt{2}\,. \tag{4.99c}$$

(d) The F_{2g} representation occurs once, originating from the reduction of $F_{1u} \times F_{1u}$ [cf. Sec. IV.C]. The basis triplet is

$$\xi_1 = (E_{23} + E_{32})/\sqrt{2}\,, \quad \xi_2 = (E_{31} + E_{13})/\sqrt{2}\,,$$
$$\xi_3 = (E_{12} + E_{21})/\sqrt{2}\,. \tag{4.99d}$$

(e) The F_{1u} representation occurs three times, originating once from the a part of the problem, once from the reduction of $E_g \times F_{1u}$ in the b part of the problem, and once from the reduction of $A_{1g} \times F_{1u}$ in the b part of the problem. The three sets of basis triplets are [cf. Eqs. (4.93)]

$$\begin{aligned} &\rho_1^0, \rho_2^0, \rho_3^0 \\ &\eta_1, \eta_2, \eta_3 \\ &y_1 = -(\sqrt{3}\,\xi_1^1 + \xi_1^2)/2, \quad y_2 = (\sqrt{3}\,\xi_2^1 - \xi_2^2)/2, \quad y_3 = \xi_3^2\,. \end{aligned} \tag{4.99e}$$

(f) The F_{2u} representation occurs once, originating from the reduction of $E_g \times F_{1u}$. The basis triplet is [cf. Eqs. (4.93)]

$$z_1 = (\xi_1^1 - \sqrt{3}\,\xi_1^2)/2, \quad z_2 = (\xi_2^1 + \sqrt{3}\,\xi_2^2)/2, \quad z_3 = -\xi_3^1\,. \tag{4.99f}$$

The transformation properties of the coordinates (4.99) are summarized below:

(a) A_{1g} representation

$$L_{(k)}\zeta_0=\zeta_0\,. \tag{4.100a}$$

(b) E_g representation

$$L_{(1)}\begin{pmatrix}\xi_a\\ \xi_b\end{pmatrix}=\begin{pmatrix}1/2 & \sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix}\begin{pmatrix}\xi_a\\ \xi_b\end{pmatrix},$$

$$L_{(2)}\begin{pmatrix}\xi_a\\ \xi_b\end{pmatrix}=\begin{pmatrix}1/2 & -\sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix}\begin{pmatrix}\xi_a\\ \xi_b\end{pmatrix}, \tag{4.100b}$$

$$L_{(3)}\begin{pmatrix}\xi_a\\ \xi_b\end{pmatrix}=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}\xi_a\\ \xi_b\end{pmatrix}.$$

(c) F_{1g} representation

$$L_{(k)}\begin{pmatrix}\zeta_1\\ \zeta_2\\ \zeta_3\end{pmatrix}=G(k)\begin{pmatrix}\zeta_1\\ \zeta_2\\ \zeta_2\end{pmatrix},\quad k=1,2\,;$$

$$L_{(3)}\begin{pmatrix}\zeta_1\\ \zeta_2\\ \zeta_3\end{pmatrix}=\begin{pmatrix}\zeta_1\\ \zeta_2\\ \zeta_3\end{pmatrix}. \tag{4.100c}$$

(d) F_{2g} representation

$$L_{(k)}\begin{pmatrix}\xi_1\\ \xi_2\\ \xi_3\end{pmatrix}=-G(k)\begin{pmatrix}\xi_1\\ \xi_2\\ \xi_3\end{pmatrix}. \tag{4.100d}$$

(e) F_{1u} representation. Let y_1,y_2,y_3 denote any of the basis triplets (4.99e). Then

$$L_{(k)}\begin{pmatrix}y_1\\ y_2\\ y_3\end{pmatrix}=G(k)\begin{pmatrix}y_1\\ y_2\\ y_3\end{pmatrix}. \tag{4.100e}$$

(f) F_{2u} representation

$$L_{(k)}\begin{pmatrix}z_1\\ z_2\\ z_3\end{pmatrix}=-G(k)\begin{pmatrix}z_1\\ z_2\\ z_3\end{pmatrix},\quad k=1,2\,;$$

$$L_{(3)}\begin{pmatrix}z_1\\ z_2\\ z_3\end{pmatrix}=G(3)\begin{pmatrix}z_1\\ z_2\\ z_3\end{pmatrix}. \tag{4.100f}$$

The requirement that the center of mass of the system be at the origin is

$$M\vec{\rho}^{\,0}+\sqrt{6}\,m\vec{\eta}=\vec{0}\,, \tag{4.101a}$$

where M and m are the masses of the X and Y nuclei, respectively. Hence, we introduce the vector

$$\vec{x}=\sqrt{6}\,m\vec{\rho}^{\,0}-M\vec{\eta}\,. \tag{4.101b}$$

The Eckart conditions (4.48b) are satisfied by imposing

$$\zeta_i=0,\quad i=1,2,3\,. \tag{4.102}$$

We obtain the set of internal symmetry coordinates:

$$\zeta_0,\quad (\xi_a,\xi_b),\quad (\xi_1,\xi_2,\xi_3),\quad (x_1,x_2,x_3)$$
$$(y_1,y_2,y_3),\quad (z_1,z_2,z_3) \tag{4.103}$$

transforming, respectively, according to

$$A_{1g},\ E_g,\ F_{2g},\ F_{1u},\ F_{1u},\ \text{and}\ F_{2u}.$$

From the coordinates (x_1,x_2,x_3) and (y_1,y_2,y_3) we can form the invariant

$$\sum_i (a_i x_i^2+b_i x_i y_i+c_i y_i^2)\,.$$

The F_{1u} normal coordinates are thus obtained by diagonalizing a simple quadratic form. The remaining coordinates in the set (4.103) are already normal coordinates. [See Moret-Bailly (1959) for the normal coordinates.]

V. GROUPS OF COORDINATE TRANSFORMATIONS

We are now prepared to answer fully the question: What are the particle motions which are compatible with the Eckart frame? The answer is as follows: *The particles may have any set of displacements* $\vec{\rho}^{\,1},\vec{\rho}^{\,2},\ldots,\vec{\rho}^{\,N}$ *having components given by*

$$\vec{\rho}^{\,\alpha}\cdot\hat{f}_j=\sum_{\gamma=1}^{h}\sum_{i=1}^{h_\gamma} l_{ij}^{\gamma\alpha}\,q_i^\gamma\,, \tag{5.1}$$

in which the normal coordinates q_i^γ *may assume arbitrary values.*

This result appears somewhat paradoxical in view of the role that the operators $\mathfrak{L}_\mathfrak{G}$ played in the determination of the q_i^γ. This paradox is removed when we realize that the Eckart frame is a quite general concept—it must admit a variety of motions compatible with it, even when there is no symmetry, i.e., $G(\mathfrak{A})$ contains only the identity. In this case, of course, the q_i^γ are determined solely by diagonalizing the quadratic potential energy form. Even when the symmetry group $G(\mathfrak{A})$ contains many elements, a wide variety of motions must be admitted by the Eckart frame, e.g., the set of all pure harmonic motions.

Having arrived at the result, Eq. (5.1), whose interpretation seems to diminish the role of the group $G(\mathfrak{A})$, we demonstrate in this section that this is not the case, at least for molecules possessing a high degree of symmetry in the static model.

We begin by presenting a variety of transformation properties of the Eckart frame and the normal coordinates, apart from any physical problem, leaving until Sec. VI the task of tying these properties to the actual molecular problem.

A. A larger invariance group of the Eckart frame

Let R denote an arbitrary real, orthogonal matrix of dimension h_γ. We introduce the following linear transformations L_R of the normal coordinates $q_1^\gamma,\ldots,q_{h_\gamma}^\gamma$:

$$L_R\begin{bmatrix}q_1^\gamma\\ \cdot\\ \cdot\\ \cdot\\ q_{h_\gamma}^\gamma\end{bmatrix}=R\begin{bmatrix}q_1^\gamma\\ \cdot\\ \cdot\\ \cdot\\ q_{h_\gamma}^\gamma\end{bmatrix}. \tag{5.2}$$

The product $L_{R'}L_R$ of two transformations is defined in

the usual manner to be the rule of first applying L_R followed by applying $L_{R'}$. Thus,

$$\begin{aligned}(L_{R'}L_R)q_i^\gamma &= L_{R'}(L_R q_i^\gamma)\\ &= L_{R'}\bar{q}_i^\gamma = \sum_{j=1}^{h_\gamma} R'_{ij}\bar{q}_j^\gamma\\ &= \sum_{j=1}^{h_\gamma} R'_{ij}\sum_{k=1}^{h_\gamma} R_{jk}q_k^\gamma = \sum_{k=1}^{h_\gamma}(R'R)_{ik}q_k^\gamma\\ &= L_{R'R}q_i^\gamma ,\end{aligned}$$

where the intermediate step follows from the definition of the barred coordinates

$$\bar{q}_i^\gamma = L_R q_i^\gamma = \sum_{j=1}^{h_\gamma} R_{ij}q_j^\gamma . \tag{5.3}$$

The coordinates $\bar{q}_i^\gamma$ are again normal coordinates which describe motions within the same Eckart frame. Indeed, transformations of this type express the fact that the normal coordinates are determined only up to equivalence by the operators $L_{\mathcal{G}}$ and the quadratic form diagonalization methods. Thus, the $\bar{q}_i^\gamma$ coordinates transform according to

$$L_{\mathcal{G}}\begin{bmatrix}\bar{q}_1^\gamma\\ \cdot\\ \cdot\\ \cdot\\ \bar{q}_h^\gamma\end{bmatrix} = \bar{R}\Gamma^\gamma(\mathcal{G})R\begin{bmatrix}\bar{q}_1^\gamma\\ \cdot\\ \cdot\\ \cdot\\ \bar{q}_{h_\gamma}^\gamma\end{bmatrix} , \tag{5.4}$$

whenever the q_i^γ transform according to Eq. (4.51b). We could, in fact, have replaced R in Eq. (5.2) by any nonsingular matrix. For the type of problem (the molecular motions) under study, this extra generality is not required.

If we let k_1, k_2, and k_3 denote the number of sets of one-, two-, and three-dimensional normal coordinates, then we see that *the following direct product group is an invariance group of the Eckart frame:*

$$O_1\times\cdots\times O_1\times O_2\times\cdots\times O_2\times O_3\times\cdots\times O_3 , \tag{5.5}$$

$$|\leftarrow k_1 \text{ times}\rightarrow|\leftarrow k_2 \text{ times}\rightarrow|\leftarrow k_3 \text{ times}\rightarrow|$$

where O_i denotes the group of transformations

$$\{L_{R_i} : R_i \in O_i\}$$

in which O_i is the group of real, orthogonal matrices of dimension i. The elements of the group (5.5) are the ordered $(k_1+k_2+k_3)$-tuples of transformations:

$$(L_{R_1(1)},\ldots,L_{R_1(k_1)};L_{R_2(1)},\ldots,L_{R_2(k_2)};L_{R_3(1)},\ldots,L_{R_3(k_3)}), \tag{5.6}$$

where $R_i(\gamma)$ denotes an orthogonal matrix of dimension i. Each $L_{R_i(\gamma)}$ in this ordered h-tuple $(h=k_1+k_2+k_3)$ acts only on its corresponding normal coordinate set $(q_1^\gamma,\ldots,q_{h_\gamma}^\gamma)$, according to the action expressed by Eq. (5.2).

We will denote the group (5.5) by the abbreviated notation $G(O)$, and call it *a group of the internal motions*. We do not mean to imply by this designation that $G(O)$ is the only possible group of transformations relating internal coordinates which are compatible with the Eckart frame. It is *one* such group, and it is the group of relevance if the motions of the particles are pure harmonic (a mathematical possibility, if not often a physical situation—except as an important approximation).

In order to keep the notation reasonably unencumbered, we will symbolize an element (5.6) of the group $G(O)$ by the notation $L_{\{R\}}$, and symbolize its action on the set of normal coordinates by $L_{\{R\}}Q$. Thus $L_{\{R\}}$ now denotes a collection of operators, and $L_{\{R\}}Q$ denotes a collection of normal coordinate transformations.

In particular, note that $L_{\{\Gamma(\mathcal{G})\}}$ denotes the h-tuple (5.6) in which each $R_i(\gamma)$ is replaced by the corresponding $\Gamma_i^\gamma(\mathcal{G})$ of Eq. (4.51b). But this collection of operators expresses the action of $L_{\mathcal{G}}$ itself on the normal coordinates. Hence, we may write

$$L_{\{\Gamma(\mathcal{G})\}}Q = L_{\mathcal{G}}Q , \tag{5.7}$$

where $L_{\mathcal{G}}Q$ denotes the collection of transformations $\{L_{\mathcal{G}}q_i^\gamma\}$. Thus, *the group of normal coordinate transformations induced by the group of operators* $\{L_{\mathcal{G}} : \mathcal{G}\in G(\mathfrak{A})\}$ *is a subgroup of the normal coordinate transformations*

$$\{L_{\{R\}} : L_{\{R\}} \in G(O)\} .$$

This is, as is well known, a very important result for the molecular problem. We will return to this point later.

