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A STRATEGY TO DERIVE NEW INTERNAL COORDINATES BY PARTITIONING THE INTERNAL CONFIGURATION SPACE ACCORDING TO INVARIANCE PROPERTIES

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Abstract

A method to derive optimally orthogonal curvilinear coordinates for N-body systems is proposed. The invariance of certain subspaces under groups of linear transformations is employed to partition the configuration subspace into internal and external components. The construction is initially carried out locally by orthogonalizing typical group invariant vector fields. Integration is performed subsequently by means of integrating factors. Simple examples of orthogonal invariants illustrate the discussion.

1. Introduction

An essential step in the integration of the multivariable Schrödinger equation describing any system of N interacting particles is the selection of some optimal choice of coordinates underlying the physical description. Such coordinates must

(1) reflect in a transparent way the constraints and the symmetries which characterize the system, and
(2) provide an acceptable degree of separability of the Hamiltonian.

In any event, the selection of an appropriate set of coordinates is decided primarily from the invariance properties of the Hamiltonian under some group Γ of linear transformations. For example, relative coordinates are invariant under the group of translations in physical space $\mathbb{R}^3$, internal coordinates are invariant under orthogonal transformations in $\mathbb{R}^3$, kinematic coordinates are invariant under orthogonal transformations in $\mathbb{R}^n$, and symmetric coordinates are invariant under the symmetric group of transformations within some subspace of the internal coordinates.

To achieve Γ-invariance, the first step is to identify *integral bases* $B(\Gamma)$, i.e. sets of independent functions invariant under Γ in which any Γ-invariant function can be expressed. These coordinates are complemented by a set $\overline{B}(\Gamma)$ of functions which are not Γ-invariant. The result is a Γ-"partitioning" of the $3N$-dimensional configuration space $\mathbb{C}$ in the sense that an arbitrary function $f(\ldots x^{ia}\ldots)$ of the $3N$ Cartesian components of the configuration vector $\boldsymbol{X}$ can be expressed as a sum of products of functions of $B(\Gamma)$ and of functions $\overline{B}(\Gamma)$ since, in general, $f(\ldots x^{ia}\ldots)$ is nonlinear in $B(\Gamma)$ and $\overline{B}(\Gamma)$. Typical invariants under the usual groups of transformations are quite well known from the theory of vector invariants [1] and can serve as building blocks for more specific coordinates. For instance, the n elementary symmetric functions in the arguments x_n are invariant under the symmetric group $\Pi(n)$ and any symmetric function in x_n is expressible in the basis $B(\Pi(n))$.

In addition to the above symmetry considerations, the integrability of the multivariable Schrödinger equation is greatly facilitated by choosing orthogonal coordinates which thereby eliminate cross terms in the Hamiltonian (although more restrictive conditions are needed in order to ensure the separability of the solutions). It is then desirable

(1) to deal with mutually orthogonal invariant subspaces yielding an optimal separation of the motions, and
(2) to choose optimally orthogonal bases for the invariant subspaces themselves.

This scheme is easily applicable to the translation invariants by employing generalized Jacobi vectors (GJV) $\boldsymbol{q}_i$ ($i = 1, \ldots, N-1 \equiv n$) [2,3] instead of the usual interparticle vectors $\boldsymbol{x}_i$ ($i = 1, \ldots, N$). Their Cartesian components q^{ia} with respect to an inertial frame $\{\boldsymbol{I}_a: a = 1, 2, 3\}$ are orthonormal and span the $3N-3$ dimensional relative subspace which is itself orthogonal to the subspace spanned by the three Cartesian coordinates of the center of mass (c.m.). Both subspaces remain Euclidean and the $3N$-dimensional configuration space is simply expressed as the direct sum of the mutually orthogonal relative and the c.m. subspaces. As a result, the Hamiltonian is exactly separable into c.m. and relative components.

The situation is rather different for the rotational invariants. Although this subject has been extensively discussed in the past [4], it is worth briefly reviewing the principal results in terms of vector formalism. The proper way to construct coordinates that are invariant under physical rotations involves the specification of a non-intertial frame $\{\boldsymbol{f}_a: a = 1, 2, 3\}$ (NIF) attached in some way to the entire system (globally defined) or to a part of the system (locally defined). In the former definition, all the GJV of the system are involved in the construction of the moving frame. Typical examples are the instantaneous principal axes of the inertia frame (IPAI) [5], the equivalent symmetric frame (ES) and the irreducible symmetric frame (IS) [6]. In the latter situation, only some specific GJV are used in the definition of the frame. This model originates in the early work of Hirschfelder and co-workers [7] and has been extensively generalized in the past few years by the present authors [8]. The resulting theory has been shown to have considerable success in the discussion of systems in which certain large amplitude internal modes are involved. For either frame, the relative coordinates y^{ia} of the GJV involved in the construction of the moving frame are the invariants for the external rotations. Unfortunately, these coordinates are not independent. Indeed, the specification of the NIF imposes three relationships upon them and a new parameterization has to be sought (see, for instance, ref. [8]). Whatever this parameterization is, the transformation of the $3N$ Cartesian coordinates q^{ia} into rotational invariants $B(O(3))$ (internal) and noninvariant $\overline{B}(O(3))$ (external) coordinates is not linear and is best discussed locally rather than globally. Infinitesimal transformations are envisaged in the local tangent space and the resulting vector fields need to be integrated to provide the desired coordinates. At the local level, it is possible to construct a tangent external subspace orthogonal to the internal tangent space. This is achieved by defining a noninertial frame whose orientation with respect to the inertial frame is given by a set of three Euler angles (external variables). However, it can be shown that, irrespective of the choice of noninertial frame, the internal and external subspaces do not remain mutually orthogonal upon integration, leading to coupling terms between the internal and external components of the kinetic energy operator (see, for example, refs. [9–12]). The degree of separability obviously depends on the choice of both the parameterization for the external subspace (that is, the choice of the noninertial frame) and of the internal subspace.

In this paper, attention will be concentrated on various parameterizations of the internal subspace irrespective of the choice of external variables. Internal coordinates can either be derived from (physical) rotational invariants $B(O(3))$ depending on the interparticle vectors (or the orthogonal Jacobi vector counterparts) or from kinematic orthogonal invariants $B(O(n))$ depending on vectors belonging to the label space. However, it should be noticed that the kinematic invariants do not constitute a complete set of internal coordinates. Indeed, there exist kinematic invariants that are not internal coordinates. The usual bond distance–angle coordinates, Cartesian components of interparticle vectors in a noninertial frame and the BRI (basic rotational invariants: GJV distances and inter-GJV angles) are typical of the former family, whereas hyperspherical coordinates belong to the latter. It appears that, apart from three- and four-body systems [12–15], no general discussion of a combination of members of the two species and forming a complete set of $3N-6$ independent internal coordinates has been investigated in detail. Such a mixed set is particularly attractive in the study of systems undergoing large amplitude nuclear motion. For instance, in dissociation or rearrangement processes it is desirable to "switch" from one set of interparticle vectors before rearrangement to another set after. This switching procedure is actually a transformation in label space and needs to be described by functions belonging to $\overline{B}(O_n)$, the remaining internal coordinates being constructed from $B(O(3)) \cap B(O(n))$ in an ideally orthogonal fashion.

This paper presents a global approach to the construction of various sets of mixed invariants under the orthogonal group $O(3)$ of physical orthogonal transformations and the group $O(n)$ of label rotations, and is preparatory to a more general discussion involving other groups of linear transformations of relevance in molecular dynamics. The procedure relies on two main propositions of the theory of vector invariants. First, all invariants under a group Γ of linear transformations acting on a vector space are expressible in terms of a finite number of typical invariants referred to as an integral basis for the Γ-invariants. Secondly, if f is Γ-invariant, so is its total differential.

Conversely, if ω is a Γ-invariant differential form and if it is possible to find a Γ-invariant Lie integrating factor, then ω yields a family of Γ-invariant integral curves. In principle, this is feasible at least for the orthogonal group [16–18] when few variables are involved.

In section 2, the general procedure is applied in the particularly simple and well-known case of translational invariants. The purpose of this exercise is to illustrate the theory in a situation of linear transformations as opposed to the more general case of curvilinear transformations. The basic concepts of arbitrariness in the choice of an external complementary space (c.m. coordinates are the traditional choice, but are not unique) and of "global" orthogonality, that is, conservation of the separability upon integration (through the choice of appropriate Jacobi vectors instead of the usual bond vectors) are easily understandable and will serve as a model for more complicated situations. In section 3, the infinitesimal standpoint needed in curvilinear manipulations is introduced by means of the concepts of tangent and cotangent spaces where linear transformations (of bases) can be performed in locally defined vector spaces. The integral bases are subsequently obtained by integration, provided integrability conditions are met. The example of spherical coordinates serves as a simple illustration of orthogonal invariants in $\mathbb{R}^3$ depending on a single vector. Section 4 deals with orthogonal invariants in $\mathbb{R}^3$ and $\mathbb{R}^n$ depending on 3 and n vectors, respectively. Integral bases for physical and kinematic orthogonal invariants are derived in a simple fashion from the invariance of the Gram matrix $\mathbf{G}$ and the mass quadrupole $\mathbf{M}$, respectively. It is also demonstrated that their common non-zero eigenvalues constitute a three-dimensional integral basis for physical/kinematic common invariants. Section 5 deals with the local (infinitesimal) version of the invariant (cotangent) subspaces and the local orthogonalization of the internal vector fields. The relative vector field is integrated for a four-dimensional problem by using different partitions of the three-dimensional internal subspace.

2. Translation invariance and the subspace of relative configuration

A system of N particles moving in $\mathbb{R}^3$ is quantum mechanically described by the Schrödinger equation

$$(T + V)\Psi = E\Psi, \tag{2.1}$$

where T is the kinetic energy operator and V is the potential. The systems considered here are such that V is invariant under the translations and the rotations (proper or not) acting in the physical space $\mathbb{R}^3$. The systems we have in mind generally possess additional invariance of the potential under the action of some specific groups of transformations acting in subspaces of the configuration space (symmetric groups, alternate groups, . . .). Consequently, the coordinates in which the potential is re-expressed must obviously obey the same invariance properties and the choice for a particular system of coordinates plays the key role in the solvability of eq. (2.1).

Ideally, one seeks $3N$ coordinates $\{v^i\}$, usually derived by curvilinear transformations from the components $\{x^{ia}\}$ of the position vectors $\boldsymbol{x}_i$ with respect to the inertial frame such that both the kinetic energy operator T and the function V, once re-expressed in the coordinates (v^i), yield a solvable system of $3N$ one-dimensional Schrödinger equations. In other words, the coordinates must be such that the eigenfunctions Ψ of eq. (2.1) are factorizable in the form $\Psi = \prod_i \psi_i(v^i)$.

From its invariance properties, the potential function, either in analytic form (when available) or in the form of numerical data, suggests the choice for the coordinates. For systems where $V = 0$, eq. (2.1) reduces to the Laplace equation which can be easily solved, for example, in Cartesian coordinates. On the other hand, whenever V can be expressed as a function of a single coordinate (central potentials, for instance), the equation is exactly solvable by an appropriate change of coordinates (radial coordinate). This actually corresponds to the invariance of V under the orthogonal group acting in the whole relative configuration space. Unfortunately, V is in general a function of more than one coordinate and the best that can be done is to find those systems of coordinates for which (2.1) is optimally separable.