B. Rotation-inversion and normal coordinate transformations combined

In this section $\mathcal{R}$ denotes a rotation-inversion of the entire physical space R^3 in the sense of Theorem 6.

The first observation is the following: *A rotation-inversion* $\mathcal{R}$ *leaves the normal coordinates invariant.* This result is intuitively evident, and it may also be proved mathematically. The mathematical proof follows from three facts:

(a) $\vec{\rho}^\alpha\cdot\hat{f}_i$ is invariant under $\mathcal{R}$, i.e., $\mathcal{R}\vec{\rho}^\alpha\cdot\mathcal{R}\hat{f}_i = \vec{\rho}^\alpha\cdot\hat{f}_i$;

(b) the center of mass conditions and the Eckart conditions are invariant under $\mathcal{R}$;

(c) the normal coordinates depend only on the components $\vec{\rho}^\alpha\cdot\hat{f}_i$ and the invariant constraints of (b).

The second observation is as follows: *The motions induced by* $L_{\{R\}}$ *leave the Eckart frame invariant.* This is the result demonstrated in the last section.

Combining these two observations, we conclude: The action of the operator $\mathcal{R}L_{\{R\}}$ on the coordinates $([\hat{f}_1\hat{f}_2\hat{f}_3];Q)$ is

$$\mathcal{R}L_{\{R\}} : ([\hat{f}_1\hat{f}_2\hat{f}_3];Q)\rightarrow(\mathcal{R}[\hat{f}_1\hat{f}_2\hat{f}_3];L_{\{R\}}Q) . \tag{5.8}$$

Note that we have the operator identity

$$\mathcal{R}L_{\{R\}} = L_{\{R\}}\mathcal{R} \tag{5.9}$$

over the sets of coordinates of type $([\hat{f}_1\hat{f}_2\hat{f}_3];Q)$.

It is important to realize that while Eq. (5.9) is a correct identity on sets of coordinates $([\hat{f}_1\hat{f}_2\hat{f}_3];Q)$, it need not be a correct identity (or even defined on other sets of objects).

Because we have the relation (5.9), we can also write $\mathcal{R}L_{\{R\}}$ as an ordered pair

$$(\mathcal{R}, L_{\{R\}}) \tag{5.10}$$

with the action of this operator pair defined by Eq. (5.8). The multiplication rule for two successive transformations then works out to be

$$(\mathcal{R}', L_{\{R'\}})(\mathcal{R}, L_{\{R\}}) = (\mathcal{R}'\mathcal{R}, L_{\{R'R\}}), \tag{5.11}$$

where we remind the reader that this is an identity on the set of all coordinates $\{([\hat{f}_1\hat{f}_2\hat{f}_3];Q)\}$. The symbol $L_{\{R'R\}}$ means the operator obtained by multiplying all the corresponding R' and R pairs in (5.6). Thus, we may regard the pairs of operators (5.10) as the elements of the direct product group

$$O_3 \times G(O). \tag{5.12}$$

We have introduced this direct product structure in anticipation of the more interesting result of the next section.

C. Permutations of coordinates

We wish to study the effect of permutations (3.55) on the coordinates $([\hat{f}_1\hat{f}_2\hat{f}_3];Q)$. We first consider only those permutations $\mathcal{P} \leftrightarrow \mathcal{G}$ given by Eq. (2.32).

The first observation is that $\mathcal{P}$ *induces a rotation-inversion* $\mathcal{G}$,

$$[\hat{f}_1\hat{f}_2\hat{f}_3] \to \mathcal{G}[\hat{f}_1\hat{f}_2\hat{f}_3], \tag{5.13}$$

of the Eckart frame (Theorem 8).

The second observation is that $\mathcal{P}$ *effects the transformation of normal coordinates given by*

$$\mathcal{P}\colon\ Q \to L_{\mathcal{G}^{-1}}Q\,. \tag{5.14}$$

This result requires proof. The action of $\mathcal{P}$ is expressed correctly on a *displacement vector* $\vec{\rho}^{\,\alpha}$ by

$$\mathcal{P}\vec{\rho}^{\,\alpha} = \mathcal{G}\mathfrak{L}_{\mathcal{G}^{-1}}\vec{\rho}^{\,\alpha}\,. \tag{5.15}$$

Using Eq. (5.13), we obtain

$$\begin{aligned}\mathcal{P}\colon\ \vec{\rho}^{\,\alpha}\cdot f_i &\to \mathcal{G}\mathfrak{L}_{\mathcal{G}^{-1}}\vec{\rho}^{\,\alpha}\cdot \mathcal{G}\hat{f}_i \\ &= (\mathfrak{L}_{\mathcal{G}^{-1}}\vec{\rho}^{\,\alpha})\cdot\hat{f}_i = L_{\mathcal{G}^{-1}}\rho_i^{\alpha}\,.\end{aligned} \tag{5.16}$$

Since this action takes place on all ρ_i^{α}, the result (5.14) follows then for the normal coordinates.

Combining Eqs. (5.13) and (5.14) gives the result

$$\mathcal{P}\colon\ ([\hat{f}_1\hat{f}_2\hat{f}_3];Q) \to (\mathcal{G}[\hat{f}_1\hat{f}_2\hat{f}_3];L_{\mathcal{G}^{-1}}Q) \tag{5.17}$$

for each $\mathcal{P} \leftrightarrow \mathcal{G}$.

Equation (5.17) has a close resemblance to Eq. (5.8) when the latter is particularized to $\mathcal{G}L_{\mathcal{G}}$:

$$\mathcal{G}L_{\mathcal{G}}\colon\ ([\hat{f}_1\hat{f}_2\hat{f}_3];Q) \to (\mathcal{G}[\hat{f}_1\hat{f}_2\hat{f}_3];L_{\mathcal{G}}Q). \tag{5.18}$$

There is, however, the curious difference of having $L_{\mathcal{G}^{-1}}$ in place of $L_{\mathcal{G}}$ in Eq. (5.17). In this second case, we have already demonstrated—a special case of Eq. (5.9)—that

$$\mathcal{G}L_{\mathcal{G}} = L_{\mathcal{G}}\mathcal{G}\,. \tag{5.19}$$

We were then able to interpret Eq. (5.18) as the action of a direct product pair $(\mathcal{G}, L_{\mathcal{G}})$.

Equation (5.17) would appear to lend itself to this same direct product interpretation, i.e., for $\mathcal{P} \leftrightarrow \mathcal{G}$, we may write

$$\mathcal{P} = (\mathcal{G}, L_{\mathcal{G}^{-1}})\,. \tag{5.20}$$

It is certainly true that Eq. (5.17) establishes this identity. It is also true that

$$\mathcal{G}L_{\mathcal{G}^{-1}} = L_{\mathcal{G}^{-1}}\mathcal{G} \tag{5.21}$$

on the coordinates $([\hat{f}_1\hat{f}_2\hat{f}_3];Q)$. However, if we follow the permutation $\mathcal{P}$ of Eq. (5.17) by a second permutation $\mathcal{P}' \leftrightarrow \mathcal{G}'$, we obtain

$$\mathcal{P}'\mathcal{P}\colon\ ([\hat{f}_1\hat{f}_2\hat{f}_3];Q) \to (\mathcal{G}'\mathcal{G}[\hat{f}_1\hat{f}_2\hat{f}_3];L_{(\mathcal{G}\mathcal{G}')^{-1}}Q)$$

which is *wrong,* since we know from Eq. (5.17) that $\mathcal{P}'' = \mathcal{P}'\mathcal{P}$ must have the action

$$\mathcal{P}''\colon\ ([\hat{f}_1\hat{f}_2\hat{f}_3];Q) \to (\mathcal{G}'\mathcal{G}[\hat{f}_1\hat{f}_2\hat{f}_3];L_{(\mathcal{G}'\mathcal{G})^{-1}}Q)\,. \tag{5.22}$$

The conclusion must be that *it is incorrect to interpret a permutation* $\mathcal{P} \leftrightarrow \mathcal{G}$ *as a rotation–inversion* $\mathcal{G}$ *of the Eckart frame and a transformation* $L_{\mathcal{G}^{-1}}$ *of the normal coordinates in a sense such that these operations act independently on the two parts of the coordinates.* The reason for this is intuitively clear: The permutations $\mathcal{P}, \mathcal{P}', \ldots$ know only how to change the label indices of the $\vec{\rho}^{\,\alpha}$. The action of the $\mathfrak{L}_{\mathcal{G}}$ is to change $\vec{\rho}^{\,\alpha}$ to $\vec{\eta}^{\,\alpha}$, and if a $\mathcal{P}'$ encounters *directly* an $\vec{\eta}^{\,\alpha}$, its action can be defined only by transforming back to a $\vec{\rho}^{\,\alpha}$.

The way out of the dilemma is the following: We must modify the *product rule* such that the relations

$$\mathcal{P} = (\mathcal{G}, L_{\mathcal{G}^{-1}})\,, \tag{5.23a}$$

$$\mathcal{P}' = (\mathcal{G}', L_{(\mathcal{G}')^{-1}}) \tag{5.23b}$$

imply

$$\mathcal{P}'\mathcal{P} = (\mathcal{G}'\mathcal{G}, L_{(\mathcal{G}'\mathcal{G})^{-1}})\,. \tag{5.23c}$$

This rule is easily found to be *the semidirect product rule for multiplying pairs* (Lomont, 1959; Biedenharn *et al.*, 1968):

$$\begin{aligned}&(\mathcal{G}', L_{\mathcal{G}'^{-1}})(\mathcal{G}, L_{\mathcal{G}^{-1}}) \\ &\quad = (\mathcal{G}'\mathcal{G}, (\mathcal{G}^{-1}L_{\mathcal{G}'^{-1}}\mathcal{G})L_{\mathcal{G}^{-1}}) \\ &\quad = (\mathcal{G}'\mathcal{G}, L_{(\mathcal{G}'\mathcal{G})^{-1}}).\end{aligned} \tag{5.24}$$

That this is the correct multiplication rule follows upon proving the operator identity

$$\mathfrak{L}_{(\mathcal{G}'\mathcal{G})^{-1}} = (\mathcal{G}^{-1}\mathfrak{L}_{\mathcal{G}'^{-1}}\mathcal{G})\mathfrak{L}_{\mathcal{G}^{-1}} \tag{5.25}$$

on the set of displacement vectors $\vec{\rho}^{\,1}, \vec{\rho}^{\,2}, \ldots, \vec{\rho}^{\,N}$. This proof goes as follows:

$$\begin{aligned}&\mathcal{G}^{-1}\mathfrak{L}_{\mathcal{G}'^{-1}}\mathcal{G}\mathfrak{L}_{\mathcal{G}^{-1}}[\vec{\rho}^{\,1}\vec{\rho}^{\,2}\cdots\vec{\rho}^{\,N}] \\ &\quad = \mathcal{G}^{-1}\mathfrak{L}_{\mathcal{G}'^{-1}}[\vec{\rho}^{\,1}\vec{\rho}^{\,2}\cdots\vec{\rho}^{\,N}]S(\mathcal{G}) \\ &\quad = \mathcal{G}^{-1}\mathcal{G}'^{-1}[\vec{\rho}^{\,1}\vec{\rho}^{\,2}\cdots\vec{\rho}^{\,N}]S(\mathcal{G}')S(\mathcal{G}) \\ &\quad = (\mathcal{G}'\mathcal{G})^{-1}[\vec{\rho}^{\,1}\vec{\rho}^{\,2}\cdots\vec{\rho}^{\,N}]\tilde{S}((\mathcal{G}'\mathcal{G})^{-1}) \\ &\quad = \mathfrak{L}_{(\mathcal{G}'\mathcal{G})^{-1}}[\vec{\rho}^{\,1}\vec{\rho}^{\,2}\cdots\vec{\rho}^{\,N}]\,.\end{aligned} \qquad \text{Q.E.D.}$$

Summary. The group of permutations $\{\mathcal{P}\}$ which is isomorphic to the group of rotation–inversion operators $\{\mathcal{G}\colon\ \mathcal{G} \in G(\mathfrak{A})\}$ has the following action on the coordinates $([\hat{f}_1\hat{f}_2\hat{f}_3];Q)$: For $\mathcal{P} \leftrightarrow \mathcal{G}$, we have

$$\mathcal{P} = (\mathcal{G}, L_{\mathcal{G}^{-1}})\,, \tag{5.26a}$$

where

$$(\mathcal{G}, L_{\mathcal{G}^{-1}})\colon\ ([\hat{f}_1\hat{f}_2\hat{f}_3];Q) \to (\mathcal{G}[\hat{f}_1\hat{f}_2\hat{f}_3];L_{\mathcal{G}^{-1}}Q). \tag{5.26b}$$

The rule for multiplying two such permutations (5.26a)

is the semidirect product rule (5.24), the whole effect of this rule being to put in the product $\mathcal{G}'\mathcal{G}$ appearing in $L_{(\mathcal{G}'\mathcal{G})^{-1}}$ opposite to what occurs in the usual direct product multiplication rule.

Hougen (1975) implements the action of a permutation correctly according to Eq. (5.26b), although it appears that he bases his result on the intuitive notion that the two parts of $\mathcal{P}=\mathcal{G}\mathcal{L}_{\mathcal{G}^{-1}}$ [cf. Eq. (3.63)] act independently on $[\hat{f}_1\hat{f}_2\hat{f}_3]$ and Q. Our result shows that this is only correct when the pair (5.26a) multiplies by the semidirect product rule.

We would insist that one learns nothing intrinsically new by writing a permutation in the form (5.26a). This way of writing a permutation (rather, certain permutations) does facilitate the study of the action of these permutations on the coordinates $([\hat{f}_1\hat{f}_2\hat{f}_3];Q)$.

There are, of course, many other permutation operators in the group $\prod_\lambda G(S_{n_\lambda})$ which cannot be written in the form (5.26a). Eventually, one must account for the effect of all the permutation operators which relabel the position vectors of identical particles (Wilson, 1935).

We present now a definition which has a significant bearing on the identical particles problem. The Eckart frame concept is fundamental to the definition, which is our reason for introducing it here. Definition: *An operator is said to be a feasible operator for a molecule if it is an element of the permutation–inversion group whose action on the Eckart frame in the coordinates* $([\hat{f}_1\hat{f}_2\hat{f}_3];Q)$ *is a pure rotation.*

The inversion operator occurring in this definition is the inversion of the whole space R^3, i.e., $\mathcal{G}\vec{x}=-\vec{x}$, each $\vec{x}\in R^3$.

The group of feasible operators is easily enumerated. This is so because it is only those $\mathcal{P}=\mathcal{G}$ of Eq. (2.32) which effect rotation–inversions of the Eckart frame. Thus, the permutation–inversions which effect a pure rotation of the Eckart frame are those $\mathcal{P}$ and $\mathcal{G}\mathcal{P}'$ belonging to the following sets:

$$\begin{aligned}\mathcal{P}&\in\{(\mathcal{G},L_{\mathcal{G}^{-1}}):\mathcal{G}\in G(\mathfrak{A}) \text{ and } \det G=1\},\\ \mathcal{G}\mathcal{P}'&\in\{(\mathcal{G}\mathcal{G},L_{\mathcal{G}^{-1}}):\mathcal{G}\in G(\mathfrak{A}) \text{ and } \det G=-1\}.\end{aligned}\tag{5.27}$$

One easily verifies, using the product rule (5.24), that these operators form a group.

If $G(\mathfrak{A})=T_d$, the group of feasible operators is isomorphic to T_d, and is the group introduced by Hougen (Hougen, 1971, 1975) for methane.

If $G(\mathfrak{A})=O_h$, the group of feasible operators is isomorphic to O_h. Quite generally the group of feasible operators is isomorphic to $G(\mathfrak{A})$.

Remarks. It has been principally Longuet-Higgens and Hougen who have promoted the concept of "feasible operators." It is here, we feel, that they have made an important contribution. Clearly, the notion of feasible operators has definitive implications for accommodating the Pauli principle and, hence, for the calculation of statistical weights (as already shown by these authors). Neither of these authors seems, however, to have introduced a formal definition for this concept.

D. Transformations of the laboratory and Eckart frames

Up to this point, we have not introduced a laboratory frame. However, a basic concept in the molecular problem is the intuitive notion that to zero-order approximation the energy of the molecule can be written as the sum of its rotational kinetic energy and its internal vibrational energy, the latter being that calculated by an observer in the Eckart frame. (We ignore the translational energy of the center of mass). It is this concept which motivates developing the equations of motion, that is, the writing out of the Hamiltonian, in terms of physical quantities which are expressed relative to the Eckart frame. Since the Eckart frame is noninertial, we must now account for such kinematical terms in the Hamiltonian as the Coriolis interaction. The only simple means we have of accomplishing this is to introduce a laboratory frame (the assumed inertial frame). This provides the vehicle for describing the motion of the Eckart frame, hence, the origin of kinematical interactions as seen by an observer in the Eckart frame.

This section is quite difficult, despite the seemingly uncomplicated title. Let us try to understand why this is true. It stems from rather intricate points of detail which must be kept straight at each level of the development. The reason so many details creep into the analysis is that we are dealing with a situation in which two spaces play a role. However, the spaces are not independent of one another—for example, if we rotate one, we must rotate the other. Rather delicate questions of group isomorphisms versus group anti-isomorphisms arise which require careful treatment. The action of operators on spaces must be carefully defined if one is to understand the group structures which arise.

It may be helpful to outline the contents of this section. We first introduce the two spaces involved, developing notational conventions for each. Essential features of each space are developed independently. Then the geometrical relation between the spaces is introduced and its significance analyzed. The rest of the section is devoted to the construction of the abstract group structures which preserve the geometrical relation between the spaces.

We introduce the notation $\hat{l}_1,\hat{l}_2,\hat{l}_3$ for a triad of right-handed unit vectors whose orientation is fixed with respect to the laboratory. We call this triad the laboratory frame.

We now have two frames $[\hat{f}_1\hat{f}_2\hat{f}_3]$ and $[\hat{l}_1\hat{l}_2\hat{l}_3]$ to keep track of. The situation is, in fact, a bit more intricate than this. *We have two spaces to keep track of.* We first discuss these two spaces separately, ignoring any connection between them.

We have, first, the space R^3 with basis $[\hat{l}_1\hat{l}_2\hat{l}_3]$ in which $\hat{f}_1,\hat{f}_2,\hat{f}_3$ appear as vectors. In R^3, the frame $[\hat{f}_1\hat{f}_2\hat{f}_3]$ is attached to the molecule, and all internal motions are referred to it in the manner previously described. In order to keep straight what vectors are basis vectors of R^3 and what quantities are vectors in R^3, we introduce the notation

$$([\hat{l}],(\hat{f})),\tag{5.28a}$$

where the square bracket $[\hat{l}]=[\hat{l}_1\hat{l}_2\hat{l}_3]$ symbolizes the basis vectors and $(\hat{f})=(\hat{f}_1,\hat{f}_2,\hat{f}_3)$ symbolizes the Eckart triad of vectors in R^3. For the purpose of this discussion, we also regard all vectors referring to the molecule to be expressed in the form

$$\vec{x} = \sum_i x_i \hat{f}_i \tag{5.28b}$$

so that what happens to such a vector under $\mathcal{R}$ is inferred from $\vec{x} \to \mathcal{R}\vec{x} = \sum_i x_i (\mathcal{R}\hat{f}_i)$. Hence, we may omit all such $\vec{x}$ and other "internal" coordinates from the set (5.28a).

The vectors $\hat{f}_j$ may, of course, be expressed in terms of the basis vectors of R^3:

$$\hat{f}_j = \sum_i ([\hat{l}_i] \cdot \hat{f}_j)[\hat{l}_i], \tag{5.29}$$

where we place a square bracket around a single vector to emphasize its role as basis vector. Equations (5.28b) and (5.29) may be combined if one wishes to express a vector $\vec{x} \in R^3$ in terms of the basis of R^3. However, for the reason given following Eq. (5.28b), it is convenient to adopt the convention of writing vectors $\vec{x} \in R^3$ in the form (5.28b) unless otherwise noted.

The basis vectors $[\hat{l}]$ of R^3 are to be regarded as attached to the laboratory, and objects in the laboratory undergo no transformations under a rotation–inversion $\mathcal{R}$: $R^3 \to R^3$. Thus, using the symbolism of Eq. (5.28), we may express the action of $\mathcal{R}$ on the space R^3 by

$$\mathcal{R}: \ ([\hat{l}], (\hat{f})) \to ([\hat{l}], (\mathcal{R}\hat{f})). \tag{5.30}$$

This same action may be expressed in matrix form by defining a matrix C with elements

$$C_{ij} = [\hat{l}_i] \cdot \hat{f}_j . \tag{5.31}$$

The transformation (5.30) then becomes

$$\mathcal{R}: \ C \to RC, \tag{5.32a}$$

where R is the matrix representing $\mathcal{R}$ on the basis $[\hat{l}]$, i.e.,

$$R_{ij} = [\hat{l}_i] \cdot \mathcal{R}[\hat{l}_j] . \tag{5.32b}$$

Observe also that the columns of C are the matrices representing the vectors $\hat{f}_1, \hat{f}_2, \hat{f}_3$ on the basis $[\hat{l}]$, i.e.,

$$C = [f_1 f_2 f_3], \tag{5.33a}$$

where

$$f_j = \mathrm{col}([\hat{l}_1] \cdot \hat{f}_j, [\hat{l}_2] \cdot \hat{f}_j, [\hat{l}_3] \cdot \hat{f}_j) . \tag{5.33b}$$

The product of two rotation–inversions of R^3, $\mathcal{R}$ followed by $\mathcal{R}'$, is given by the usual rule:

$$\mathcal{R}'\mathcal{R}: \ ([\hat{l}], (\hat{f})) \to ([\hat{l}], (\mathcal{R}'(\mathcal{R}\hat{f}))) . \tag{5.34a}$$

Correspondingly, the matrix transformation (5.32a) is

$$\mathcal{R}'\mathcal{R}: \ C \to R'(RC) = (R'R)C. \tag{5.34b}$$

Thus, we have an isomorphism

$$\mathcal{R} \leftrightarrow R \tag{5.34c}$$

between the group of rotation–inversions of R^3 and the group of orthogonal matrices $\{R\}$, where the latter is realized as transformations of the matrix C.

In the molecular problem, we must also keep track of the world external to the molecule as seen by an observer in the Eckart frame. For this observer, using basis $[\hat{f}] = [\hat{f}_1 \hat{f}_2 \hat{f}_3]$, the vectors $(\hat{l}) = (\hat{l}_1, \hat{l}_2, \hat{l}_3)$ appear simply as vectors in the external world—the space we will call S^3. Thus, the vectors $[\hat{f}]$ are a basis of S^3. The vectors $(\hat{l})$ appear as a sort of "Eckart frame" for describing the positions $\vec{X}$ of objects external to the molecule:

$$\vec{X} = \sum_i X_i \hat{l}_i . \tag{5.35}$$

We may then describe S^3 by the set of vectors

$$([\hat{f}], (\hat{l})), \tag{5.36}$$

where $[\hat{f}]$ is the basis, and $(\hat{l})$ is a triad of vectors for describing everything (of relevance) in the external world. What happens to vectors in the external world under a rotation–inversion $\mathcal{S}$ of S^3 is to be inferred from $\vec{X} \to \mathcal{S}\vec{X} = \sum_i X_i (\mathcal{S}\hat{l}_i)$, so that again we may omit external vectors from the set (5.36).

As in the case of Eq. (5.29), we may also express the vectors $\hat{l}_i$ in terms of the basis $[\hat{f}]$ of the space S^3:

$$\hat{l}_i = \sum_i ([\hat{f}_j] \bullet \hat{l}_i)[\hat{f}_j] . \tag{5.37}$$

We have introduced a large dot to designate the dot product of vectors in S^3. While this distinction of dot products in R^3 and S^3 is formal, it serves to emphasize that we are dealing with two spaces. The dot product of two vectors $\vec{x}$, $\vec{y} \in R^3$ may then be calculated from Eq. (5.28b),

$$\vec{x} \circ \vec{y} = \sum_i x_i y_i , \tag{5.38a}$$

while the dot product for two vectors $\vec{X}$, $\vec{Y} \in S^3$ is obtained from Eq. (5.35):

$$\vec{X} \bullet \vec{Y} = \sum_i X_i Y_i . \tag{5.38b}$$

The basis vectors $[\hat{f}]$ of S^3 are attached to the molecule, and they undergo no transformation under a rotation-inversion $\mathcal{S}$: $S^3 \to S^3$. Thus, using the symbolism of Eqs. (5.35) and (5.36), we may express the action of $\mathcal{S}$ on the space S^3 by

$$\mathcal{S}: ([\hat{f}], (\hat{l})) \to ([\hat{f}], (\mathcal{S}\hat{l})) . \tag{5.39}$$

This same action may be expressed in matrix form by defining a matrix C' with elements

$$C'_{ij} = [\hat{f}_i] \bullet \hat{l}_j , \tag{5.40}$$

The transformation (5.39) then becomes

$$\mathcal{S}: C' \to SC', \tag{5.41}$$

where S is the matrix representing $\mathcal{S}$ on the basis $[\hat{f}]$, i.e.,

$$S_{ij} = [\hat{f}_i] \bullet \mathcal{S}[\hat{f}_j] . \tag{5.42}$$

Observe also that the columns of C' are the matrices representing $\hat{l}_1, \hat{l}_2, \hat{l}_3$ on the basis $[\hat{f}]$, i.e.,

$$C' = [l_1 l_2 l_3], \tag{5.43a}$$

where

$$l_i = \mathrm{col}([\hat{f}_1] \bullet \hat{l}_i, [\hat{f}_2] \bullet \hat{l}_i, [\hat{f}_3] \bullet \hat{l}_i) . \tag{5.43b}$$

The product of two rotation–inversions of S^3, $\mathcal{S}$ followed by $\mathcal{S}'$, is given by the standard rule:

$$\mathcal{S}'\mathcal{S}: ([\hat{f}], (\hat{l})) \to ([\hat{f}], (\mathcal{S}'(\mathcal{S}\hat{l}))) . \tag{5.44a}$$

Correspondingly, the matrix transformation (5.41) is

$$\mathcal{S}'\mathcal{S}: C' \to S'(SC') = (S'S)C' . \tag{5.44b}$$

Thus, we have an isomorphism

$$\mathcal{S} \longrightarrow S \tag{5.44c}$$

between the group of rotation–inversions of S^3 and the group of orthogonal matrices $\{S\}$, where the latter is realized as transformations of the matrix C'.