2.1. GENERAL PROCEDURE

The general strategy aimed at achieving the above goal requires construction of coordinates by first taking advantage of their invariance under the action of the relevant groups of transformations acting in some subspace of the $3N$-dimensional configuration space: translation and orthogonal group acting in the Euclidean physical space $\mathbb{R}^3$, orthogonal group acting in the Cartesian label space $\mathbb{R}^n$, symmetric group acting in subspaces of the Riemannian internal space, etc. The invariance under a group Γ yields a partition of the underlying *local* vector space $T_P^*\mathbb{C}$ of the differential forms defined on $\mathbb{C}$ (the so-called *cotangent* space [19] at P) into the *internal* subspace $I(\Gamma)$ and an *external* subspace $E(\Gamma)$, arbitrarily defined as a complementary space to $I(\Gamma)$ in the $T_P^*\mathbb{C}$. The bases spanning $I(\Gamma)$ and $E(\Gamma)$ are, respectively, the generators of the integral functions which are Γ-invariant and the integral functions which are not invariant under Γ. Briefly, if γ is a covariant vector (differential form) of $I(\Gamma)$, then, by integration, γ may (if integrability conditions are met) generate a function (really a family of functions) invariant under any element of Γ. In addition, if $\lambda \in E(\Gamma)$, by integration, λ would generate an external function. Since $I(\Gamma)$ is a finite dimensional vector space, the Γ-invariant functions are expressible in terms of a finite number of them, the so-called integral basis $B(\Gamma)$. With the usual scalar product defining the contravariant metric $\tilde{g}$ on $T_P^*\mathbb{C}$, the orthogonality of the coordinates and their separability properties are encoded in the metric subtensors $\tilde{g}_{\text{int}}$ (internal) and $\tilde{g}_{\text{ext}}$ (external). The coupling tensor $\tilde{g}_{ie}$ reflects the separability of the two subspaces. Whenever $\tilde{g}_{ie} = 0$, $E(\Gamma)$ is the orthogonal complement to $I(\Gamma)$,

$$T_P^*C = I(\Gamma) \oplus E(\Gamma),$$

and the metric $\tilde{g}$ is block-diagonal. In general, whereas $E(\Gamma)$ can be locally constructed orthogonally to $I(\Gamma)$ (i.e. $\tilde{g}_{ie}|_P = 0$), the orthogonality cannot be conserved by the integration $I_P(\Gamma) \to B(\Gamma)$ and the lack of a "global" orthogonality between $B(\Gamma)$ and $\overline{B}(\Gamma)$ is mainly responsible for the inevitable couplings between the internal and the external motions: $\tilde{g}$ is no longer block-diagonal. Nevertheless, there exists a great deal of flexibility in the choice of a basis for $I(\Gamma)$ and in the construction of $E(\Gamma)$, from which optimal orthogonalizations (hence separability) can be envisaged. The same situation prevails in the orthogonalization within each of the subspaces (couplings between internal motions, for instance) and it is very unlikely that a completely internal (or external) orthogonal basis can be constructed.

2.2. STRUCTURE AND METRIC OF THE CONFIGURATION SPACE

The metric space in which the transformations of coordinates take place is conveniently defined as the tensor product of the Euclidean "physical" space and a "label" space. Let the system of N interacting particles (whose masses are m_i) be described by the N position vectors $\boldsymbol{x}_i$. With a fixed origin and an arbitrary fixed (inertial) orthonormal frame $\{\boldsymbol{l}_a;\, a = 1, 2, 3\}$ centered at the origin, the $3N$ scalar products

$$x^{ia} = (\boldsymbol{x}_i, \boldsymbol{l}_a) \qquad (i = 1, 2, \ldots, N;\ a = 1, 2, 3) \tag{2.2}$$

are the components of the position vectors with respect to the inertial frame $\{\boldsymbol{l}_a\}$:

$$\boldsymbol{x}_i = \sum_a x^{ia} \boldsymbol{l}_a \,. \tag{2.3}$$

The ordered set of the $3N$ components x^{ia} can be viewed as the $3N$ components of a vector $\boldsymbol{X}$ describing the instantaneous configuration. In this way, instead of considering N particles moving in $\mathbb{R}^3$, we consider one particle moving in $\mathbb{R}^{3N}$. The covariant metric for the $3N$-dimensional configuration space is given by [2]

$$\underset{\sim}{g}(x) = \mathrm{diag}(D_N, D_N, D_N)\,, \tag{2.4}$$

where

$$D_N = \mathrm{diag}(m_1, \ldots, m_N)\,. \tag{2.5}$$

This representation suggests interpretation of the configuration space as the tensor product of the physical space $\mathbb{R}^3$ and a label space $\mathbb{R}^N$. The ordered set of $3N$ components x^{ia} can be viewed as the $3N$ coordinates of the configuration vector $\boldsymbol{X}$ in the basis $\{\boldsymbol{\varphi}_{ia}\}$, tensor product of the label basis $\{\boldsymbol{c}_i\}$ and the physical basis $\{\boldsymbol{l}_a\}$,

$$\boldsymbol{\varphi}_{ia} = \boldsymbol{c}_i \otimes \boldsymbol{l}_a \,, \tag{2.6}$$

$$\boldsymbol{X} = \sum_{ia} x^{ia} \boldsymbol{\varphi}_{ia} \,. \tag{2.7}$$

The metric tensor (covariant) is then the tensor product of the physical metric $\mathbf{I}_3$ and the label metric $\mathbf{D}_N$ (diagonal but not normed).

The configuration vector may additionally be interpreted as the set of $3N$ components x^{ia} of three N-dimensional label vectors γ_a,

$$\gamma_a = \sum_i x^{ia} c_i \,. \tag{2.3'}$$

This interpretation (see fig. 1) proves useful in the discussion of the mass quadrupole (tensor of inertia) whenever noninertial frames are defined: the scalar products of the vectors γ_a are related to the momenta of inertia of the molecular frame with respect to the inertial frame.

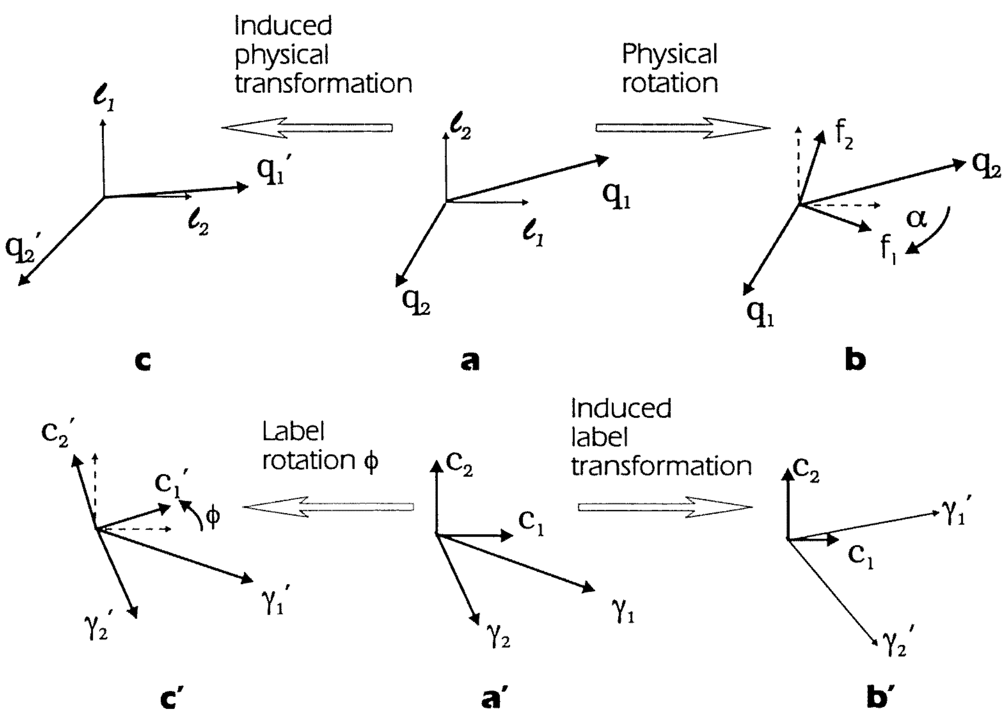

Fig. 1. Physical and label orthogonal transformations. (a) The internal configuration is represented in terms of the two Jacobi vectors q_1 and q_2 in the inertial frame $\{l_1, l_2\}$. (b) The same configuration in the noninertial frame $\{f_1, f_2\}$ obtained by the rotation $R(\alpha)$. (c) The internal configuration (a) is represented in terms of a new set of Jacobi vectors q_1' and q_2' obtained by the label rotation $\rho(\phi)$. (a′) The kinematic configuration in the label basis $\{c_1, c_2\}$ for the system referred to the inertial frame. (b′) The same kinematic configuration for the system referred to the noninertial frame. (c′) The same configuration in the label basis $\{c_1', c_2'\}$.

Under a linear transformation represented by the $3N \times 3N$ matrix **A**, the base vectors φ_{ia} transform into ε_{jb} according to the *covariant* law,

$$\varepsilon_{jb} = \sum_{ia} A_{jb}^{ia} \varphi_{ia} . \tag{2.8}$$

The metric tensor $\underset{\sim}{g}(x)$ transforms covariantly into $\underset{\sim}{g}(y)$,

$$\underset{\sim}{g}(y) = A\, \underset{\sim}{g}(x) A^{t}. \tag{2.9}$$

In this new coordinate system, the configuration has components y^{jb} obtained *contravariantly* from the coordinates x^{ia} in such a way that

$$x^{ia} = \sum_{jb} A_{jb}^{ia} y^{jb} . \tag{2.10}$$

Equation (2.10) is usually viewed as the law of transformation of the dual basis $\{x^{ia}\}$ (spanning the dual configuration space $\mathbb{C}^*$ of the linear forms defined on $\mathbb{C}$) whose metric tensor is obtained by inversion of $\underset{\sim}{g}(x)$:

$$\tilde{g}(x) = \underset{\sim}{g}^{-1}(x) = (D_N^{-1}, D_N^{-1}, D_N^{-1}) .$$

To avoid any confusion, the following symbolism will be used in this paper. A list of symbols appears in the appendix.

basis for C	components	basis for C^*	components
e_{ia}	x^{ia}	e^{ia}	x_{ia}
configuration vectors X		dual vectors χ (linear forms)	
contravariant		covariant	
$X = \sum_{ia} x^{ia} e_{ia}$		$\chi = \sum_{ia} x_{ia} e^{ia}$	

2.3. TRANSLATION INVARIANTS AND THE JACOBI VECTORS

The first step to be taken in the procedures directed towards separation of variables is trivially achieved by considering the invariance of the relative positions of the particles under translations in the physical space $\mathbb{R}^3$, yielding a partitioning of the $3N$-dimensional configuration space $\mathbb{C}$ into a $(3N-3)$-dimensional relative space $\mathcal{R}$ and a three-dimensional center-of-mass space $\mathcal{G}$

$$\mathbb{C} = \mathcal{R} \oplus \mathcal{G}.$$

Although the separation of the relative motion is a quite trivial matter, it is worth re-interpreting the whole procedure since it is a simplified version of the theory discussed subsequently. Translation invariant coordinates are obtained from a *linear process* as opposed to *curvilinear transformations* characterizing the other group invariants. Moreover, the choice for an external subspace (complementary space to the space generated by the translation invariants) being arbitrary, the coordinates of the center-of-mass are chosen since they generate a subspace orthogonal to the relative subspace.

Indeed, under any translation acting in the physical space, the position vectors $\boldsymbol{x}_i$ transform as

$$\boldsymbol{x}_i \to \boldsymbol{x}_i + \boldsymbol{a} \tag{2.11}$$

and any function $f(\boldsymbol{x}_i - \boldsymbol{x}_j \equiv \boldsymbol{r}_{ij})$ is left invariant under the group of physical translations. In particular, the scalar functions $r_{ij}^a = (\boldsymbol{x}_i - \boldsymbol{x}_j, \boldsymbol{l}_a)$ provide a rational integral basis for translation invariants, that is, any function $f(x^{ia})$ of the coordinates x^{ia} invariant under the group of the translations in the physical space is expressible in terms of the r_{ij}^a.

It should be noticed at this point that the relative vectors $\boldsymbol{r}_{ij}$ are not necessarily all independent $(\boldsymbol{r}_{ij} + \boldsymbol{r}_{jk} = \boldsymbol{r}_{ik})$. $\mathcal{R}$ is spanned by choosing an appropriate set of $N-1$ independent label vectors $\boldsymbol{c}_i - \boldsymbol{c}_j = \boldsymbol{e}_k$,

$$\mathcal{R} = \text{SPAN}(\boldsymbol{e}_k \otimes \boldsymbol{l}_a \equiv \boldsymbol{\varepsilon}_{ka}).$$

The dual space $\mathcal{R}^*$ may be spanned by any set of $3N-3$ linearly independent linear combinations of the covariant vectors ε^{ka}. For instance, the internal space with respect to the physical translations could be spanned by the $(3N-3)$-dimensional basis

$$\begin{aligned} e^{1a} &= \varepsilon^{1a} - \varepsilon^{2a}, \\ e^{2a} &= \varepsilon^{1a} - \varepsilon^{3a}, \\ &\dots \\ e^{N-1,a} &= \varepsilon^{1a} - \varepsilon^{N,a} \qquad (a = 1, 2, 3). \end{aligned}$$

With this basis, the metric $\tilde{g}$ for $\mathcal{R}^*$ is no longer diagonal,

$$\tilde{g} = \begin{bmatrix} m_1^{-1} + m_2^{-1} & m_1^{-1} & \cdots & m_1^{-1} \\ m_1^{-1} & m_1^{-1} + m_3^{-1} & \cdots & m_1^{-1} \\ \cdots & \cdots & \cdots & \cdots \\ m_1^{-1} & m_1^{-1} & \cdots & m_1^{-1} + m_N^{-1} \end{bmatrix}.$$

The complementary subspace is spanned by a set of three linear combinations of the base vectors ε^{ka} which are linearly independent with respect to the vectors

e^{ja}, for instance, the three vectors $E^a = \sum_i \varepsilon^{ia}$ ($a = 1, 2, 3$) are linearly independent with respect to the set $\{e^{ja}; j = 1, \ldots, N-1\}$ since the determinant of the linear transformation

$$\{\varepsilon^{ia}\} \rightarrow \{e^{ja}, E^a\}$$

is not zero.

It is easily demonstrated that if $\boldsymbol{x}_G$ is the position vector of the center-of-mass, the three vectors $\boldsymbol{x}_G \otimes \boldsymbol{l}_a$ span the complementary subspace $\mathcal{G}$ and, consequently, $\mathcal{G}^*$ is spanned by the corresponding dual basis $\{\varepsilon^{G_a}\}$. Both subspaces $\mathcal{R}^*$ and $\mathcal{G}^*$ are mutually orthogonal and Ψ is expressible as the product $\psi_R \psi_G$, whereas $T = T_R + T_G$, yielding an exact separation of the relative and center-of-mass motions.

With a view to diagonalizing T_R, another transformation is performed by converting the nonorthonormal label basis $\{\boldsymbol{e}_i\}$ (metric g) into an orthonormal counterpart $\{\boldsymbol{n}_i\}$ (metric $\mathbf{I}_N$) by a so-called label orthonormalizing transformation $\mathbf{O}$:

$$\mathbf{O}\colon\ \varepsilon \rightarrow \phi = \mathbf{O}\varepsilon \tag{2.12}$$

satisfying

$$\mathbf{O}\,\tilde{g}\,\mathbf{O}^{\mathrm{t}} = \mathbf{I}_N \,.$$

The configuration vector is now expressed as

$$\boldsymbol{x} = \sum_{ia} q^{ia} \boldsymbol{\phi}_{ia} \,, \tag{2.13}$$

where

$$\boldsymbol{\phi}_{ia} = \boldsymbol{n}_i \otimes \boldsymbol{l}_a$$

are orthonormal base vectors

$$(\boldsymbol{\phi}_{ia}, \boldsymbol{\phi}_{jb}) = \delta_{ij}\, \delta_{ab} \,.$$

Procedure (2.12) is not unique and can be determined by considering specific criteria such as the symmetry of the system, etc. As a result, the set of $N-1$ interparticle vectors $\{\boldsymbol{r}_{ij}\}$ is transformed into a set of so-called Jacobi vectors $\{\boldsymbol{q}_j\}$ orthonormal in label space

$$\boldsymbol{q}_i = \sum_a q^{ia} \boldsymbol{l}_a \,, \tag{2.14}$$

where $q^{ia} = (\boldsymbol{q}_i, \boldsymbol{l}_a)$ are $3N-3$ orthogonal translation invariant coordinates. With this procedure, $\mathcal{R}$ has recovered its Euclidean property, hence simplifying further transformation.

3. Tangent and cotangent spaces

The next step in the procedure is to consider the invariance properties with respect to orthogonal transformations in both the physical and the label spaces. In this case, any attempt to partition the relative subspace into a rotational invariant subspace and its complement involves considering curvilinear transformations of the $3n$ ($n \equiv N-1$] Cartesian coordinate q^{ia}: the elements of the matrix A in eq. (2.8) are no longer constants, as can easily be seen by examining the transformation of the inertial frame $\{\boldsymbol{l}_a\}$ into a noninertial frame $\{\boldsymbol{f}_a\}$. The new components of the Jacobi vectors are given by

$$(\boldsymbol{q}_i, \boldsymbol{f}_a) = q'^{ia} = \sum_b R_{ba} q^{ib}, \tag{3.1}$$

where R_{ba} are the direction cosines of $\boldsymbol{f}_a$ with respect to $\boldsymbol{l}_a$. The requirement for $\{\boldsymbol{f}_a\}$ to be noninertial implies that the R_{ab} are functions of the q^{ib} [6]. The same situation prevails with rotations in label space. Any orthogonal transformation in label space (represented by the $n \times n$ matrix ρ) transforms the set of Jacobi vectors $\{\boldsymbol{q}_i\}$ into a new set $\{\boldsymbol{y}_j\}$ whose components in the noninertial frame $\{\boldsymbol{f}_a\}$ are given by

$$y^{ia} = \sum_j \rho_{ji} q^{ja} \tag{3.2}$$

and where once again ρ_{ji} are given functions of the q^{ja}.

The construction of curvilinear coordinates is approached via linear transformations in the cotangent space [19] at a point P. Locally, the usual co- and contravariant laws given by, respectively, eqs. (2.8) and (2.9) are applicable. The elements of the matrix A are now functions of the coordinates q^{ia} evaluated at the point P.

The relative configuration basis $\{\phi_{ia}\}$ defined in the previous section (eq. (2.13)) is orthonormal and is used as a basis $\{\phi_{ia}|_P\}$ for the vector space $T_P\mathbb{C}$ tangent at $P \in \mathbb{C}$. Any linear combination of the base vectors $\phi_{ia}|_P$ with C^∞-coefficients evaluated at P is a vector of $T_P\mathbb{C}$, providing by integration a vector field. Let $\{u^k; k = 1, \ldots, 3n\}_P$ be a set of $3n$ independent C^∞-functions of q^{ia} (the Jacobian of the transformation is non-zero). The set $\{u^k\}$ defines a basis $\{\varepsilon_k\}$ for $T_P\mathbb{C}$,

$$\varepsilon_k = \sum_{ia} \frac{\partial q^{ia}}{\partial u^k}\Big|_P \phi_{ia}. \tag{3.3}$$

ε_k is obviously directed tangent to the curve defined by u^k (u^i are constant for $i \neq k$). With this interpretation [20], the elements of the matrix A are the contravariant components of ε_k in the Cartesian basis and (3.3) represents the linear transformation of the Cartesian basis $\{\varphi_{ia}\}$ into the basis $\{\varepsilon_k\}$. After having temporarily re-labeled the indices "ia" with a single index j and by using matrix notation, the following holds:

$$A_{kj} = \frac{\partial q^j}{\partial u^k}. \tag{3.4}$$

The covariant metric tensor in the coordinates u^k is given by

$$\underset{\sim}{g}(u) = A\,\underset{\sim}{g}(q)A^{\mathrm{t}} = AA^{\mathrm{t}}. \tag{3.5}$$

Its elements are in general functions of the coordinates.

The dual configuration space $\mathbb{C}^*$ (vector space of the linear forms defined on $\mathbb{C}$) is spanned by the basis $\{\phi^j\}$ dual to $\{\phi_j\}$ which transforms according to the contravariant law:

$$\varepsilon^k = \sum_j B_{jk}\phi^j, \tag{3.6}$$

where

$$B_{jk} = \frac{\partial u^k}{\partial q^j} \tag{3.7}$$

are the elements of the matrix $B = A^{-1}$.

In particular, if the functions u^k are linear expressions in q^j, the above relations reduce to the usual linear transformations since the matrix A has constant elements:

$$u^k = \sum_j B_{jk} q^j. \tag{3.8}$$

The contravariant metric tensor $\tilde{g}$ is obtained by inverting $\underset{\sim}{g}$,

$$\tilde{g} = \underset{\sim}{g}^{-1}.$$

3.1. CONDITIONS OF INTEGRABILITY

At P, the dual basis $\{\phi^j\}$ spans the cotangent space $T_P^*\mathbb{C}$ and any linear combination of the base vectors with C^∞ coefficients evaluated at P defines a 1-form χ (covariant vector)

$$\chi = \sum_j \chi_j \phi^j,$$

where the covariant components χ_j are $3n$ C^∞ functions of q^{ia}. By integration, the form χ will provide a function $w(q^{ia})$ which satisfies the same invariance properties. In principle, the integration of χ can be carried out by means of finding integrating factors μ making $\mu\chi$ an exact differential. If the form χ is immediately integrable, that is, without multiplication by any factor, its primitive w can be obtained by quadrature of $\mathrm{d}\chi = 0$. If the differential is not exact, as is usually the case, a set of integrating factors μ can always be found to make exact the differential $\mathrm{d}(\mu\chi)$. In this case, the partial differential coefficients of the primitive w are proportional to the coefficients χ_j,

$$w_j = \mu\chi_j$$

and the conditions of integrability

$$w_{ij} = (\mu\chi_i)_j$$

imply that

$$\mu(\chi_{ij} - \chi_{ji}) = \chi_j\,\mu_i - \chi_i\,\mu_j. \tag{3.9}$$

A direct evaluation of μ depends upon equations of more advanced character than the ordinary first-order equations under consideration. Apart from some very few special cases, these differential equations cannot be solved analytically [17] although various numerical methods can be successfully used. Hopefully, for the orthogonal groups we are concerned with here, the problem can be somewhat simplified as illustrated below.

3.2. RATIONAL INTEGRAL BASES

It is a well-known result from the theory of the vector invariants that all invariants with respect to most of the usual groups Γ of linear transformations acting on a vector space are expressible in terms of a finite number among them. For instance, a typical table of the basic invariants of the orthogonal group and depending on m vectors $\boldsymbol{x}_i$ consists of all the m^2 scalar products $(\boldsymbol{x}_i, \boldsymbol{x}_j)$. In particular, the invariants depnding on the n Jacobi vectors $\boldsymbol{q}_i$ are expressible in terms of the n^2 scalar products $(\boldsymbol{q}_i, \boldsymbol{q}_j)$ constituting the Gram matrix $\mathbf{G}$. On the other hand, the invariants depending on the three label vectors $\boldsymbol{\gamma}_a$ defined in eq. (2.3′) are expressible in terms of the nine scalar products (γ_a, γ_b), elements of the mass quadrupole $\mathbf{M}$. This finite number of typical invariants constitutes a rational integral basis for any Γ-invariant function.