The preceding analysis treats the spaces R^3 and S^3 as distinct entities. Let us now note, however, that the spaces R^3 and S^3 are related to one another by a very particular rule, namely,

$$[\hat{l}_i]\cdot\hat{f}_j = [\hat{f}_j]\bullet\hat{l}_i \tag{5.45a}$$

for all $i,j=1,2,3$. Let us explain this relation further. $[\hat{l}_1],[\hat{l}_2],[\hat{l}_3]$ are any arbitrary orthonormal basis vectors of R^3; $[\hat{f}_1],[\hat{f}_2],[\hat{f}_3]$ are any arbitrary orthonormal basis vectors of S^3 (draw two pictures, one depicting R^3 with its basis $[\hat{l}_1],[\hat{l}_2],[\hat{l}_3]$, the other depicting S^3 with its basis $[\hat{f}_1],[\hat{f}_2],[\hat{f}_3]$). We may think of $\hat{f}_1,\hat{f}_2,\hat{f}_3$ as an arbitrary, but given, triad of orthogonal vectors in the space R^3; then the vectors $\hat{l}_1,\hat{l}_2,\hat{l}_3$ are definite vectors of S^3 given by

$$\hat{l}_i = \sum_j ([\hat{l}_i]\cdot\hat{f}_j)[\hat{f}_j] . \tag{5.45b}$$

Conversely, we may think of $\hat{l}_1,\hat{l}_2,\hat{l}_3$ as an arbitrary, but given, triad of vectors in the space S^3; then the vectors $\hat{f}_1,\hat{f}_2,\hat{f}_3$ are definite vectors of R^3 given by

$$\hat{f}_i = \sum_j ([\hat{f}_i]\bullet\hat{l}_j)[\hat{l}_j] . \tag{5.45c}$$

Thus, Eq. (5.45a) establishes a one-to-one correspondence between triads of vectors $\hat{f}_1,\hat{f}_2,\hat{f}_3\in R^3$ and triads of vectors $\hat{l}_1,\hat{l}_2,\hat{l}_3\in S^3$.

One method of enumerating the set $\{\hat{f}_1,\hat{f}_2,\hat{f}_3\}$ of all triads of unit perpendicular vectors of R^3 is to pick a *particular triad* $\hat{f}_1^\circ\hat{f}_2^\circ\hat{f}_3^\circ$ and consider the set

$$\{\mathcal{R}\hat{f}_1^\circ,\mathcal{R}\hat{f}_2^\circ,\mathcal{R}\hat{f}_3^\circ : \mathcal{R}\in\mathcal{O}_3^l\} , \tag{5.46}$$

where $\mathcal{O}_3^l$ denotes the group of rotation–inversions of R^3. The set (5.46) then contains all triads $\hat{f}_1,\hat{f}_2,\hat{f}_3$. Similarly, we may enumerate the set $\{\hat{l}_1,\hat{l}_2,\hat{l}_3\}$ of all triads of unit perpendicular vectors of S^3 by

$$\{\mathcal{S}\hat{l}_1^\circ,\mathcal{S}\hat{l}_2^\circ,\mathcal{S}\hat{l}_3^\circ : \mathcal{S}\in\mathcal{O}_3^f\} , \tag{5.47}$$

where $\mathcal{O}_3^f$ denotes the group of rotation–inversions of S^3, and $\hat{l}_1^\circ,\hat{l}_2^\circ,\hat{l}_3^\circ$ is a *particular triad* of S^3.

The geometrical relation (5.45a) between the spaces R^3 and S^3 may now be expressed more vividly as

$$[\hat{l}_i]\cdot\mathcal{R}\hat{f}_j^\circ = [\hat{f}_j]\bullet\mathcal{S}\hat{l}_i^\circ , \tag{5.48}$$

for each $i,j=1,2,3$ and each $\mathcal{R}\in\mathcal{O}_3^l$ (or each $\mathcal{S}\in\mathcal{O}_3^f$). In this relation, it is sufficient to consider that either $\mathcal{R}$ or $\mathcal{S}$ runs over the elements of its respective group. This is true because if we consider $\mathcal{R}$ as given, then $\mathcal{S}$ is uniquely determined—we will call it $\mathcal{S}_\mathcal{R}$. Conversely, if we consider $\mathcal{S}$ as given, then $\mathcal{R}$ is uniquely determined—we will call it $\mathcal{R}_\mathcal{S}$.

Equation (5.48) then expresses the set of all allowed relations between the spaces R^3 and S^3. From what has been said above, it is also clear that it establishes a one-to-one correspondence

$$\mathcal{R} \longrightarrow \mathcal{S} \tag{5.49}$$

between the elements of $\mathcal{O}_3^l$ and the elements of $\mathcal{O}_3^f$. We prove below that this correspondence is an anti-isomorphism of groups.

The geometrical content of Eq. (5.48) is clear: An operation that appears as a "forward rotation" of the Eckart vectors $(\hat{f}^\circ)$ in the space R^3 appears as a "backward rotation" of $(\hat{l}^\circ)$ in the space S^3.

We will now drop the cumbersome superscripts in Eq. (5.48) and write it simply as

$$[\hat{l}_i]\cdot\mathcal{R}\hat{f}_j = [\hat{f}_j]\bullet\mathcal{S}\hat{l}_i , \tag{5.50}$$

for each $i,j=1,2,3$ and each $\mathcal{R}\in\mathcal{O}_3^l$ (or each $\mathcal{S}\in\mathcal{O}_3^f$). We now regard, however, $\hat{f}_1,\hat{f}_2,\hat{f}_3$ and the corresponding $\hat{l}_1,\hat{l}_2,\hat{l}_3$ as given, but arbitrary. *The important point to remember is that each distinct choice of* $\hat{f}_1,\hat{f}_2,\hat{f}_3$ *(or* $\hat{l}_1,\hat{l}_2,\hat{l}_3$*) determines a different correspondence* $\mathcal{R}\to\mathcal{S}$.

Let us now discuss further the properties of the correspondence (5.49). It is essential in deducing the specific mapping that the vectors $\hat{f}_j$ and $\hat{l}_i$ be kept *fixed* [$\hat{f}_j^\circ$ and l_i° in Eq. (5.48)]. Let us illustrate this point with an example. In R^3, we take $\hat{f}_j=[\hat{l}_j]$, $j=1,2,3$ so that $\hat{l}_i=[\hat{f}_i]$, $i=1,2,3$, in S^3. A rotation $\mathcal{R}$ of $\pi/2$ about $[\hat{l}_3]$ then corresponds to a rotation of $\pi/2$ about $-[\hat{f}_3]$ in S^3. On the other hand, if we choose $\hat{f}_1=[\hat{l}_2],\hat{f}_2=[\hat{l}_3],\hat{f}_3=[\hat{l}_1]$ in R^3, and, hence, $\hat{l}_1=[\hat{f}_3],\hat{l}_2=[\hat{f}_1],\hat{l}_3=[\hat{f}_2]$ in S_3, the rotation $\mathcal{R}$ of $\pi/2$ about $[\hat{l}_3]$ is described in S^3 as a rotation of $\pi/2$ about $-[\hat{f}_2]$. Thus, in order that the map-mapping $\mathcal{R}\to\mathcal{S}$ be unambiguous, *one must make all such correspondences relative to a fixed set of* $\hat{f}_1,\hat{f}_2,\hat{f}_3$ (or $\hat{l}_1,\hat{l}_2,\hat{l}_3$).

We may illustrate, by example, that the correspondence (5.49) is an anti-isomorphism. Choose again $\hat{f}_j=[\hat{l}_j]$ in R^3 ($\hat{l}_i=[\hat{f}_i]$ in S^3). If we follow $\mathcal{R}=\pi/2$ about $[\hat{l}_3]$ by $\mathcal{R}'=\pi/2$ about $[\hat{l}_1]$, the result is $\mathcal{R}'\mathcal{R}=2\pi/3$ about $([\hat{l}_1]-[\hat{l}_2]+[\hat{l}_3])/\sqrt{3}$. In the correspondence, we have $\mathcal{R}\to\mathcal{S}=\pi/2$ about $-[\hat{f}_3]$, $\mathcal{R}'\to\mathcal{S}'=\pi/2$ about $-[\hat{f}_1]$, and $\mathcal{R}'\mathcal{R}$ corresponds to $2\pi/3$ about $-([\hat{f}_1]-[\hat{f}_2]+[\hat{f}_3])/\sqrt{3}$, which is the product $\mathcal{S}\mathcal{S}'$, not $\mathcal{S}'\mathcal{S}$. The general proof that we have an anti-isomorphism is given below.

It is also useful to express Eq. (5.50) in matrix form: The left-hand side becomes

$$[\hat{l}_i]\cdot\mathcal{R}\hat{f}_j = (RC)_{ij} , \tag{5.51a}$$

where R is the matrix representing $\mathcal{R}$ on the basis $[\hat{l}]$, and C is the matrix representing $[\hat{f}_1\hat{f}_2\hat{f}_3]$ on the basis $[\hat{l}]$, i.e.,

$$C_{ij} = [\hat{l}_i]\cdot\hat{f}_j . \tag{5.51b}$$

The right-hand side of Eq. (5.50) becomes

$$[\hat{f}_j]\bullet\mathcal{S}\hat{l}_i = (S\tilde{C})_{ji} = (C\tilde{S})_{ij} , \tag{5.51c}$$

where S is the matrix representing $\mathcal{S}$ on the basis $[\hat{f}]$. Thus, Eq. (5.50) expresses the identity

$$RC = C\tilde{S} . \tag{5.52}$$

We can now prove that the correspondence established by Eq. (5.50) is an anti-isomorphism. Let us suppose that $\mathcal{R}$ and $\mathcal{R}'$ are given so that we are solving Eq. (5.50) for $\mathcal{S}$. We must prove that the two equations

$$[\hat{f}_j]\bullet\mathcal{S}_\mathcal{R}\hat{l}_i = [\hat{l}_i]\cdot\mathcal{R}\hat{f}_j , \tag{5.53a}$$

$$[\hat{f}_j]\bullet \mathcal{S}_{\mathcal{R}'}\hat{l}_i=[\hat{l}_i]\cdot\mathcal{R}'\hat{f}_j \tag{5.53b}$$

imply

$$[\hat{f}_j]\bullet \mathcal{S}_{\mathcal{R}}\mathcal{S}_{\mathcal{R}'}\hat{l}_i=[\hat{l}_i]\cdot\mathcal{R}'\mathcal{R}\hat{f}_j\,. \tag{5.53c}$$

To show this, we proceed in the following manner, starting from Eq. (5.53b):

$$\begin{aligned}\mathcal{S}_{\mathcal{R}}(\mathcal{S}_{\mathcal{R}'}\hat{l}_i)&=\sum_j([\hat{l}_i]\cdot\mathcal{R}\hat{f}_j)\mathcal{S}_{\mathcal{R}}[\hat{f}_j]\\&=\sum_{j,k}(R'C)_{ij}(\tilde{S}_R)_{ik}[\hat{f}_k]\\&=\sum_k(R'C\tilde{S}_R)_{ik}[\hat{f}_k]=\sum_j(R'RC)_{ij}[\hat{f}_j]\\&=\sum_j([l_i]\circ\mathcal{R}'\mathcal{R}\hat{f}_j)[\hat{f}_j],\end{aligned}$$

where $C\tilde{S}_R=CR$ is a consequence of Eq. (5.52). Since we also have

$$[\hat{f}_j]\bullet \mathcal{S}_{\mathcal{R}'\mathcal{R}}\hat{l}_i=[\hat{l}_i]\circ\mathcal{R}'\mathcal{R}\hat{f}_j\,,$$

if follows from Eq. (5.53c) that

$$\mathcal{S}_{\mathcal{R}}\mathcal{S}_{\mathcal{R}'}=\mathcal{S}_{\mathcal{R}'\mathcal{R}}\,. \tag{5.54}$$

Thus, we have proved that

$$\mathcal{R}\to\mathcal{S}_{\mathcal{R}}\ \text{and}\ \mathcal{R}'\to\mathcal{S}_{\mathcal{R}'} \tag{5.55a}$$

imply

$$\mathcal{R}\mathcal{R}'\to\mathcal{S}_{\mathcal{R}'\mathcal{R}}\,. \tag{5.55b}$$

Since the correspondence set up by Eq. (5.50) is one-to-one onto, this rule of associating rotation–inversions of R^3 with rotation–inversions of S^3 is an anti-isomorphism.