3.3. INVARIANT COTANGENT SUBSPACES

A second useful result of the theory of vector invariants will serve as the keystone of the suggested procedure. It can be stated as follows: the total differential (covariant vector) of a Γ-invariant is Γ-invariant. Conversely, if $\chi(q^{ia})$ is a Γ-invariant differential form

$$\chi(q_{ia}) = \sum_j \chi_j \phi^j, \tag{3.10}$$

then a Γ-invariant integrating factor μ can be found. The form $\mu\chi$ is integrable by quadrature and the primitives of $\mathrm{d}(\mu\chi) = 0$ are Γ-invariant. This is illustrated below for the orthogonal group. A more general discussion (involving the symmetric groups) is currently in preparation. The problem of constructing Γ-invariants can be reduced in a first step to the infinitesimal level (cotangent space) and, subsequently, by integration, moved back to the level of rational integral functions.

Formally, let Γ be a group of linear transformations acting in the cotangent space $T_P^*\mathbb{C}$. The subspace W is invariant under Γ if, for any $\gamma \in \Gamma$,

$$\gamma W \subset W. \tag{3.11}$$

In such a case, Γ defines a g-dimensional bases $\{\sigma^1, \ldots, \sigma^g\}$ in W in which γ can be represented by the triangular matrix

$$\gamma = \begin{pmatrix} \gamma_{11} & 0 \\ \gamma_{12} & \gamma_{22} \end{pmatrix}, \tag{3.12}$$

where γ_{11} and γ_{22} are, respectively, $g \times g$ and $(3n - g) \times$ matrices.

Any linear combination χ of the base vectors $\{\sigma^1, \ldots, \sigma^g\}$ with Γ-invariant coefficients is an invariant covariant vector with respect to Γ and generates by integration a family of functions which are Γ-invariant. Similarly, any linear combination of the dual basis which is not expressible as the linear combination of $\{\sigma^1, \ldots, \sigma^g\}$ is not invariant under Γ. By integration, the linear combination will generate (if integrable) a function which is not Γ-invariant (external coordinate with respect to Γ). Any set of $3n - g$ such linearly independent combinations will span the Γ-external cotangent subspace. In this way, the configuration space has been partitioned into an internal Γ-invariant subspace $I(\Gamma)$ and an external space $E(\Gamma)$ with respect to Γ-invariance. Obviously, the two subspaces are disjoint only if $E(\Gamma)$ is the orthogonal complement to $I(\Gamma)$,

$$I(\Gamma) \cup E(\Gamma) = T_P^*C \to I(\Gamma) \cap E(\Gamma) \neq \phi,$$

$$I(\Gamma) \oplus E(\Gamma) = T_P^*C \to I(\Gamma) \cap E(\Gamma) = \phi.$$

The basis of $\{\phi^1, \ldots, \phi^g\}$ can be orthogonalized by any standard procedure [2,3] (Gram–Schmidt, ES, IS, ...). However, the generators obtained after the orthogonalization are not necessarily integrable into a Γ-invariant solution. Indeed, let $\{\chi^i\colon i = 1, \ldots, g\}$ be an orthonormal basis obtained by the orthogonalization represented by the $g \times g$ matrix O. The generators χ^i have the form

$$\chi^i = \sum_j O_{ij}\phi^j \quad (j = 1, \ldots, g).$$

For χ^i to generate a Γ-invariant solution, the two following points must hold:

(1) the coefficients O_{ij} are Γ-invariant,

(2) the integrating factor is Γ-invariant.

For the orthogonal group $O(n)$, it is shown in the next section that the elements (σ^k, σ^l) of the contravariant metric g are functions of the elements G^{ij} of the Gram matrix $\mathbf{G}$ which constitute a rational basis for the orthogonal invariants. Any orthonormalization O transforms the basis $\{\sigma^k\}$ into an orthonormal basis $\{\eta^k\}$ according to

$$O \underset{\sim}{g} O^t = I,$$

where I is the g-dimensional unit tensor. Hence,

$$\eta^k = \sum_l O_{kl}(G^{ij})\sigma^l.$$

By rescaling the η^k (integrating factor $\mu_k(G^{ij})$), the forms $\mu_k\eta^k$ are made integrable and provide the set of g orthogonal $O(n)$-invariants. Although conceptually simple, the procedure requires the tremendous task of finding analytic expressions for the integrating factors μ_k.

The procedure is shown in the following scheme:

basic Γ-invariants —derivation→ cotangent base vectors

| orthonormalization ↓

orthonormal basis

| rescaling ↓

orthogonal Γ-invariants ←integration— integrable basis

The concept of partitioning can be easily extended to more than one group of linear transformations and common invariants could be envisaged. For instance, let Γ_1 and Γ_2 be two groups whose generators are, respectively, $\{\sigma^1, \ldots, \sigma^g\}$ and $\{\lambda^1, \ldots, \lambda^h\}$. Assuming that $\mathrm{SPAN}\{\sigma^1, \ldots, \sigma^g\} \cap \{\lambda^1, \ldots, \lambda^h\}$ is not empty, there exist common generators for which integrating factors can be found and providing common invariant integral curves.

3.4. EXAMPLE: SPHERICAL COORDINATES

Spherical coordinates are derived here in order to illustrate how the concept of orthogonal invariance is used in the construction of globally orthogonal coordinates. This simple example is typical of orthogonal invariants in a three-dimensional space and depending on a single vector. The procedure followed hereafter is generalized in the next section for orthogonal invariants in n-dimensional space and depending on an arbitrary number $k \leq n$ of vectors. For this reason, it is worthwhile to work out the scheme in some detail.

Let $\boldsymbol{x}$ be a vector of $\mathbb{R}^3$ whose components with respect to the orthonormal basis $\{\boldsymbol{l}_a\}$ are x^a,

$$\boldsymbol{x} = x^1 \boldsymbol{l}_1 + x^2 \boldsymbol{l}_2 + x^3 \boldsymbol{l}_3.$$

At the point P, $\{\boldsymbol{l}_a\}_P$ is a basis for the tangent space, whereas $\{\boldsymbol{l}^a\}_P$ is the dual basis (cotangent space at P):

$$g_P = I_3.$$

The only invariant under $O(3)$ acting in $\mathbb{R}^3$ and depending on the vector $\boldsymbol{x}$ is

$$r(x^a) = (\boldsymbol{x}, \boldsymbol{x}) = \sum_a (x^a)^2,$$

which constitutes a one-dimensional integral basis for $O(3)$-invariants. It should be noticed that it is the length $r^{1/2}$ that is usually used as a coordinate. One seeks two coordinates (preferably orthogonal) to complement r in $\mathbb{R}^3$.

At P, let the covariant vector $e^r|_P$ be defined by (after having divided by a factor of 2)

$$e^r|_P = \sum_a x_a l^a|_P .$$

$e^r|_P$ is a basis for the one-dimensional internal subspace. Two external coordinates can be generated by any linear combination of $\{l^a\}|_P$ which are linearly independent with respect to $e^r|_P$. For instance, an easy choice would be

$$\varepsilon^1|_P = -x_2 l^1|_P + x_1 l^2|_P ,$$

$$\varepsilon^2|_P = x_1 l^1|_P - x_3 l^3|_P .$$

The metric tensor is not diagonal: the elements (evaluated at P) are as follows:

$$\begin{array}{lll} g^{rr} = r & g^{r1} = 0 & g^{r2} = x_1^2 - x_3^2 \\ & g^{11} = x_1^2 + x_2^2 & g^{12} = -x_1 x_2 \\ & & g^{22} = x_1^2 + x_3^2 . \end{array}$$

g can be diagonalized in several ways by any orthogonalization procedure. For instance, by a "non-normalizing" Gram–Schmidt procedure, one obtains

$$(1) \qquad \varepsilon^1|_P = -x_2 l^1|_P + x_1 l^2|_P ,$$

$$(2) \qquad \varepsilon^2|_P = -x_1 x_3 l^1|_P - x_2 x_3 l^2|_P + \left(x_1^2 + x_2^2\right) l^3|_P .$$

The metric tensor is now

$$\begin{array}{lll} g^{rr}=r & g^{r1}=0 & g^{r2}=0 \\ & g^{11}=x_1^2+x_2^2 & g^{12}=0 \\ & & g^{22}=r(x_1^2+x_2^2)\,. \end{array}$$

The integrability of the two differential forms (1) and (2) is not immediate:

(1) By choosing $\mu = 1/x_1x_2$ as an integrating factor, $\mu\varepsilon^1|_P$ becomes an exact differential generating the solutions $F(x_1/x_2)$: for instance, $\Theta = \tan^{-1}(x_1/x_2)$.

(2) In addition, by choosing $\lambda = [x_1^2 + x_2^2]^{-1/2}$ as an integrating factor for (2), $\lambda\varepsilon^2|_P$ generates the solutions $F(x_3/[x_1^2+x_2^2+x_3^2]^{1/2})$: for instance, $\Phi = \cos^{-1}(x_3/[x_1^2+x_2^2+x_3^2]^{1/2})$.

This achieves the separation of the curvilinear coordinates into a rotational invariant (r) and two external, orthogonal coordinates (Θ and Φ). However, different orthogonalizations can be carried out in the cotangent space by a rotation $R(\alpha)$ of the vectors $(\mu\varepsilon^1|_P, \lambda\varepsilon^2|_P)$ in the plane orthogonal to $\varepsilon^r|_P$. The integrability of the resulting 1-forms $(\varepsilon'^1|_P, \varepsilon'^2|_P)$ of course imposes conditions on the function $\alpha(x^1, x^2, x^3)$. Indeed, any function depending only on r can be used as an angle for the rotation providing an integrable set $(\varepsilon'^1, \varepsilon'^2)$.

4. Rotational invariants: integral bases

Orthogonal invariants depending on n vectors $\boldsymbol{q}_i$ of a k-dimensional vector space ($n \leq k$) are expressible in terms of the n^2 scalar products

$$G^{ij} = (\boldsymbol{q}_i, \boldsymbol{q}_j) = \sum_a q^{ia}q^{ja}\,. \tag{4.1}$$

G^{ij} are the elements of the so-called symmetric Gram matrix (really a contravariant tensor) $\mathbf{G}$ of the vectors $\boldsymbol{q}_i$. The n^2 invariants G^{ij} are not all independent:

(1) from $G^{ij} = G^{ji}$, there are n independent diagonal orthogonal invariants G^{ii} and $n(n-1)/2$ different off-diagonal elements G^{ij},

(2) depending on the dimensions n and k, the different G^{ij} are not necessarily independent ($\rho(\mathbf{G}) - n$, where $\rho(\mathbf{G})$ is the rank of $\mathbf{G}$, is the number of relationships among the off-diagonal elements).

For instance, there are $3n - 3$ independent orthogonal invariants in $\mathbb{R}^3$ and depending on n vectors, that is,

n "radial" invariants G^{ii},

$2n - 3$ independent "angular" invariants G^{ij} $(i \neq j)$,

$(n^2 - 5n + 6)/2$ relationships between the different G^{ij}.

For $n = 2$ or 3, $\rho(\mathbf{G}) = 2$ or 3 and all the off-diagonal elements are independent.

The procedure for generating curvilinear coordinates invariant under the orthogonal group acting in different subspaces of the configuration space is illustrated in this section for the three-dimensional physical space and the n-dimensional label space. Integral bases for both the internal and the external subspaces are obtained in a natural fashion from the invariance properties of the Gram matrix **G** of the Jacobi vectors and the mass quadrupole **M** of the noninertial frame.

4.1. MASS QUADRUPOLE M AND GRAM MATRIX G

The discussion is greatly simplified by using the dyadic formalism [21]. Let Q be the configuration dyadic defined as the tensor product of the label and physical dyads d_n and d_3,

$$Q = d_n \otimes d_3. \tag{4.2}$$

Q is represented by the $n \times 3$ matrix of the Cartesian coordinates q^{ia},

$$Q = \begin{pmatrix} q^{11} & q^{12} & q^{13} \\ q^{21} & q^{22} & q^{23} \\ \cdots & \cdots & \cdots \\ q^{n1} & q^{n2} & q^{n3} \end{pmatrix}. \tag{4.3}$$

Two fundamental tensors **M** and **G** are obtained by dyadics product:

(1) the mass quadrupole M defined as

$$\mathbf{M} = Q^{\mathrm{t}} Q, \tag{4.4}$$

(2) the Gram tensor G defined as

$$\mathbf{G} = Q Q^{\mathrm{t}}. \tag{4.5}$$

Explicitly, **M** and **G** can be represented by the matrices

$$M^{ab} = \sum_i q^{ia} q^{ib} \qquad (3 \times 3), \tag{4.6}$$

$$G^{ij} = \sum_a q^{ia} q^{ja} \qquad (n \times n). \tag{4.7}$$

The mass quadrupole **M** is related to the more conventional tensor of inertia I by

$$I = \mathrm{Tr}\,\mathbf{M}\ \mathbf{I}_3 - \mathbf{M}. \tag{4.8}$$

Geometrically, M^{ab} is the scalar product of the label vectors γ_a and γ_b,

$$\gamma_a = \sum_i q^{ia} c_i , \tag{4.9}$$

where $\{c_i\}$ are the label base vectors defined in eq. (2.6) and G^{ij} is the scalar product of the Jacobi vectors q_i and q_j.

4.2. PROPERTIES OF M AND G

(1) **M** and **G** are both symmetric, real and positive definite matrices. They are diagonalizable by real proper orthogonal matrices acting in, respectively, the 3×3 physical and the $n \times n$ label space,

$$\mathbf{R}^t\mathbf{M}\mathbf{R} = \Lambda, \tag{4.10}$$

$$\rho^t\mathbf{G}\rho = \Gamma, \tag{4.11}$$

where

$$\Lambda = \mathrm{diag}(\lambda_1, \lambda_2, \lambda_3), \tag{4.12}$$

$$\Gamma = \mathrm{diag}(\gamma_1, \gamma_2, \ldots, \gamma_n). \tag{4.13}$$

(2) **M** and **G** have the same trace,

$$t \equiv \mathrm{Tr}\,\mathbf{M} = \mathrm{Tr}(Q^tQ) = \mathrm{Tr}(QQ^t) = \mathrm{Tr}\,\mathbf{G}. \tag{4.14}$$

(3) **M** and **G** have the same determinant,

$$d \equiv \det \mathbf{M} = \det(Q^tQ) = \det(QQ^t) = \det \mathbf{G}. \tag{4.15}$$

(4) The eigenvalues of **G** are as follows:

$$\gamma_a = \lambda_a \quad \text{for } a = 1, 2, 3; \quad \gamma_a = 0 \quad \text{for } a > 3. \tag{4.16}$$

In particular, for $n = 2$ or 3,

$$R^t\mathbf{M}R = \lambda = \rho^t\mathbf{G}\rho. \tag{4.17}$$

Proof

The eigenvalue equation for **M** is

$$\mathbf{M}p_a = \lambda_a p_a,$$

where p_a is the (physical space) eigenvector corresponding to the eigenvalue λ_a. By premultiplying by Q, we conclude that λ_a is also an eigenvalue for **G** with corresponding (label space) eigenvector Qp_a,

$$Q\mathbf{M}p_a = \lambda_a Qp_a = (QQ^t)Qp_a = \lambda_a(Qp_a) = \mathbf{G}(Qp_a).$$

By using the trace identity and the non-negative property of the eigenvalues λ_a and γ_a, the theorem is proved.

The three vectors p_a constitute a noninertial frame in which the mass quadrupole (hence, the tensor of inertia) is diagonal: the instantaneous principal axes of inertia frame (IPAI). With respect to this frame, the components of p_a are (R_{1a}, R_{2a}, R_{3a}). Therefore, the components of Qp_a are the Cartesian components y^{ia} of the Jacobi vectors q_i with respect to the principal axes frame $\{p_a\}$,

$$Qp_a = \mathrm{col}(y^{1a}, y^{2a}, \ldots, y^{na}).$$

After normalization and recalling the definition of the eigenvalues λ_a,

$$\lambda_a = \sum_k (y^{ka})^2,$$

the eigenvalue equation for $\mathbf{G}$ in terms of the label base vectors c_k is

$$\mathbf{G}g_a = \lambda_a^{-1/2} \sum_k y^{ka} c_k .$$

The eigenvectors g_a $(a > 3)$ corresponding to the zero eigenvalues of $\mathbf{G}$ are degenerate and they span an $(n-3)$ dimensional subspace of the label space orthogonal to the subspace spanned by g_1, g_2 and g_3.

For $n = 2$ or 3, the problem is particularly simple since there are as many g_a as c_i so that the components of g_a with respect to the label basis c_i are the elements of the rotation matrix ρ,

$$\rho_{ia} = g^{ia} = (g_a, c_i)$$

and can be parameterized by one (for $n = 2$) or three (for $n = 3$) Euler angles Φ_i.

4.3. ANALYTIC EXPRESSIONS FOR THE EIGENVALUES λ_a

For $n = 2$, the eigenvalues are obtained easily by solving the secular equation $|\mathbf{G} - \Lambda| = 0$,

$$\lambda_1 = \tfrac{1}{2}[t + (t^2 - 4d)^{1/2}], \quad \lambda_2 = \tfrac{1}{2}[t - (t^2 - 4d)^{1/2}]. \tag{4.18}$$

For $n = 3$, the secular equation for G reads as

$$\lambda^3 - t\lambda^2 + s\lambda - d = 0,$$

where s is the sum of the three principal minors of $\det G$. The solutions of this cubic equation are obtained from the Cardan formulae [22]

$$\lambda_1 = t/3 + P + Q, \quad \lambda_2 = t/3 + \omega P + \omega^2 Q, \quad \lambda_3 = t/3 + \omega^2 P + \omega Q, \tag{4.19}$$

where ω is a cubic root of 1 ($\neq 1$) and P and Q are given by

$$P = [-q/2 + (p^3/27 + q^2/4)^{1/2}]^{1/2}, \quad Q = [-q/2 - (p^3/27 + q^2/4)^{1/2}]^{1/2},$$

where

$$p = s - t^2/3, \quad q = -2t^3/27 + ts/3 - d.$$

4.4. INVARIANCE PROPERTIES FOR M AND G

Under a physical linear transformation T, the dyadic $Q(q)$ transforms into $Q'(q)$,

$$Q(q) \xrightarrow{T} Q'(q) = Q(q)T. \tag{4.20}$$

With a passive interpretation, T represents a change of basis in the physical space, whereas the Jacobi vectors remain fixed with respect to the inertial frame. With an active interpretation, the Jacobi vectors are transformed into a new set of physical vectors.

M and **G** transform according to

$$\mathbf{M}' = T^t Q^t(q) Q(q) T = T^t \mathbf{M} T, \tag{4.21a}$$

$$\mathbf{G}' = Q(q) T T^t Q^t(q). \tag{4.21b}$$

In particular, if T is orthogonal,

$$\mathbf{G}' = \mathbf{G}.$$

Under a label linear transformation L, the dyadic $Q(q)$ transforms into $Q(r)$,

$$Q(q) \xrightarrow{L} Q(r) = LQ(q), \tag{4.22}$$

where $Q(r)$ is the configuration dyadic of the components of a set $\{\boldsymbol{r}_i\}$ of linearly independent physical vectors representing the same configuration.

M and **G** transform according to

$$\mathbf{M}(r) = Q^t(r) Q(r) = Q^t(q) L^t L Q(q), \tag{4.23a}$$

$$\mathbf{G}(r) = Q(r) Q^t(r) = L Q(q) Q^t(q) L^t. \tag{4.23b}$$

In particular, if L is orthogonal, the set $\{\boldsymbol{r}_i\}$ is another set of Jacobi vectors $\{\boldsymbol{q}'_i\}$ and **M** is invariant under label orthogonal transformations

$$\mathbf{M}(q') = \mathbf{M}(q).$$

4.5. INTERNAL AND EXTERNAL SUBSPACES

Since **G** is invariant under physical orthogonal transformations, the elements G^{ij} constitute an integral basis for the internal subspace $I \equiv B(O(3))$ and are referred to as the basic internal coordinates. The set $\{G^{ij}\}$ spans the internal subspace.

The diagonalization of **G** by the label orthogonal matrix ρ provides n angles Φ_i (kinematic external coordinates spanning the complement $L \equiv \overline{B}(O(n))$ of the kinematic space $K \equiv B(O(n))$. This yields a partition into

(1) n radial coordinates Q_i:

$$Q_i = \left[\sum_a (q^{ia})^2 \right]^{1/2},$$

(2) $n(n-1)/2$ angular coodinates θ_{ij}:

$$\theta_{ij} = \cos^{-1} \left[\sum_a q^{ia} q^{ja} \right] / Q_i \, Q_j \, .$$

The metric tensors are discussed in the next section, together with the orthogonalization after the infinitesimal bases have been introduced.

Since **M** is invariant under label orthogonal transformations, the elements M^{ab} are the basic kinematic coordinates spanning the subspaces K (M is a 3×3 matrix; hence, all six matrix elements $M^{ab} = M^{ba}$ are independent). This yields a partition into

(1) three radial kinematic coordinates:

$$\Gamma_a = \left[\sum_i (q^{ia})^2 \right]^{1/2},$$

(2) three angular kinematic coordinates:

$$\Psi_{ab} = \cos^{-1} \left[\sum_i q^{ia} q^{ib} \right] / \, \Gamma_a \Gamma_b \, .$$

From diagonalization of **M** by the physical orthogonal matrix R, one deduces the external coordinates $R_{ab}(\alpha_i)$ parameterized by the three external angles α_i spanning the external subspace $E \equiv \overline{B}(O(3))$ (complementary space for the internal subspace I) and describing the rotation of the principal axes with respect to the inertial frame.

The partition of the configuration space is achieved in two ways,

$$I \cup E = \mathbb{C} \rightarrow I \cap E = \varnothing,$$

$$K \cup L = \mathbb{C} \rightarrow K \cap L = \varnothing, \qquad \varnothing\text{: empty set.}$$

Since **M** and **G** have the same eigenvalues λ_a, the set $\{\lambda_a\}$ is invariant under both physical and label orthogonal transformations and constitutes an integral basis for the subspace $K \cap I$.

An alternate set could be $\{t, d, s\}$ since the λ_a are expressed in terms of these three "geometrical" invariants: hyperradius (trace t), sum of the principal minors s (surface of the parallelipiped) and the volume v (determinant) (from eqs. (4.18) and (4.19).

4.6. DIMENSIONS

$K \cap I$ generates coordinates which are internal and label invariant,

$$(K \cap I) \cup L \cup E = C = I \cup E,$$

hence,

$$\dim C = \dim(K \cap I) + \dim L + \dim E,$$

$$3n = 3 + (3n - 6) + 3;$$

this agrees with

$$\dim(K \cup I) = \dim C = \dim K + \dim I - \dim(K \cap I),$$

$$3n = 6 + (3n - 3) - 3.$$

For instance, $n = 3$;

$$9 = 6 + 6 - 3.$$

5. Rotational invariants: infinitesimal standpoint

As discussed in the previous section, under a physical orthogonal transformation R, the configuration dyadic $Q(q)$ in the representation $\{q\}$ transforms according to

$$Y(q) = Q(q)R, \tag{5.1a}$$

where $Y(q)$ is the dyadic in the same representation but referred to the noninertial frame. The separation of the internal and external coordinates is formally expressed by the relation

$$q^{ia} = \sum_k R_{ak}(\Theta^s) y^{ik}(u^r), \tag{5.2a}$$

where the external coordinates Θ^s are the Euler angles parameterizing the rotation matrix R (from inertial to noninertial frames) and $u^r(G^{ij})$ are some set of $3n - 3$ independent functions deduced from the elements of the Gram matrix.