It is an intrinsic property of the geometrical relation of Eq. (5.50) that the correspondence is an anti-isomorphism: If we insist that the rotation–inversions $\{\mathcal{R}\}$ of R^3 and rotation–inversions $\{\mathcal{S}\}$ of S^3 multiply by the usual rules, then we have no choice—the correspondence set up by (5.50) multiplies backwards.

Let us now give the explicit relation between the correspondences resulting from different choices of the vectors $\hat{f}_1,\hat{f}_2,\hat{f}_3$. Let

$$\mathcal{R}\to\mathcal{S}_{\mathcal{R}} \tag{5.56a}$$

be the anti-isomorphism which is established by

$$[\hat{l}_i]\circ\mathcal{R}\hat{f}_j=[\hat{f}_j]\bullet\mathcal{S}_{\mathcal{R}}\hat{l}_i\,. \tag{5.56b}$$

We wish to determine the anti-isomorphism which is established by the vectors $\hat{f}'_1,\hat{f}'_2,\hat{f}'_3$, i.e.,

$$[\hat{l}_i]\cdot\mathcal{R}\hat{f}'_j=[\hat{f}_j]\bullet\mathcal{S}'_{\mathcal{R}}\hat{l}'_i \tag{5.57a}$$

Let the vectors $\hat{f}'_j$ be related to the $\hat{f}_j$ by $\mathcal{R}_0$, i.e., $\hat{f}'_j=\mathcal{R}_0\hat{f}_j$. Then the $\hat{l}'_i$ are related to the $\hat{l}_i$ appearing in Eq. (5.56b) by $\hat{l}'_i=\mathcal{S}_{\mathcal{R}_0}\hat{l}_i$, where $\mathcal{R}_0\to\mathcal{S}_{\mathcal{R}_0}$ is the correspondence (5.56a) determined by Eq. (5.56b). Using these results and Eqs. (5.56b) and (5.57a), it is straightforward to prove that the anti-isomorphism established by Eq. (5.57a) is

$$\mathcal{R}\to\mathcal{S}'_{\mathcal{R}}=\mathcal{S}_{\mathcal{R}_0}^{-1}\mathcal{S}_{\mathcal{R}\mathcal{R}_0}\,. \tag{5.57b}$$

A more explicit relation may be given for the $\mathcal{S}_{\mathcal{R}}$ in the correspondence $\mathcal{R}\to\mathcal{S}_{\mathcal{R}}$ in terms of the parameters $\hat{n}$, θ. Let $\hat{f}_1,\hat{f}_2,\hat{f}_3$ be specified. Let

$$\mathcal{R}=\text{rotation of }\theta\text{ about }\hat{n}\,. \tag{5.58a}$$

Then

$$\mathcal{S}_{\mathcal{R}}=\text{rotation of }\theta\text{ about }-\hat{N}\,, \tag{5.58b}$$

where

$$\hat{N}=\sum_{i,j}([\hat{l}_i]\cdot\hat{f}_j)(\hat{n}\cdot[\hat{l}_i])[\hat{f}_j]\,. \tag{5.58c}$$

Note, in particular, that $\hat{f}_1,\hat{f}_2,\hat{f}_3$ enter explicitly into the determination of $\hat{N}$, and hence, of $\mathcal{S}_{\mathcal{R}}$.

At the opening of this section, we pointed out that the introduction of a laboratory frame is necessary for understanding the origin of kinematical interactions in a Hamiltonian expressed in coordinates relative to the Eckart frame. It is clear that the group of operators $\{\mathcal{S}\}$ must have a significant role in this problem. However, the groups $\{\mathcal{S}\}$ and $\{\mathcal{R}\}$ are not entirely independent because they are intrinsically related in our problem through Eq. (5.50). This does not imply that we need to consider only one of the groups, i.e., one of the spaces R^3 or S^3. It means we must keep track of both and consider simultaneously the effect of the rotation–inversions $\mathcal{R}$ of R^3 and the rotation–inversions $\mathcal{S}$ of S^3. This we now do, after introducing some notation.

We introduce the Cartesian product space $R^3\times S^3$ which is the set of ordered pairs of vectors

$$\{(\vec{\mathbf{x}},\vec{\mathbf{X}}):\vec{\mathbf{x}}\in R^3,\ \vec{\mathbf{X}}\in S^3\}\,. \tag{5.59}$$

Through the formalism introduced by Eqs. (5.28) and (5.36), we replace the set (5.59) by

$$\left\{\begin{array}{l}([\hat{l}],(\hat{f})):(\hat{f})\text{ is a triad of perpendicular unit vectors in }R^3\\[2ex]([\hat{f}],(\hat{l})):(\hat{l})\text{ is a triad of perpendicular unit vectors in }S^3\end{array}\right\}\,. \tag{5.60a}$$

We are interested only in a subspace of $R^3\times S^3$, namely, the subspace such that

$$[\hat{l}_i]\cdot\hat{f}_j=[\hat{f}_j]\bullet\hat{l}_i\,, \tag{5.60b}$$

for $i,j=1,2,3$, where $\hat{f}_1,\hat{f}_2,\hat{f}_3$ (or $\hat{l}_1,\hat{l}_2,\hat{l}_3$) run now over all triads. We denote this subspace of $R^3\times S^3$ by the notation

$$R^3*S^3\,. \tag{5.60c}$$

Remark. The basis vectors $[\hat{l}]$ and $[\hat{f}]$ appearing in the definition of R^3*S^3 may be arbitrarily selected, and we do not distinguish between spaces corresponding to different choices of bases.

We next consider mappings of R^3*S^3 onto itself. With each $\mathcal{R}\in\mathcal{O}_3^l$ (the group of rotation–inversions of R^3), we associate the following transformation of the space R^3*S^3:

$$\mathcal{R}:R^3*S^3\to R^3*S^3\,, \tag{5.61}$$

where the action of $\mathcal{R}$ on an *arbitrary* element of R^3*S^3 is defined by

$$\begin{aligned}\mathcal{R}:\ &([\hat{l}],(\hat{f}))\to([\hat{l}],(\mathcal{R}\hat{f}))\\&([\hat{f}],(\hat{l}))\to([\hat{f}],(\mathcal{S}'_{\mathcal{R}}\hat{l}))\,,\end{aligned} \tag{5.61a}$$

where

$$\mathcal{R} \to \mathcal{S}^f_{\mathcal{R}} \tag{5.61b}$$

is the anti-isomorphism determined by

$$[l_i]\cdot\mathcal{R}\hat{f}_j = [\hat{f}_j]\bullet \mathcal{S}^f_{\mathcal{R}}\hat{l}_i\,. \tag{5.61c}$$

It is now of utmost importance to make explicit the fact that the anti-isomorphism (5.61c) depends on the initial set of vectors $(\hat{f})$, and this is the reason for attaching f to the symbol $\mathcal{S}_{\mathcal{R}}$.

Observe that by its very definition $\mathcal{R}$ maps $R^3 * S^3$ onto itself. Hence, $\mathcal{R}$ preserves the geometrical relation between the spaces R^3 and S^3.

Suppose we now follow the transformation $\mathcal{R}$ by a second transformation $\mathcal{R}'$. We have

$$\mathcal{R}': \begin{matrix} ([\hat{l}],(\hat{f}')) \to ([\hat{l}],(\mathcal{R}'\hat{f}')) \\ ([\hat{f}],(\hat{l}')) \to ([\hat{f}],(\mathcal{S}^{f'}_{\mathcal{R}'}\hat{l}')), \end{matrix} \tag{5.62a}$$

where $\hat{f}'_j = \mathcal{R}\hat{f}_j$ and $\hat{l}'_i = \mathcal{S}^f_{\mathcal{R}}\hat{l}_i$. But, from Eq. (5.57b), we have

$$\mathcal{S}^{f'}_{\mathcal{R}'} = \mathcal{S}^f_{\mathcal{R}^{-1}\mathcal{R}'\mathcal{R}}\,. \tag{5.62b}$$

Thus, the transformation $\mathcal{R}$ followed by $\mathcal{R}'$ is given by

$$\mathcal{R}'\,\mathcal{R}: \begin{matrix} ([\hat{l}],(\hat{f})) \to ([\hat{l}],(\mathcal{R}'\,\mathcal{R}\hat{f})) \\ ([\hat{f}],(\hat{l})) \to ([\hat{f}],(\mathcal{S}^f_{\mathcal{R}'\,\mathcal{R}}\hat{l})), \end{matrix} \tag{5.63a}$$

since

$$\mathcal{S}^{f'}_{\mathcal{R}'}\,\mathcal{S}^f_{\mathcal{R}} = \mathcal{S}^f_{\mathcal{R}^{-1}\mathcal{R}'\mathcal{R}}\mathcal{S}^f_{\mathcal{R}} = \mathcal{S}^f_{\mathcal{R}'\mathcal{R}}\,. \tag{5.63b}$$

Thus, the transformation $\mathcal{R}$ *followed* by $\mathcal{R}'$ is the same as the transformation $\mathcal{R}'' = \mathcal{R}'\mathcal{R}$.

It is tempting to associate a pair of operators with the transformation (5.61a) such as $(\mathcal{R}, \mathcal{S}^f_{\mathcal{R}})$. However, since it must be possible to choose the initial element $([\hat{l}],(\hat{f}))$; $([\hat{f}],(\hat{l}))$ of the space $R^3 * S^3$ arbitrarily, there is no consistent way of associating a single pair with the transformation.

The reader may find it helpful to verify geometrically the preceding multiplication rule in some simple examples. An illustrative example is the following: Choose $\hat{f}_i = [\hat{l}_i]$ in R^3 and, hence, $\hat{l}_i = [\hat{f}_i]$ in S^3, for the initial set of Eq. (5.61a). Suppose we now rotate R^3 by $\mathcal{R} = \pi/2$ about $[\hat{l}_3]$; then the corresponding rotation of S^3 is given by $\mathcal{S}^f_{\mathcal{R}} = \pi/2$ about $-[\hat{f}_3]$. Thus, the action of $\mathcal{R}$ on the chosen initial element of $R^3 * S^3$ is to give a new element of $R^3 * S^3$,

$$\hat{f}'_1 = [\hat{l}_2], \hat{f}'_2 = -[\hat{l}_1], \hat{f}'_3 = [\hat{l}_3];$$
$$\hat{l}'_1 = -[\hat{f}_2], \hat{l}'_2 = [\hat{f}_1], \hat{l}'_3 = [\hat{f}_3].$$

This element becomes the initial element for the next rotation $\mathcal{R}'$ of $R^3 * S^3$. We choose $\mathcal{R}'$ to be a rotation of R^3 given by $\mathcal{R}' = \pi/2$ about $[\hat{l}_1]$; then the corresponding rotation of S^3 is given by $\mathcal{S}^{f'}_{\mathcal{R}'} = \pi/2$ about $[\hat{f}_2]$. Thus, the action of $\mathcal{R}'$ on the element of $R^3 * S^3$ produced by $\mathcal{R}$ is the new element

$$\hat{f}''_1 = [\hat{l}_3], \hat{f}''_2 = -[\hat{l}_1], \hat{f}''_3 = -[\hat{l}_2];$$
$$\hat{l}''_1 = -[\hat{f}_2], \hat{l}''_2 = -[\hat{f}_3], \hat{l}''_3 = [\hat{f}_1].$$

It should be noted that in drawing pictures corresponding to the above operations *we do not in any sense consider the spaces R^3 and S^3 as superposed.* We depict the space R^3 with its fixed basis frame $[\hat{l}_1], [\hat{l}_2], [\hat{l}_3]$ on one sheet of paper, and we depict the space S^3 with its fixed basis frame $[\hat{f}_1], [\hat{f}_2], [\hat{f}_3]$ on a second sheet of paper. We do not align the bases of the two spaces in any particular way with respect to one another. It is only the relationship of triads of vectors $\{\hat{f}_1, \hat{f}_2, \hat{f}_3\}$ to the basis of R^3 and of triads of vectors $\{\hat{l}_1, \hat{l}_2, \hat{l}_3\}$ to the basis of S^3 as determined by $[\hat{l}_i]\cdot\hat{f}_j = [\hat{f}_j]\bullet\hat{l}_i$ which is important, and which is preserved by the transformation $\mathcal{R}$ of $R^3 * S^3$.