Similarly, under the change of representation $\{q\} \to \{q'\}$, represented by the label orthogonal transformation L

$$Q(q') = LQ(q) \tag{5.1b}$$

and the separation of the variables is formally expressed by

$$q^{ka} = \sum_i L_{ik}(\Phi^s) q'^{ia}(\upsilon^r), \tag{5.2b}$$

where $\{\Phi^s\}$ is a set of Euler angles (*K*-external variables) parameterizing the $n \times n$ label orthogonal matrix L and $\upsilon^r(M^{ab})$ are some functions of the six kinematic orthogonal invariants deduced from the mass quadrupole in a given noninertial frame.

In the following, details of the discussion are worked out for the $O(3)$-invariants (physical space). The generalization for $O(n)$ (label space) presents no problem.

5.1. INTERNAL COORDINATES FOR PHYSICAL ROTATIONS

Since the elements G^{ij} of the symmetric Gram matrix remain invariant under external rotations ($\mathbf{R}\mathbf{G}R^t = \mathbf{G}$), they constitute a basis for the internal variables, that is, any internal coordinate may be expressed as a function of the variables G^{ij}.

The variables G^{ij} are expressible in terms of the q^{ia} according to

$$G^{ij} = \sum_a q^{ia} q^{ja} = G^{ji} \tag{5.3}$$

or, after renaming,

$$\text{radial coordinates:} \quad G^{ii} \equiv r^i = \sum_a (q^{ia})^2, \tag{5.4}$$

$$\text{angular coordinates:} \quad G^{ij} \equiv a^k = \sum_a q^{ia} q^{ja} \qquad (i \neq j). \tag{5.5}$$

The transformation of the Cartesian coordinates into the internal base functions r^i and a^k is curvilinear. Let $\mathrm{d}r^i$ and $\mathrm{d}a^k$ be the total differentials,

$$\mathrm{d}r^i = \sum_{k\ a} \partial_{ka} r^i \,\mathrm{d}q^{ka}, \quad \mathrm{d}a^k = \sum_{i\ a} \partial_{ia} a^k \,\mathrm{d}q^{ia}, \tag{5.6}$$

where ∂_{ia} stands for the partial differential with respect to q^{ia}. Locally, the covariant vectors (internal generators)

$$\varepsilon^i = \left(\partial_{11} r^i, \partial_{12} r^i, \ldots, \partial_{n3} r^i\right), \quad \varphi^k = \left(\partial_{11} a^k, \partial_{12} a^k, \ldots, \partial_{n3} a^k\right) \tag{5.7}$$

define a basis for the internal cotangent subspace. The $\partial_{jb} r^i$ and $\partial_{jb} a^i$ are the covariant components in the orthonormal basis $\{\phi^{jb}\}$. The components of the generators are readily obtained,

$$\partial_{ia} r^j = 2q^{ja}\delta_{ij}\,, \quad \partial_{ia} a^k = q^{ja}. \tag{5.8}$$

The scalar products $(\varepsilon^i, \varepsilon^j)$ are the elements of the contravariant internal subtensor I

$$\begin{pmatrix} r^1 & 0 & 0 & 0 & a^2 & a^3 \\ 0 & r^2 & 0 & a^1 & 0 & a^3 \\ 0 & 0 & r^3 & a^1 & a^2 & 0 \\ 0 & a^1 & a^1 & r^2+r^3 & a^3 & a^2 \\ a^2 & 0 & a^2 & a^3 & r^1+r^3 & a^1 \\ a^3 & a^3 & 0 & a^2 & a^1 & r^1+r^2 \end{pmatrix}, \tag{5.9}$$

which is not diagonal.

Any internal variable υ (that is, any function of the internal integrity base functions) is generated by a vector ε^υ which is a linear combination of the generators ε^i and φ^k,

$$\varepsilon^\upsilon = \sum_i A_i \varepsilon^i + \sum_k B_k \varphi^k, \tag{5.10}$$

where the coefficients A_i and B_k are the partial derivatives of υ with respect to r^i and a^k. The norm n_υ of the generator ε^υ is

$$n_\upsilon = (\varepsilon^\upsilon, \varepsilon^\upsilon)^{1/2}, \tag{5.11}$$

whereas the relative orientation of ε^υ with respect to the generators ε^i and φ^k is given by

$$\cos(\upsilon, r^i) = n_\upsilon^{-1} (r^i)^{-1/2} (\varepsilon^\upsilon, \varepsilon^i), \tag{5.12a}$$

$$\cos(\upsilon, a^i) = n_\upsilon^{-1} (r^j + r^k)^{-1/2} (\varepsilon^\upsilon, \varphi^k). \tag{5.12b}$$

As can be seen from the above relations, both the norm and the relative orientations of the generator ε^υ are functions of r^i and a^k (this is a general feature for curvilinear coordinates).

Conversely, let ε^u be a linear combination of the internal generators,

$$\varepsilon^u \equiv \sum_i a_i \varepsilon^i + \sum_k b_k \varphi^k, \tag{5.13}$$

where a_i and b_k are some given functions of r^i and a^k. The question is to find the internal variable u obtained by integrating ε^u. This can be done by solving the ordinary differential equation of the first order and of the first degree,

$$\sum_i a_i \,\mathrm{d}r^i + \sum_k b_k \,\mathrm{d}a^k = 0. \tag{5.14}$$

If this differential is immediate, that is, without multiplication by any factor, expressible in the form $\mathrm{d}u$, where u is a function of r^i and a^k, then the equation is exact and its primitive u can be obtained by quadrature. If the differential is not exact, as is usually the case, an integrating factor $\mu(r^i, a^k)$ can be found to make the differential exact

$$\mu\left(\sum_i a_i \,\mathrm{d}r^i + \sum_k b_k \,\mathrm{d}a^k\right) = 0. \tag{5.15}$$

In this case, the partial differential coefficients of the primitive $u(r^i, a^k)$ are proportional to the coefficients a_i and b_k,

$$u_i = \mu a_i, \quad u_k = \mu b_k, \tag{5.16}$$

Then

$$\frac{\partial(\mu a_i)}{\partial r^j} = \frac{\partial^2 u}{\partial r^j \,\partial a^i} \tag{5.17}$$

(condition of integrability)
$$= \frac{\partial^2 u}{\partial r^i \,\partial r^j}$$

$$= \frac{\partial(\mu a_j)}{\partial r^i} \quad \ldots \tag{5.18}$$

that is,

$$\mu\left\{\frac{\partial a_i}{\partial r^j} - \frac{\partial a_j}{\partial r^i}\right\} = a_j\mu_i - a_i\mu_j \quad \ldots \tag{5.19}$$

Geometrically, the integrating factor acts as a rescaling factor for the generator ε^u permitting the integrability of the differential,

$$\left(\sum_i a_i \,\mathrm{d}r^i + \sum_k b_k \,\mathrm{d}a^k\right).$$

In short, if the differential is not exact, ε^u is not generating the function u but a function μ (integrating factor) may be found in order to rescale ε^u into the integrable Ξ^u.

5.2. EXTERNAL VARIABLES FOR PHYSICAL ROTATIONS

Any set of three independent functions $\Theta^s = \Theta^s(q^{ia})$ which cannot be expressed as a function of the internal integrity base functions can be chosen as external variables. The concept of functional independence can be expressed mathematically as follows.

Let the total differential of Θ^s be

$$d\Theta^s = \sum_{i\ a} \partial_{ia}\Theta^s \, dq^{ia}$$

and let the local base vectors be

$$\tau^s \equiv \left(\partial_{11}\Theta^s, \partial_{12}\Theta^s, \ldots, \partial_{n3}\Theta^s\right). \tag{5.20}$$

In order to be linearly independent, the functions Θ^s must satisfy

(1) $\sum_s a_s\tau^s = 0$ iff $a_1 = a_2 = a_3 = 0$,

(2) $\sum_k b_k\varepsilon^k + c_s\tau^s = 0$ iff $b_1 = b_2 = \ldots = c_s = 0$ for $s = 1, 2, 3$,

(3) $\sum_k d_k\varphi^k + h_s\tau^s = 0$ iff $d_1 = d_2 = \ldots = h_s = 0$ for $s = 1, 2, 3$.

In short, if Z is the curvilinear transformation $(q^{ia}) \to (r^r, a^t, \Theta^s)$, the curvilinear coordinates are independent if the Jacobian of the transformation is not zero,

$$\det Z \neq 0.$$

It is easily verified that the three functions

$$\Theta^s = \sum_i q^{ir}q^{it} \quad (r, s, t \text{ are cyclic permutations}) \tag{5.21}$$

obey the above three criteria and therefore constitute an integrity basis for the external variables.

The components of the external generators are

$$\partial_{ir}\Theta^s = q^{it} \tag{5.22}$$

and the external sub-tensor E is

$$\begin{pmatrix} \Lambda^1 & \Theta^3 & \Theta^2 \\ \Theta^3 & \Lambda^2 & \Theta^1 \\ \Theta^2 & \Theta^1 & \Lambda^3 \end{pmatrix}, \tag{5.23}$$

where

$$\Lambda^1 = \sum_i [(q^{i2})^2 + (q^{i3})^2],$$
$$\Lambda^2 = \sum_i [(q^{i1})^2 + (q^{i3})^2],$$
$$\Lambda^3 = \sum_i [(q^{i2})^2 + (q^{i1})^2] \tag{5.24}$$

are the diagonal elements of the mass quadrupole of the Jacobi vectors in the inertial frame.

Any external variable is generated by a linear combination of at least one external generator and any internal generators:

$$\tau' = \sum_s a_s \tau^s + \sum_i b_i \varepsilon^i + \sum_j c_j \varphi^j, \tag{5.25}$$

where

$$(a_1, a_2, a_3) \neq (0, 0, 0).$$

The external variable Θ' is obtained by integrating the differential $d\Theta'$. The same comments concerning the exactness of the differential apply as above. Integrating factors are used in order to make exact $d\Theta'$.

With the internal rational basis (r^i, a^k) and the external basis (Θ^s), the two subspaces are not orthogonal: the coupling sub-tensor C is

$$\begin{pmatrix} q^{12}q^{12} & q^{11}q^{13} & q^{11}q^{12} \\ q^{22}q^{23} & q^{21}q^{23} & q^{21}q^{22} \\ q^{32}q^{33} & q^{31}q^{33} & q^{31}q^{32} \\ q^{22}q^{33} + q^{32}q^{23} & q^{31}q^{23} + q^{21}q^{33} & q^{31}q^{22} + q^{32}q^{21} \\ q^{13}q^{32} + q^{12}q^{33} & q^{31}q^{13} + q^{11}q^{33} & q^{12}q^{31} + q^{11}q^{32} \\ q^{13}q^{22} + q^{12}q^{23} & q^{21}q^{13} + q^{11}q^{23} & q^{21}q^{12} + q^{22}q^{11} \end{pmatrix}.$$

The global orthogonalization of the two subspaces cannot be achieved by any basis transformation, as illustrated in the following example.

5.3. FOUR-DIMENSIONAL PROBLEM

Let a system of three particles (ABC) be described by means of two Jacobi vectors $(\boldsymbol{q}_1, \boldsymbol{q}_2)$ in the two-dimensional physical space $\mathbb{R}^2$. It may happen that two different configurations are better described by two different GJV representations. This is the case, for instance, in processes involving dissociation-rearrangements. In fig. 1, the configuration (a) is better described by two Jacobi vectors $\{\boldsymbol{q}_i\}$ such that $\boldsymbol{q}_1$ is directed along the bond BC and $\boldsymbol{q}_2$ is along the line joining A to the center-of-mass of BC (this representation was called a "mobile" representation by Hirschfelder and co-workers [7]). In configuration (b), the most appropriate choice would be to take $\boldsymbol{q}_1'$ along the bond AB and $\boldsymbol{q}_2'$ along the line joining the center-of-mass of AB to C. The "physical" evolution of the system from (a) to (c) induces a "switching" of the set $\{\boldsymbol{q}_i\}$ to the set $\{\boldsymbol{q}_i'\}$. This transformation occurs in label space and is represented by a 2×2 orthogonal matrix ρ whose parameter is the kinematic variable ϕ (fig. 1c′).

5.4. INTEGRAL BASES

As usual, the Gram matrix $\mathbf{G}$ and the mass quadrupole $\mathbf{M}$,

$$G^{ij} = (\boldsymbol{q}_i, \boldsymbol{q}_j) = q^{i1}q^{j1} + q^{i2}q^{j2}, \tag{5.26a}$$

$$M^{ab} = (\boldsymbol{\gamma}_a, \boldsymbol{\gamma}_b) = q^{1a}q^{1b} + q^{2a}q^{2b}, \tag{5.26b}$$

provide integral bases for $O(2)$-invariants depending, respectively, on

(1) the two vectors $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$ of the physical space $\mathbb{R}^2$ referred to the inertial frame $\{\boldsymbol{l}_1, \boldsymbol{l}_2\}$ whose origin is at the center-of-mass and

(2) the two vectors $\boldsymbol{\gamma}_1$ and $\boldsymbol{\gamma}_2$ of the label space $\mathbb{R}^2$ referred to the label basis $\{\boldsymbol{c}_1, \boldsymbol{c}_2\}$.

The separation of variables is formally achieved by choosing as external variables the parameters of the 2×2 orthogonal matrices representing, respectively,

(1) physical space rotations $R(\Theta)$ transforming the inertial frame $\{\boldsymbol{l}_1, \boldsymbol{l}_2\}$ into a given noninertial frame $\{\boldsymbol{f}_1, \boldsymbol{f}_2\}$,

$$R(\Theta)\mathbf{M}(\boldsymbol{l})R^{\mathrm{t}}(\Theta) = \mathbf{M}(\boldsymbol{f}),$$

(2) label space rotations $\rho(\Phi)$ switching the representation $\{\boldsymbol{q}_i\}$ into $\{\boldsymbol{q}_i'\}$,

$$\rho(\Phi)G(\boldsymbol{q})\rho^{\mathrm{t}}(\Phi) = G(\boldsymbol{q}').$$

With respect to physical rotation invariance, the four variables are partitioned into $(G^{11}, G^{22}, G^{12}) \cup (\Theta)$ and with respect to kinematic invariance into $(M^{11}, M^{22}, M^{12}) \cup (\Phi)$.

5.5. INTERNAL COTANGENT SUBSPACES

In the orthonormal basis $\boldsymbol{\phi}_{ia} = \boldsymbol{c}_i \otimes \boldsymbol{l}_a$, the configuration vector $\boldsymbol{X}$ has components $(q^{11}, q^{12}, q^{21}, q^{22})$. For a configuration P, the four-dimensional cotangent space $T_P^*\mathbb{C}$ is spanned by the orthonormal dual basis $(\varepsilon^{11}, \varepsilon^{12}, \varepsilon^{21}, \varepsilon^{22})$.

The infinitesimal invariants for physical and kinematic orthogonal transformations are spanned by, respectively, the bases obtained from the orthogonal invariance of the elements of the Gram matrix $\mathbf{G}$ and the mass quadrupole $\mathbf{M}$:

physical $O(2)$-invariant subspace I:

$$\begin{aligned} {}^{1}\rho &= 2(q^{11}, q^{12}, 0, 0), \\ {}^{2}\rho &= 2(0, 0, q^{21}, q^{22}), \\ \alpha^3 &= (q^{21}, q^{22}, q^{11}, q^{21}), \end{aligned} \tag{5.27}$$

whose metric $g(I)$ is

$$\begin{array}{cccc} & \rho^1 & \rho^2 & \alpha^3 \\ & \downarrow & \downarrow & \downarrow \\ \rho^1 \rightarrow & 4G^{11} & 0 & 2G^{12} \\ \rho^2 \rightarrow & & 4G^{22} & 2G^{12} \\ \alpha^3 \rightarrow & & & G^{11} + G^{22} \end{array} \; ; \tag{5.28}$$

kinematic $O(2)$-invariant subspace K:

$$\begin{aligned} \delta^1 &= 2(q^{11}, 0, q^{21}, 0), \\ \delta^2 &= 2(0, q^{12}, 0, q^{22}), \\ \kappa^3 &= (q^{12}, q^{11}, q^{22}, q^{21}), \end{aligned} \tag{5.29}$$

whose metric $g(K)$ is

$$\begin{array}{cccc} & \delta^1 & \delta^2 & \kappa^3 \\ & \downarrow & \downarrow & \downarrow \\ \delta^1 \rightarrow & 4M^{11} & 0 & 2M^{12} \\ \delta^2 \rightarrow & & 4M^{22} & 2M^{12} \\ \kappa^3 \rightarrow & & & M^{11} + M^{22} \end{array} \; . \tag{5.30}$$

The two metrics (5.28) and (5.30) can be diagonalized in various ways by using any orthonormalization procedure since the metrics are defined locally.

For instance, the discussion at the end of section 2 is illustrated here for a Gram–Schmidt orthogonalization. By noticing that ρ^1, ρ^2 (δ^1, δ^2) are already orthogonal:

(1) normalize ρ^1 and ρ^2 (δ^1 and δ^2),

(2) orthogonalize α^3 (κ^3) with respect to ρ^1 and ρ^2 (δ^1, δ^2).

(1) Normalization (for $i = 1, 2$):

$$\rho^i \rightarrow \rho'^i = [(q^{i1})^2 + (q^{i2})^2]^{-1/2} \rho^i = Q_i^{-1} \rho^i, \tag{5.31a}$$

$$\varepsilon^a \rightarrow \Xi^a = [(q^{1a})^2 + (q^{2a})^2]^{-1/2} \varepsilon^a = \Gamma_a^{-1} \varepsilon^a. \tag{5.31b}$$

These forms are exact differentials and, by immediate integration, the integral functions are, respectively:

$$\rho'^{i} \rightarrow [G_{ii}]^{1/2} = Q_i\,, \tag{5.32}$$

$$\Xi^{a} \rightarrow [M_{aa}]^{1/2} = \Gamma_a\,. \tag{5.33}$$

(2) Orthogonalization:

By using a straight Gram–Schmidt orthonormalization involving ρ^1, ρ^2 and α^3, one obtains the normalized vector

$$\alpha'^{3} = -N\left(\frac{G_{12}}{G_{11}}\rho^1 + \frac{G_{12}}{G_{22}}\rho^2 - 2\alpha^3\right), \tag{5.34'}$$

where the normalization function is

$$N = \tfrac{1}{2}[G_{11}G_{22}]^{1/2}t^{-1/2}d^{-1}.$$

The form α'^3 is not integrable; nonetheless, the expression between parentheses in (5.34) can be made integrable by using $1/G_{12}$ as an integrating factor, and the form

$$\alpha''^{3} = \frac{1}{G_{11}}\rho^1 + \frac{1}{G_{22}}\rho^2 - \frac{2}{G_{12}}\alpha^3$$

can be integrated directly. The solutions generated by α''^3 are

$$F\left(\frac{G_{11}G_{22}}{(G^{12})^2}\right),$$

that is, any function of $G_{11}G_{22}(G_{12})^{-2}$ satisfies (5.34′). In particular, it can easily be seen that, by taking

$$\cos^{-1}[G_{12}(G_{11}G_{22})^{-1/2}]$$

as a particular solution, one recovers the usual angle θ between the two Jacobi vectors in the physical space:

$$\theta = \tan^{-1}\left(\frac{q^{11}q^{22} - q^{12}q^{21}}{q^{11}q^{21} + q^{12}q^{22}}\right). \tag{5.35}$$

The internal metric transforms into

$$\begin{array}{cccc} & \rho'^1 & \rho'^2 & \alpha''^3 \\ & \downarrow & \downarrow & \downarrow \\ \rho'^1 \rightarrow & 1 & 0 & 0 \\ \rho'^2 \rightarrow & & 1 & 0 \\ \alpha''^3 \rightarrow & & & Q_1^{-2} + Q_2^{-2} \end{array} \quad . \tag{5.36}$$

The set (Q_1, Q_2, θ) constitutes an orthogonal integral basis for $O(2)$-invariants depending on the two vectors q_1, q_2 of the physical space $\mathbb{R}^2$. It should be noticed that the coefficients in the expansion (5.34) are $O(2)$-invariant, as is the integrating factor $1/G^{12}$.

Other orthogonalization procedures may be used. In any case, the coefficients and the integrating factors are $O(2)$-invariant. One might be interested, for instance, in three equivalent symmetric orthogonal coordinates derived from G^{11}, G^{12} and G^{22}. This is a particularly attractive system of internal coordinates for triatomic molecules A_3. The orthonormalization matrix O_{es} needed is symmetric and is given by

$$O_{es} = g(I)^{-1/2},$$

where $g(I)$ is the metric (5.28). The elements of O_{es} are obviously $O(2)$-invariant. However, analytic expressions for the integrating factors are not available at the present time. Other orthogonalizations can be used. Among them, the three eigenvectors obtained from the equation

$$g(I)\Lambda = \lambda\Lambda.$$

Concerning the kinematic invariants, a similar discussion yields

$$\Phi = \tan^{-1}\left(\frac{q^{11}q^{22} - q^{12}q^{21}}{q^{11}q^{12} + q^{21}q^{22}}\right)$$

for the general solutions of κ''^3. Similarly, the internal kinematic metric transforms into

$$\begin{array}{cccc} & \Xi^1 & \Xi^2 & \kappa''^3 \\ & \downarrow & \downarrow & \downarrow \\ \Xi^1 \rightarrow & 1 & 0 & 0 \\ \Xi^2 \rightarrow & & 1 & 0 \\ \kappa''^3 \rightarrow & & & \Gamma_1^{-2} + \Gamma_2^{-2} \end{array} \quad . \tag{5.37}$$

5.6. EXTERNAL SUBSPACES

The external subspaces can be spanned arbitrarily by any linear combinations ε which are linearly independent with respect to the internal generators $(\rho'^1, \rho'^2, \alpha''^3)$, that is, such that the determinant of the Gram matrix of the vectors $(\rho'^1, \rho'^2, \alpha''^3, \varepsilon)$ is not zero. For instance, one can choose the vector

$$\varepsilon = (-q^{12}, q^{11}, -q^{22}, q^{21}).$$

This form is not an exact differential. However, it should be noticed that the vector fields

$$\varepsilon^1 = (-q^{12}, q^{11}, 0, 0), \quad \varepsilon^2 = (0, 0, -q^{22}, q^{21})$$

can be made integrable by choosing $\mu_1 = 1/q^{11}q^{12}$ and $\mu_2 = 1/q^{21}q^{22}$ as respective integrating factors. By recalling that any linear combination of integrable forms is integrable, one obtains the integrable form

$$\Xi'^3 = \mu_1\varepsilon^1 + \mu_2\varepsilon^2 = (-1/q^{11}, 1/q^{12}, -1/q^{21}, 1/q^{22}) \tag{5.38}$$

$$\xrightarrow{\text{integration}}$$

$$\alpha = q^{12}/q^{11} + q^{22}/q^{21}. \tag{5.39}$$

Notice that Ξ'^3 is orthogonal to ρ'^1, ρ'^2 but not α''^3. Geometrically, the angle α represents the rotation of the inertial frame axis l_1 to the noninertial axis f_1 directed along the Jacobi vector $\boldsymbol{q}_1$.