One might now imagine that we are through, since we have seemingly accounted for the relation between the two spaces R^3 and S^3, and found a group of transformations which preserve $R^3 * S^3$. This is, however, not the case. We can turn the correspondence (5.50) around and solve for $\mathcal{R}$ in terms of $\mathcal{S}$ (as already pointed out). We will show that this does lead to new transformations of the space $R^3 * S^3$. We only summarize the relevant properties of the anti-isomorphism, since the results parallel those already given for the $\mathcal{S}_{\mathcal{R}}$.

Let

$$\mathcal{S} \to \mathcal{R}_{\mathcal{S}} \tag{5.64a}$$

be the anti-isomorphism which is established by

$$[\hat{f}_j]\bullet\mathcal{S}\hat{l}_i = [\hat{l}_i]\cdot\mathcal{R}_{\mathcal{S}}\hat{f}_j \tag{5.64b}$$

for $i, j = 1, 2, 3$, each $\mathcal{S}\in\mathcal{O}^f_3$, and for a definite selection of $\hat{l}_1, \hat{l}_2, \hat{l}_3 \in S^3$. Then the anti-isomorphism

$$\mathcal{S} \to \mathcal{R}'_{\mathcal{S}} \tag{5.65a}$$

which is established by

$$[\hat{f}_j]\bullet\mathcal{S}\hat{l}'_i = [\hat{l}_i]\cdot\mathcal{R}'_{\mathcal{S}}\hat{f}'_j \tag{5.65b}$$

for $i, j = 1, 2, 3$, each $\mathcal{S}\in\mathcal{O}^f_3$, and $\hat{l}'_i = \mathcal{S}_0\hat{l}_i$, hence, $\hat{f}'_j = \mathcal{R}_{\mathcal{S}_0}\hat{f}_j$ is

$$\mathcal{S} \to \mathcal{R}'_{\mathcal{S}} = \mathcal{R}_{\mathcal{S}_0^{-1}\mathcal{S}\,\mathcal{S}_0}. \tag{5.65c}$$

The analogs of Eqs. (5.58) are easily obtained by inverting Eq. (5.58c): If

$$\mathcal{S} = \text{rotation of } \theta \text{ about } \hat{N}, \tag{5.66a}$$

then

$$\mathcal{R}_{\mathcal{S}} = \text{rotation of } \theta \text{ about } -\hat{n}, \tag{5.66b}$$

where

$$\hat{n} = \sum_{i,j}([\hat{f}_i]\bullet\hat{l}_j)(\hat{N}\bullet[\hat{f}_i])[\hat{l}_j], \tag{5.66c}$$

in which $\hat{l}_1, \hat{l}_2, \hat{l}_3$ are regarded as specified.

With each $\mathcal{S}\in\mathcal{O}^f_3$, we now associate the following transformation of the space $R^3 * S^3$:

$$\mathcal{S}:\ R^3 * S^3 \to R^3 * S^3, \tag{5.67a}$$

where the action of $\mathcal{S}$ on an arbitrary element of $R^3 * S^3$ is defined by

$$\mathcal{S}: \begin{matrix} ([\hat{l}],(\hat{f})) \to ([\hat{l}],(\mathcal{R}^l_{\mathcal{S}}\hat{f})) \\ ([\hat{f}],(\hat{l})) \to ([\hat{f}],(\mathcal{S}\hat{l})), \end{matrix} \tag{5.67b}$$

where

$$\mathcal{S} \to \mathcal{R}^l_{\mathcal{S}} \tag{5.67c}$$

is the anti-isomorphism determined by Eq. (5.64b). If we follow $\mathcal{S}$ by a second transformation $\mathcal{S}'$, then we verify that the transformation is that for $\mathcal{S}'' = \mathcal{S}'\mathcal{S}$.

We now come to one of the principal results of this lengthy section: *For each* $\mathcal{R} \in \mathcal{O}_3^I$ *and for each* $\mathcal{S} \in \mathcal{O}_3^f$, *we have the operator identity*

$$[\mathcal{R}, \mathcal{S}] = \mathcal{R}\mathcal{S} - \mathcal{S}\mathcal{R} = 0 \tag{5.68}$$

on the space $R^3 * S^3$.

This important result may be proved in several ways. We choose a method which presents much of the previous abstract transformation theory in a useful matrix form.

We first observe that the space $R^3 * S^3$ is in one-to-one correspondence with the set of orthogonal matrices:

$$R^3 * S^3 \longleftrightarrow \{C : C\tilde{C} = I\}. \tag{5.69}$$

Proof. Given any element of $R^3 * S^3$, we define the matrix C by $C_{ij} = [\hat{l}_i] \cdot \hat{f}_j = [\hat{f}_j] \bullet \hat{l}_i$. Conversely, given any orthogonal matrix C, we define the vectors $\hat{f}_1, \hat{f}_2, \hat{f}_3 \in R^3$ by $\hat{f}_j = \sum_i C_{ij}[\hat{l}_i]$ and the vectors $\hat{l}_1, \hat{l}_2, \hat{l}_3 \in S^3$ by $\hat{l}_i = \sum_i C_{ij}[\hat{f}_j]$. Then the point $([\hat{l}], (\hat{f}))$; $([\hat{f}]; (\hat{l}))$ is an element of $R^3 * S^3$.

The fact that the space $R^3 * S^3$ can be represented by the set of orthogonal matrices means that we can transcribe all the previous transformations of the abstract space into transformations on an orthogonal matrix, *without loss of content.*

The transformation (5.61) becomes

$$\mathcal{R}: \quad C \to RC \tag{5.70}$$

for each $\mathcal{R} \in \mathcal{O}_3^I$, and each orthogonal C, where R is the matrix representing $\mathcal{R}$ on the basis $[\hat{l}]$.

The transformation (5.67) becomes

$$\mathcal{S}: \quad C \to C\tilde{S}, \tag{5.71}$$

for each $\mathcal{S} \in \mathcal{O}_3^f$, and each orthogonal matrix C, where S is the matrix representing $\mathcal{S}$ on the basis $[\hat{f}]$.

The fact that $\mathcal{R}$ and $\mathcal{S}$ commute is now apparent: First $\mathcal{R}$, followed by $\mathcal{S}$, is the transformation

$$\mathcal{S}\mathcal{R}: \quad C \to (RC)\tilde{S} = RC\tilde{S}; \tag{5.72a}$$

first $\mathcal{S}$, followed by $\mathcal{R}$ is the transformation

$$\mathcal{R}\mathcal{S}: \quad C \to R(C\tilde{S}) = RC\tilde{S}. \tag{5.72b}$$

We denote the group of rotation-inversion transformations which maps the space $R^3 * S^3$ onto itself by the notation

$$\mathcal{O}_3^I * \mathcal{O}_3^f. \tag{5.73a}$$

In its action on C, an element of this group may be represented by an ordered pair

$$(\mathcal{R}, \mathcal{S}): \ \mathcal{R} \in \mathcal{O}_3^I, \ \ \mathcal{S} \in \mathcal{O}_3^f, \tag{5.73b}$$

where the action on C is given by

$$(\mathcal{R}, \mathcal{S}): \quad C \to RC\tilde{S}. \tag{5.73c}$$

The product of two such transformations is that of a direct product.

The emergence of such a simple matrix transformation property of the space $R^3 * S^3$ is quite satisfying. It suggests, perhaps, that much of the abstract analysis of this section could be done away with. We do not believe this to be the case. Matrix transformations lend themselves to many interpretations, and it would have been nontrivial to start with Eq. (5.73c) and arrive at the interpretation we have given it (although we now know how to do this).

E. Transformations of $R^3 * S^3$ induced by $\mathcal{L}_\mathcal{G}$

The coordinates which describe the motions of the particles in a polyatomic molecule are now taken to be

$$\{(C; Q)\}, \tag{5.74}$$

where C is an arbitrary orthogonal matrix representing an element of the space $R^3 * S^3$, and Q denotes the collection of normal coordinates.

We have previously deduced the action of $\mathcal{L}_\mathcal{G}$ on the normal coordinates:

$$\mathcal{L}_\mathcal{G}: Q \to L_\mathcal{G} Q. \tag{5.75}$$

It is somewhat less obvious what the action of $\mathcal{L}_\mathcal{G}$ is on C. From initial considerations, because $C_{ij} = [\hat{l}_i] \cdot \hat{f}_j$, one would be inclined to think that $\mathcal{L}_\mathcal{G}$ induces no transformation of C. This conclusion seems to follow from the fact that $\mathcal{L}_\mathcal{G}$ leaves the Eckart frame vectors $\hat{f}_i$ invariant, and it seems to do nothing to the basis vectors $[\hat{l}]$ of R^3. The second inference must, however, be carefully examined. We have emphasized in Sec. III.B that the $\mathcal{G}$ tag on $\mathcal{L}_\mathcal{G}$ does not designate a rotation–inversion of the space R^3, and it does not necessarily follow that $\mathcal{L}_\mathcal{G}$ does nothing to C.

To determine the action of $\mathcal{L}_\mathcal{G}$ on C, we examine the action of $\mathcal{L}_\mathcal{G}$ on the total angular momentum of the particles:

$$\vec{\mathrm{j}} = \sum_\alpha m_\alpha \vec{\mathrm{x}}^\alpha \times \vec{\mathrm{v}}^\alpha. \tag{5.76}$$

Under the action of $\mathcal{L}_\mathcal{G}$, we have

$$\mathcal{L}_\mathcal{G}: \vec{\mathrm{x}}^\alpha \to \sum_\beta (\mathcal{G}\vec{\mathrm{x}}^\beta) S_{\alpha\beta}(\mathcal{G}), \tag{5.77a}$$

$$\vec{\mathrm{v}}^\alpha = d\vec{\mathrm{x}}^\alpha/dt \to \sum_\beta (\mathcal{G}\vec{\mathrm{v}}^\beta) S_{\alpha\beta}(\mathcal{G}). \tag{5.77b}$$

It follows that

$$\mathcal{L}_\mathcal{G}: \vec{\mathrm{j}} \to \mathcal{G}\vec{\mathrm{j}} = \sum_{i,j} (\vec{\mathrm{j}} \cdot \hat{f}_j) G_{ij} \hat{f}_i \quad \text{if } \det G = 1, \tag{5.78}$$

$$\vec{\mathrm{j}} \to -\mathcal{G}\vec{\mathrm{j}} = -\sum_{i,j} (\vec{\mathrm{j}} \cdot f_j) G_{ij} \hat{f}_i \quad \text{if } \det G = -1.$$

Since we are not bound to interpreting $\mathcal{G}$ as a rotation of R^3, we insist that the action of $\mathcal{L}_\mathcal{G}$ on $\vec{\mathrm{j}}$ be such as to preserve the angular momentum $\vec{\mathrm{j}}$, i.e., that $\vec{\mathrm{j}}$ and $\mathcal{G}\vec{\mathrm{j}}$ (or $-\mathcal{G}\vec{\mathrm{j}}$) are one and the same vector as seen from the laboratory frame. This can be the case if and only if $\mathcal{L}_\mathcal{G}$ induces a transformation of the laboratory frame determined by

$$\mathcal{L}_\mathcal{G}: [\hat{l}_i] \to [\hat{l}'_i], \tag{5.79a}$$

where

$$\begin{aligned} &[\hat{l}_i] \cdot \vec{\mathrm{j}} = [\hat{l}'_i] \cdot \mathcal{G}\vec{\mathrm{j}}, \quad \det G = 1, \\ &[\hat{l}_i] \cdot \vec{\mathrm{j}} = -[\hat{l}'_i] \cdot \mathcal{G}\vec{\mathrm{j}}, \quad \det G = -1. \end{aligned} \tag{5.79b}$$

Thus, we obtain

$$[\hat{l}_i'] = \det G\, \mathcal{G}[\hat{l}_i] = (\det G)\sum_j (CG\tilde{C})_{ji}[\hat{l}_j]. \tag{5.79c}$$

The action of $\mathcal{L}_\mathcal{G}$ on C is now determined from

$$\mathcal{L}_\mathcal{G}: [\hat{l}_i]\cdot\hat{f}_j \to [\hat{l}_i']\cdot\hat{f}_j, \tag{5.80a}$$

that is,

$$\mathcal{L}_\mathcal{G}: C \to (\det G)C\tilde{G}. \tag{5.80b}$$

The nature of the space $R^3 * S^3$ is such that if we change the basis of the space R^3, we must also change the basis of the space S^3. Since the transformation (5.79a) is a change of basis, $\mathcal{L}_\mathcal{G}$ must also induce a change of basis of S^3 given by

$$\mathcal{L}_\mathcal{G}: [\hat{f}_i] \to [\hat{f}_i'], \tag{5.81a}$$

where

$$[\hat{l}_i']\cdot\hat{f}_j = [\hat{f}_j'] \bullet \hat{l}_i. \tag{5.81b}$$

Using Eq. (5.79c), we now calculate

$$[\hat{f}_i'] = \det G \sum_j G_{ij}[\hat{f}_j], \tag{5.82}$$

$$\mathcal{L}_\mathcal{G}: C \to (\det G)C\tilde{G}, \tag{5.83}$$

which agrees with Eq. (5.80b).

We have now proved that $\mathcal{L}_\mathcal{G}$ is a mapping of the space $R^3 * S^3$ into itself, and that this mapping corresponds to a *change of basis* of the space. If we represent an element of $R^3 * S^3$ by C, then C is mapped into $(\det G)C\tilde{G}$. The action of $\mathcal{L}_\mathcal{G}$ on the coordinates (5.74) is thus expressed by

$$\mathcal{L}_\mathcal{G}: (C; Q) \to ((\det G)C\tilde{G};\ L_\mathcal{G}Q). \tag{5.84}$$

VI. INVARIANCE PROPERTIES OF THE HAMILTONIAN OF A POLYATOMIC MOLECULE

In Sec. V, we have discussed various groups of operators which have an action on the coordinates which are usually used to characterize the motions of the nuclei in a polyatomic molecule. We still must relate these groups to the description of the molecular motions. This is accomplished by determining the properties which the Hamiltonian of the physical system possesses with respect to these groups.

We wish to do this in a general way without going through a detailed development of the Hamiltonian, using only general principles. We begin by examining the physical quantities which enter into the Hamiltonian, where the physical quantities are to be referred to the Eckart frame.

The Hamiltonian is made up of a potential energy term and a kinetic energy term. The potential energy $V(Q)$ is assumed to depend (in a given electronic configuration) only on the normal coordinates. The kinetic energy term is more complicated, but will be seen to be comprised of functions of the normal coordinates $\{Q\}$, the conjugate momenta $\{P\}$, and the components of the *total angular momentum* $\vec{\mathrm{j}}$ of the system (Wilson, 1955). These components are to be calculated relative to the Eckart frame. We have

$$\vec{\mathrm{j}} = \sum_i j_i[\hat{l}_i] = \sum_i J_i\hat{f}_i, \tag{6.1a}$$

and the components in question are

$$J_i = \hat{f}_i\cdot\vec{\mathrm{j}}. \tag{6.1b}$$

Note that both $\vec{\mathrm{j}}$ and $\hat{f}_i$ are *vectors* in the space R^3. Thus, the physical quantities on which the Hamiltonian is defined are certain scalar and pseudoscalar parameters and the dynamical variables

$$J_1, J_2, J_3, \{Q\}, \{P\}. \tag{6.2}$$

A. Transformations of angular momentum

Let us next examine the transformation properties of $\vec{\mathrm{j}}$ and the J_i. The total angular momentum of the system of particles is given by

$$\vec{\mathrm{j}} = \sum_{\alpha=1}^{N} m_\alpha \vec{\mathrm{x}}^\alpha \times \vec{\mathrm{v}}^\alpha, \tag{6.3}$$

where $\vec{\mathrm{x}}^1, \vec{\mathrm{x}}^2, \ldots, \vec{\mathrm{x}}^N$ are the position vectors of the particles relative to the center of mass and the $\vec{\mathrm{v}}^1, \vec{\mathrm{v}}^2, \ldots, \vec{\mathrm{v}}^N$ are the corresponding velocities. Under a rotation-inversion $\mathcal{R}$ of the space R^3, we have

$$\begin{aligned} &\mathcal{R}: \vec{\mathrm{j}} \to \mathcal{R}\vec{\mathrm{j}} \text{ if } \mathcal{R} \text{ is a rotation} \\ &\qquad \vec{\mathrm{j}} \to \vec{\mathrm{j}} \text{ if } \mathcal{R} = \mathcal{I}. \end{aligned} \tag{6.4}$$

Under a permutation $\mathcal{P}$ of identical particles, we have

$$\mathcal{P}: \vec{\mathrm{j}} \to \vec{\mathrm{j}}. \tag{6.5}$$

Under the action of $\mathcal{L}_\mathcal{G}$, we have from Sec. V.E that

$$\begin{aligned} \mathcal{L}_\mathcal{G}: \vec{\mathrm{j}} &\to (\det G)\mathcal{G}\vec{\mathrm{j}} \\ &= (\det G)\sum_{i,j} J_j G_{ij}\hat{f}_i. \end{aligned} \tag{6.6}$$

On the other hand, the Eckart frame vectors behave in the following manner:

$$\begin{aligned} &\mathcal{R}: \hat{f}_i \to \mathcal{R}\hat{f}_i \text{ if } \mathcal{R} \text{ is a rotation} \\ &\qquad \hat{f}_i \to -\hat{f}_i \text{ if } \mathcal{R} = \mathcal{I}. \end{aligned} \tag{6.7}$$

For each $\mathcal{P} \leftrightarrow \mathcal{G}$ of the static molecular model, we have

$$\mathcal{P}: \hat{f}_i \to \mathcal{G}\hat{f}_i, \mathcal{G} \in \mathcal{O}_3^l, \tag{6.8}$$

where we recall that if $\mathcal{G}$ is described in the static model as a rotation of θ about $\hat{n} = \sum_i n_i\hat{e}_i$, the definition of $\mathcal{G} \in \mathcal{O}_3^l$ is that $\mathcal{G}$ is a rotation of θ about $\hat{n} = \sum_i n_i\hat{f}_i \in R^3$. In addition, we know that the operators $\mathcal{L}_\mathcal{G}$ leave the Eckart frame invariant.

Using the above information, we may now deduce the following properties of the J_i: For each $\mathcal{R} \in \mathcal{O}_3^l$, we have

$$\begin{aligned} &\mathcal{R}: J_i \to J_i \text{ if } \mathcal{R} \text{ is a rotation} \\ &\qquad J_i \to -J_i \text{ if } \mathcal{R} = \mathcal{I}. \end{aligned} \tag{6.9}$$

For each $\mathcal{P} \leftrightarrow \mathcal{G}$, we have

$$\mathcal{P}: J_i \to (\mathcal{G}\hat{f}_i)\cdot\vec{\mathrm{j}} = \sum_j G_{ji}J_j, \tag{6.10a}$$

or, equivalently,

$$\mathcal{P}: \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} \to \tilde{G}\begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix}, \tag{6.10b}$$

where we note that the matrix representing $\mathcal{G} \in \mathcal{O}_3^l$ on the

Eckart frame is the same as the matrix G representing $\mathcal{G}$ on the principal axes of the static model. For each $\mathfrak{L}_{\mathcal{G}}, \mathcal{G} \in \mathcal{G}(\mathfrak{A})$, we have

$$\mathfrak{L}_{\mathcal{G}}: J_i \to (\det G) \sum_j G_{ij} J_j , \tag{6.11a}$$

or, equivalently,

$$\mathfrak{L}_{\mathcal{G}}: \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} \to (\det G) G \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} . \tag{6.11b}$$

Note that the matrix $(\det G)G$ is always proper, orthogonal.

The determination of the transformation properties of the J_i under $\mathcal{S} \in \mathcal{O}_3^f$ is somewhat more delicate. First of all, in our definition (5.36) of the space S^3, we deliberately did not include "molecular vectors" in this space for the simple reason that such vectors do not undergo transformations under $\mathcal{S}$, which by design describes rotation-inversions *of the external world* as seen by an observer in the Eckart frame. This observer, however, knows that he is in a noninertial reference frame and that the rotations of the external world which he observes are, in fact, due to his own motion with respect to the inertial frame. He takes this into account by considering that the angular momentum $\vec{j}$ is a vector belonging to the external world, i.e., that the angular momentum $\vec{j}$ is given in his space by the vector $\vec{J}$ defined by

$$\vec{J} = \sum_i j_i \hat{l}_i = \sum_i J_i [\hat{f}_i] , \tag{6.12a}$$

where the components j_i and J_i are the same as those occurring in Eq. (6.1a):

$$j_i = [\hat{l}_i] \cdot \vec{j} = \hat{l}_i \bullet \vec{J} , \tag{6.12b}$$

$$J_i = \hat{f}_i \cdot \vec{j} = [\hat{f}_i] \bullet \vec{J} . \tag{6.12c}$$

The transformation properties of the J_i under $\mathcal{S} \in \mathcal{O}_3^f$ are now easily obtained:

$$\mathcal{S}: J_i \to [\hat{f}_i] \bullet \mathcal{S}\vec{J} = \sum_j S_{ij} J_j , \tag{6.13a}$$

or, equivalently,

$$\mathcal{S}: \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} \to S \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} . \tag{6.13b}$$

It is noteworthy that the group of matrix transformations on the components J_1, J_2, J_3 effected by the $\{\mathfrak{L}_{\mathcal{G}}\}$ [cf. Eqs. (6.11)] is a subgroup of the group of matrix transformations effected by the $\{\mathcal{S}\}$ [cf. Eq. (6.13)].

It is also noteworthy that the action of a permutation $\mathcal{P} \to \mathcal{G}$ on the components J_1, J_2, J_3 is identical to that of $(\det G)\mathfrak{L}_{\mathcal{G}^{-1}}$ [compare Eqs. (6.10b) and (6.11b)]. *This result implied that the action of any element $\mathcal{F}$ of the group of feasible operators on J_1, J_2, J_3 is precisely that of the corresponding* $\mathfrak{L}_{\mathcal{G}^{-1}}$. This corresponding $\mathfrak{L}_{\mathcal{G}^{-1}}$ is determined as follows: The static model establishes the one-to-one correspondence $\mathcal{P} \to \mathcal{G}$ between certain elements of the permutation group and the $\mathcal{G} \in G(\mathfrak{A})$. If $\det G = +1$, then $\mathcal{F} = \mathcal{P}$ and the $\mathcal{G}$ in $\mathfrak{L}_{\mathcal{G}^{-1}}$ is the $\mathcal{G}$ corresponding to $\mathcal{P}$; if $\det G = -1$, then $\mathcal{F} = \mathcal{I}\mathcal{P}$, and the $\mathcal{G}$ in $\mathfrak{L}_{\mathcal{G}^{-1}}$ is the $\mathcal{G}$ corresponding to $\mathcal{P}$.

B. Invariance group of the full Hamiltonian

We are now prepared to discuss the invariance properties of the Hamiltonian of a polyatomic molecule. We present this discussion from two points of view, the first one following, more or less, traditional concepts regarding the role of the point group, and the second one following, more or less, new concepts regarding the role of the group of feasible operators (Longuet-Higgens, 1963; Hougen, 1975).

A result common to each viewpoint follows from property (6.9) and the fact that the normal coordinate, hence, also the conjugate momenta, are invariants under each $\mathcal{R} \in \mathcal{O}_3^l$: *Any Hamiltonian built out of the physical quantities $J_1, J_2, J_3, \{Q\}, \{P\}$ is automatically invariant under each rotation $\mathcal{R}$ of the space R^3.* The Hamiltonian must, of course, also be invariant under the inversion of R^3. This implies either that the Hamiltonian is quadratic in the J_i or that terms linear in J_i are multiplied by quantities which are pseudoscalars under $\mathcal{I} \in \mathcal{O}_3^l$. It is the latter situation which prevails. These results imply that the rotation-inversions of the space R^3 play no role in the subsequent discussions of the invariance properties of the Hamiltonian.

The traditional viewpoint (Wilson, 1955) holds that the Hamiltonian must be invariant with respect to the group of operators $\{\mathfrak{L}_{\mathcal{G}}\}$. The basis for this principle is clear: These operators generate internal motions of the particles which are compatible with the Eckart frame, and the Hamiltonian which describes these motions must accordingly be invariant—it is the largest group possessing this property which can be derived from a group which preserves the geometry of the static model.

The second viewpoint (Longuet-Higgens, 1963; Hougen, 1975) holds that the Hamiltonian must be invariant under the elements of the group of feasible operators. However, since the action of a feasible operator $\mathcal{F}$ on the set of normal coordinates, the conjugate momenta, and angular momenta given by (6.2) is expressed by a $\mathfrak{L}_{\mathcal{G}^{-1}}$, *it follows that the two viewpoints coincide insofar as the invariance properties of the Hamiltonian are concerned.* This should come as no surprise in view of Eq. (5.14). The "rotational part" of a feasible operator is "wiped out," not only in its action on a normal coordinate [$\mathcal{O}_3^l$ scalars], but also in its action on the $\mathcal{O}_3^l$ pseudoscalars J_1, J_2, J_3.

We have now proved the result: *The invariance group of the Hamiltonian of a polyatomic molecule is the direct product group* $\mathcal{O}_3^l \times \{\mathfrak{L}_{\mathcal{G}}\}$.

We hasten to note that while invariance under the group of feasible operators and the group $\{\mathfrak{L}_{\mathcal{G}}\}$ imply the same properties for the Hamiltonian, this does not mean that there is no distinction in the consequences of these invariances. This is so because the action on coordinates of operators taken from these two groups is distinct. Let us develop these properties explicitly.

C. Transformation of coordinates

The coordinates of the molecular problem are the quantities in the set

$$\{(C;Q)\}, \tag{6.14}$$

where C is an arbitrary orthogonal matrix representing an element of the space $R^3 * S^3$, and Q denotes the set of normal coordinates.

The action of a permutation $\mathcal{P} \leftrightarrow \mathcal{G}$ on the coordinates (6.14) is obtained from Eq. (5.17):

$$\mathcal{P}\colon (C;Q) \to (G'C; L_{\mathcal{G}^{-1}}Q), \tag{6.15a}$$

where G' is the matrix representing $\mathcal{G} \in \mathcal{O}_3^l$ on the basis $[\hat{l}]$. For $\mathcal{G} \in \mathcal{O}_3^l$ we have

$$\mathcal{G}\colon (C;Q) \to (-C;Q). \tag{6.15b}$$

These two results allow us to write out the action on the coordinates of any element of the group of feasible operators. Observe that it is intrinsic to the definition of a permutation that the $\mathcal{G}$ occurring in $\mathcal{P} = (\mathcal{G}, L_{\mathcal{G}^{-1}})$ [cf. Eq. (5.20)] is an element of $\mathcal{O}_3^l$.

The action of $\mathcal{L}_{\mathcal{G}}$ on the coordinates $(C;Q)$ was determined in Sec. V.E:

$$\mathcal{L}_{\mathcal{G}}\colon (C;Q) \to ((\det G)C\tilde{G}; L_{\mathcal{G}}Q). \tag{6.16}$$

In the quantum mechanical description of the molecule, the wave functions describing a given state of energy will undergo different types of transformations under the induced action of operators drawn from the group of feasible operators and those drawn from the group $\{\mathcal{L}_{\mathcal{G}}\}$. We will develop the details of these transformations in a subsequent paper, but the principal result may already be anticipated: The group of feasible operators has little to do with the molecular motions problem—it is the key concept in implementing the Pauli principle.

D. Larger symmetries and symmetry breaking

In Sec. V.D, we introduced a group of transformations $\mathcal{O}_3^l * \mathcal{O}_3^f$ on the space $R^3 * S^3$. The action of an element of the group on C was that of a direct product group:

$$(\mathcal{R}, \mathcal{S})\colon C \to RC\tilde{S}. \tag{6.17}$$

In Sec. V.A, we also introduced the group of transformations $G(O)$ with elements $L_{\{R\}}$ whose action on the normal coordinates is symbolized by

$$L_{\{R\}}\colon Q \to L_{\{R\}}Q. \tag{6.18}$$

We may consider the ordered triplet of operators

$$(\mathcal{R}, \mathcal{S}, L_{\{R\}}) \tag{6.19a}$$

to be an element of the direct product group

$$\mathcal{O}_3^l * \mathcal{O}_3^f \times G(O), \tag{6.19b}$$

where we recall that $G(O)$ is itself a direct product group $G(O) = \prod_i O_i$. The action of the group element (6.19a) on the coordinates $(C;Q)$ is defined by

$$(\mathcal{R}, \mathcal{S}, L_{\{R\}})\colon (C;Q) \to (RC\tilde{S}; L_{\{R\}}Q), \tag{6.20}$$

where we recall that R is the matrix representing $\mathcal{R}$ on the basis $[\hat{l}]$, and S is the matrix representing $\mathcal{S}$ on the basis $[\hat{f}]$. (The $\{R\}$ subscript on L has nothing to do with the matrix R representing $\mathcal{R}$.)

One readily proves that the product rule first $(\mathcal{R}, \mathcal{S}, L_{\{R\}})$ followed by $(\mathcal{R}', \mathcal{S}', L_{\{R'\}})$ defines the direct product multiplication

$$(\mathcal{R}', \mathcal{S}', L_{\{R'\}})(\mathcal{R}, \mathcal{S}, L_{\{R\}}) = (\mathcal{R}'\mathcal{R}, \mathcal{S}'\mathcal{S}, L_{\{R'R\}}). \tag{6.21}$$

What is the role of the group (6.19) in the molecular problem? The answer is to be found in perturbation theory. One expects the Hamiltonian H to be approximated to zero order by an H_0 which is a pure rotational part plus a pure harmonic motion part (Casimir, 1931). If the rotator is spherical, *then the group* (6.19b) *with elements* (6.19a) *is the invariance group of the Hamiltonian H_0.*

Suppose further that the molecule is in a mode of excitation such that the principal perturbing term is (Jahn, 1935, 1939)

$$H_1 = \zeta(J_1L_1 + J_2L_2 + J_3L_3), \tag{6.22}$$

where (L_1, L_2, L_3) are the components of angular momentum carried by a triply degenerate mode of oscillation. Then the invariance group of $H_0 + H_1$ is the following subgroup of the group (6.19b):

$$\mathcal{O}_3^l * \mathcal{O}_3^f \textcircled{d} O_3 \times G'(O), \tag{6.23}$$

where the new symbols have the following meaning: $G'(O)$ includes all products in the direct product group given by Eq. (5.5), except the O_3 which is the invariance group of the 3-dimensional oscillator which carries the angular momentum (L_1, L_2, L_3); the symbol $\mathcal{O}_3^f \textcircled{d} O_3$ designates the so-called diagonal subgroup of $\mathcal{O}_3^f \times O_3$—it is the group consisting of the pairs $(\mathcal{S}, L_S)$, where the subscript S is the matrix representing $\mathcal{S}$ on the basis $[\hat{f}]$. The corresponding transformation properties of the angular momenta occurring in H_1 are

$$\mathcal{S}: \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} \to S \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix}, \tag{6.24a}$$

$$L_S: \begin{pmatrix} L_1 \\ L_2 \\ L_3 \end{pmatrix} \to S \begin{pmatrix} L_1 \\ L_2 \\ L_3 \end{pmatrix}. \tag{6.24b}$$

Thus, H_1 is invariant.

Let us now examine the relation of the invariance group $\mathcal{O}_3^l \times \{\mathcal{L}_{\mathcal{G}}\}$ of the full Hamiltonian to the group (6.19b). The elements of $\mathcal{O}_3^l \times \{\mathcal{L}_{\mathcal{G}}\}$ are the ordered pairs

$$(\mathcal{R}, \mathcal{L}_{\mathcal{G}}). \tag{6.25a}$$

The action of this element on $(C;Q)$ is [cf. Eq. (6.16)]

$$(\mathcal{R}, \mathcal{L}_{\mathcal{G}})\colon (C;Q) \to (RC\tilde{S}'(\mathcal{G}); L_{\mathcal{G}}Q), \tag{6.25b}$$

where we have written

$$S'(\mathcal{G}) = (\det G)G. \tag{6.25c}$$

Comparing this result with Eq. (6.20), we see that *as matrix transformations on the coordinates $(C;Q)$, the transformations* (6.25b) *are a subgroup of the matrix transformation on $(C;Q)$ given by* (6.20). This result should not be too astonishing in view of the fact that the group of (passive) transformations $\{\mathcal{L}_{\mathcal{G}}\}$ on the basis of $R^3 * S^3$ is isomorphic to a group of (active) transformations on the vectors of $R^3 * S^3$.

Let us introduce the following notations: $G(Q)$ denotes the subgroup of transformations, $G(Q) \subset G(O)$, on the normal coordinates given by $Q \to L_{\mathcal{G}}Q$, each $\mathcal{G} \in G(\mathfrak{A})$

[cf. Eq. (5.7)]. G^f denotes the subgroup of active transformations, $G^f \subset \mathcal{O}_3^f$ of $R^3 * S^3$ such that $\mathcal{S}'(\mathcal{G}) \in G^f$ has the action

$$\mathcal{S}'(\mathcal{G}): \; C \to C\tilde{S}'(\mathcal{G}), \tag{6.26a}$$

where

$$S'(\mathcal{G}) = (\det G)G. \tag{6.26b}$$

Then the invariance group of the full Hamiltonian can be taken to be

$$\mathcal{O}_3^l * G^f \times G(Q) \tag{6.27a}$$

with elements

$$(\mathcal{R}, \mathcal{S}'(\mathcal{G}), L_{\mathcal{G}}). \tag{6.27b}$$

The action of an operator (6.27b) on the coordinates $(C;Q)$ is given by Eq. (6.20); it coincides with the action of $\mathcal{R}$ and $\mathcal{L}_{\mathcal{G}}$. By design it transforms the Hamiltonian H in the same manner as do $\mathcal{R}$ and $\mathcal{L}_{\mathcal{G}}$.

We also note that the group of permutations $\mathcal{P} \leftrightarrow \mathcal{G}$ (hence, the group of feasible operators) also draws its operators from the set (6.20), since

$$\mathcal{P} = (\mathcal{G}, E, L_{\mathcal{G}^{-1}}), \tag{6.28}$$

where $E \in \mathcal{O}_3^f$ is the identity operator.

From the viewpoint of perturbation theory, the structure

$$\mathcal{O}_3^l * G^f \times G(Q) \subset \mathcal{O}_3^l * \mathcal{O}_3^f \times G(O) \tag{6.29}$$

defines completely the general structure of the polyatomic molecule Hamiltonian. The problem is conveniently phrased in a language which suggests alternative algebraic methods (Biedenharn and Gamba, 1972; Louck, 1974; de Vries and van Zanten, 1974) of solution: The zero-order Hamiltonian is invariant under $\mathcal{O}_3^l * \mathcal{O}_3^f \times G(O)$; the most general interaction occurring in the full Hamiltonian must be a tensor operator with respect to the group $\mathcal{O}_3^l * \mathcal{O}_3^f \times G(O)$ and an invariant with respect to the subgroup $\mathcal{O}_3^l * G^f \times G(Q)$. [Quite naturally subgroup structures which lie between the two extremes of Eq. (6.29) are also of interest.]

In the quantum mechanical case the theory of *irreducible tensor operators* (Wigner, 1940; Racah, 1942; Rose, 1957; Edmonds, 1957; Fano and Racah, 1959; Biedenharn and van Dam, 1965) of the orthogonal groups $\mathcal{O}_3$ and $\mathcal{O}_2$, and the couplings of such operators, are therefore essential ingredients of the theory of many (Wilson, 1934) polyatomic molecules (Hecht, 1960, 1960a; Moret-Bailly, 1959, 1961, 1965; Michelot *et al.*, 1974, 1974a; Griffith, 1962).

It is particularly appropriate to note here Carl Eckart's contribution to the theory of tensor operators (Eckart, 1930).

VII. CONCLUDING REMARKS

This brings us to the conclusion of what has been essentially a classical discussion of the vibration-rotation aspects of polyatomic molecules. However, the invariance properties of the quantum mechanical Hamiltonian are the same. Furthermore, since we know how the coordinates transform under the various groups, we also know how to define (Wigner, 1959) the induced action on wave functions. We thus have available the full apparatus for studying the quantum mechanical problem from the viewpoint of the group transformations themselves.

This procedure leads to new insights into the anomalous commutation rules (van Vleck, 1951) of the angular momenta components J_1, J_2, J_3 as well as to a better understanding of the angular momentum coupling rules for molecular angular momenta, the modifications of the Racah–Wigner tensor calculus, the transformation properties of wave functions, and the calculation of statistical weights (Wilson, 1935; Longuet-Higgens, 1963; Bunker and Papoušek, 1969; Hougen, 1971; Oka, 1973; Hougen, 1975). We plan to carry out this study in a paper to be published elsewhere.

Finally, we would like to make some admittedly speculative remarks concerning nonrigid molecules (Longuet-Higgens, 1963). It is fairly clear from the generalizations of the transformations (3.18) along the lines indicated by Eq. (3.23) that the theory we have presented has a generalization to nonrigid molecules.

It appears that such a theory would involve the use of several Eckart frames; certain "local" Eckart frames would be defined from the position vectors of those nuclei which seem to comprise "rigid molecular substructures"; yet another "principal" Eckart frame would be defined on the position vectors of the center of mass vectors of the "rigid molecular parts" of the composite molecule. Interactions between the various Eckart frames would provide the mechanism for torsional interactions, etc.

We are not certain that a meaningful physical theory of the above type can be built, but it seems worth considering. It could provide a rigorous basis for the highly descriptive ideas of Longuet-Higgens (1963).

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