Any linear combination of Ξ'^3 with the internal base vectors provides a differential form that will generate, after having been made integrable, a function $\xi(q^{ia})$ similar to (5.39) associated with a particular noninertial frame $\{f_a(\xi)\}$; for instance, the angle Θ parameterizing the orthogonal matrix R which diagonalizes the mass quadrupole M. This generates the instantaneous principal axes of inertia as a noninertial frame,

$$R(\Theta)\mathbf{M}R^t(\Theta) = \mathrm{diag}(\lambda_1, \lambda_2).$$

The angle Θ is readily found as a function of (q^{ia}) by solving the above equation:

$$\tan(2\Theta) = -2\,\frac{M_{12}}{M_{11} - M_{22}},$$

where

$$M^{12} = q^{11}q^{12} + q^{21}q^{22}, \quad M^{11} = (q^{11})^2 + (q^{21})^2, \quad M^{22} = (q^{12})^2 + (q^{22})^2.$$

The external physical cotangent space is spanned by Ξ^α,

$$\Xi^\alpha = \alpha_{11}\varepsilon^{11} + \alpha_{12}\varepsilon^{12} + \alpha_{21}\varepsilon^{21} + \alpha_{22}\varepsilon^{22},$$

where Θ_{ia} is the partial derivative of $\tan(2\Theta)$ with respect to q^{ia},

$$\Theta_{11} = -2(M_{11} - M_{22})^{-2}[(M_{11} - M_{22})q^{12} - 2M_{12}q^{11}],$$
$$\Theta_{12} = -2(M_{11} - M_{22})^{-2}[(M_{11} - M_{22})q^{11} - 2M_{12}q^{12}],$$
$$\Theta_{21} = -2(M_{11} - M_{22})^{-2}[(M_{11} - M_{22})q^{22} - 2M_{12}q^{21}],$$
$$\Theta_{22} = -2(M_{11} - M_{22})^{-2}[(M_{11} - M_{22})q^{21} - 2M_{12}q^{22}]$$

and Ξ^α can be expressed as

$$\Xi^\alpha = -2(M_{11} - M_{22})^{-2}\kappa^3 + 2M_{12}(\varepsilon^1 - \varepsilon^2).$$

Any linear combination ε^ζ of ε^α with the internal base vectors $(\rho^1, \rho^2, \alpha^3)$ would provide (if integrability conditions are met) an acceptable external integral function $\zeta(q^{ia})$ generated from ε^ζ such that the mass quadrupole transforms into

$$R(z)\mathbf{M}R^{t}(z) = \mathbf{M}'.$$

Geometrically, z is the angle of the rotation of the principal axes noninertial frame into a new noninertial frame whose mass quadrupole with respect to the inertial frame is $\mathbf{M}'$. Whatever the linear combination ε^ζ is, it is impossible to generate an integral function z orthogonal to the entire internal subspace. The best that can be done is to construct a function z orthogonal to a two-dimensional subspace of I, as demonstrated in the following theorem and illustrated in fig. 2.

THEOREM

Let Θ be an independent variable, that is, the determinant of the transformation is not zero,

$$(q^{11}q^{22} - q^{12}q^{21})(\Theta_{11}q^{12} + \Theta_{21}q^{22} - \Theta_{12}q^{11} - \Theta_{22}q^{21}) \neq 0. \qquad \text{(C1)}$$

Unless the first term is zero (in which case the angle between the Jacobi vectors is zero), the independence condition is

$$(\Theta_{11}q^{12} + \Theta_{21}q^{22} - \Theta_{12}q^{11} - \Theta_{22}q^{21}) \neq 0.$$

The orthogonality conditions are

$$(r^1, \Theta): \quad \Theta_{11}q^{11} + \Theta_{12}q^{12} = 0, \qquad \text{(C2)}$$
$$(r^2, \Theta); \quad \Theta_{21}q^{21} + \Theta_{22}q^{22} = 0, \qquad \text{(C3)}$$
$$(a, \Theta): \quad \Theta_{11}q^{21} + \Theta_{21}q^{11} + \Theta_{12}q^{22} + \Theta_{22}q^{12} = 0. \qquad \text{(C4)}$$

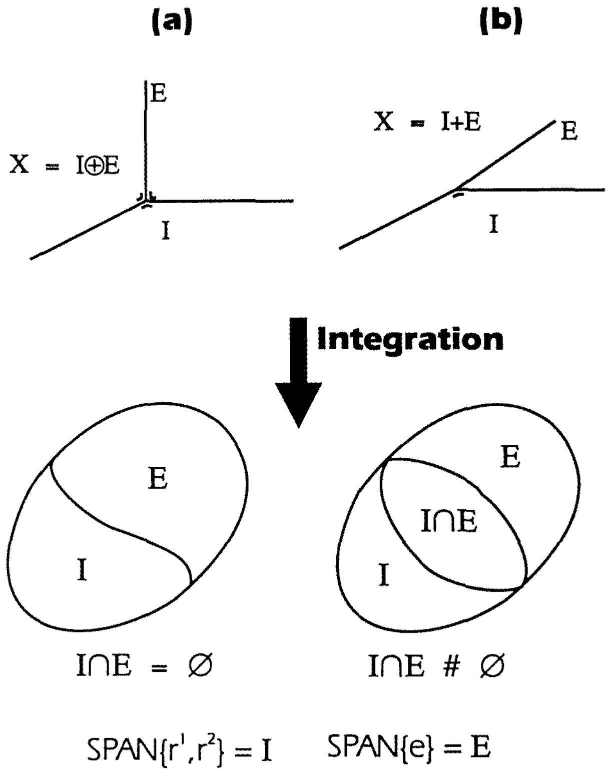

Fig. 2. Integration of the vector fields and conservation of the orthogonality of the integral curves. (a) The orthogonality of the external vector field with respect to the internal cotangent space yields by integration a complete separability in the partition. The external coordinate is "purely" independent of the choice of the internal variables. (b) The external subspace is not the orthogonal complement to the internal space. The intersection of the internal and the external spaces of the integral curves is not empty.

From (C2):

$$\Theta_{12} = -\lambda\, q^{11}, \quad \Theta_{11} = \lambda\, q^{12},$$

from (C3):

$$\Theta_{21} = -\mu\, q^{22}, \quad \Theta_{22} = \mu\, q^{21},$$

with the integrating factors λ and μ satisfying the partial differential equations:

$$q^{11}\lambda_{11} + q^{12}\lambda_{12} = 2\lambda\,, \tag{C5}$$

$$q^{21}\mu_{21} + q^{22}\mu_{22} = 2\mu\,. \tag{C6}$$

Let ε^λ and ε^μ be the generators of the integrating factors λ and μ,

$$\varepsilon^\lambda = (\partial_{11}\lambda,\ \partial_{12}\lambda,\ \partial_{21}\lambda,\ \partial_{22}\lambda), \quad \varepsilon^\mu = (\partial_{11}\mu,\ \partial_{12}\mu,\ \partial_{21}\mu,\ \partial_{22}\mu).$$

Conditions (C2) and (C3) establish that the generator ε^τ is constructed orthogonal to ρ^1 and ρ^2, respectively, that is, ε^τ lies at the intersection of the planes perpendicular to ρ^1 and ρ^2, respectively. Condition (C5) states that the generator ε^λ lies in the plane defined by ε^τ and ρ^1. In addition, (C6) ensures that the generator ε^μ of μ is in the plane defined by ε^τ and ρ^2. By replacing in (C4), one obtains

$$\lambda = -\mu$$

and Θ is orthogonal to the entire internal space if an integrating factor λ can be found such that

$$\Theta_{11} = \lambda\, q^{12}, \quad \Theta_{12} = -\lambda\, q^{11}, \quad \Theta_{21} = \lambda\, q^{22}, \quad \Theta_{22} = -\lambda\, q^{21}.$$

The common integrating factor λ must satisfy simultaneously

$$q^{11}\lambda_{11} + q^{12}\lambda_{12} = 2\lambda, \quad q^{21}\lambda_{21} + q^{22}\lambda_{22} = 2\lambda,$$

which is impossible according to the above result: ε^λ cannot be in the two planes $(\varepsilon^\tau, \rho^1)$ and $(\varepsilon^\tau, \rho^2)$ unless $\varepsilon^\tau \equiv \varepsilon^\lambda$, which would mean that λ is a constant.

The situation is analogous for the kinematic invariants. For the kinematic external space, one can choose

$$\varphi^3 = (-q^{21}, -q^{22}, q^{11}, q^{12}),$$

the angle θ parameterizing the orthogonal matrix ρ which diagonalizes the Gram matrix G in label space,

$$\rho(\theta) G \rho^t(\theta) = \mathrm{diag}(\lambda_1, \lambda_2),$$

where θ is given as a function of (q^{ia}) by

$$\tan(2\theta) = -2\,\frac{G_{12}}{G_{11} - G_{22}},$$

where

$$G^{12} = q^{11}q^{21} + q^{12}q^{22}, \quad G^{11} = (q^{11})^2 + (q^{12})^2, \quad G^{22} = (q^{21})^2 + (q^{22})^2.$$

The external kinematic cotangent space is spanned by ε^θ,

$$\varepsilon^\theta = \theta_{11}\varepsilon^{11} + \theta_{12}\varepsilon^{12} + \theta_{21}\varepsilon^{21} + \theta_{22}\varepsilon^{22},$$

where θ_{ia} is the partial derivative of θ with respect to q^{ia}. This choice of θ determines the so-called IS Jacobi vectors. As was the case for physical rotations, any linear combination ε^{ξ} of ε^{θ} with the generators (ε^1, ε^2, κ^3) would provide (if integrability conditions are met) a function χ corresponding to a new representation by means of Jacobi vectors whose Gram matrix is given by

$$\rho(\chi)\mathbf{G}\rho^{t}(\chi) = \mathbf{G}'.$$

The function $\chi(q^{ia})$ permits, therefore, a "switch" from the IS representation to another set of Jacobi vectors. For example, the switching function transforming into the "mobile" representation can be easily derived.

SUMMARY

By considering the orthogonal invariants in the physical space, the cotangent space is partitioned into

$$T_P^* C = \mathrm{SPAN}(\rho^1, \rho^2, \alpha^3) \cup \mathrm{SPAN}(\varepsilon^{\alpha})$$

and it has been shown in the previous section that SPAN(ε^{α}) cannot be kept orthogonal to SPAN(ρ^1, ρ^2, α^3) during the integration process. The metric $\tilde{g}$ assumes the form

$$\begin{pmatrix} g(I) & C \\ C^{t} & E \end{pmatrix},$$

where C ($\neq 0$) is the 3×1 coupling tensor whose elements are (ρ^1, ε^{α}), (ρ^2, ε^{α}), (α^3, ε^{α}) and $E = (\varepsilon^{\alpha}, \varepsilon^{\alpha})$.

By considering the orthogonal invariants in the label space, the cotangent space is partitioned into

$$T_P^* C = \mathrm{SPAN}(\varepsilon^1, \varepsilon^2, \kappa^3) \cup \mathrm{SPAN}(\varepsilon^{\theta}),$$

where SPAN(ε^{θ}) cannot be made orthogonal to SPAN(ε^1, ε^2, κ^3) for the same reason as above.

5.7. *K/P* INVARIANTS

The common invariants for physical and kinematic orthogonal transformations are generated by the infinitesimal basis obtained from the common trace t and the common determinant d of $\mathbf{G}$ and $\mathbf{M}$ (eqs. (4.14), (4.15)):

$K \cap I$ space:

$$\varepsilon^{t} = 2(q^{11}, q^{12}, q^{21}, q^{22}),$$

$$\varepsilon^{d} = (q^{22}, -q^{21}, -q^{12}, q^{11}).$$

By considering the common invariants, the cotangent space is partitioned into

$$T_P^* C = \mathrm{SPAN}(\varepsilon^t, \varepsilon^d) \cup \mathrm{SPAN}(\varepsilon^\alpha) \cup \mathrm{SPAN}(\varepsilon^\theta),$$

that is,

(1) two generators for the common invariants,
(2) one generator for the physical external variable,
(3) one generator for the kinematic external variables (switching functions),

where SPAN(ε^α) and SPAN(ε^θ) are orthogonal to SPAN(ε^t, ε^d) but cannot be made orthogonal one with respect to the other. The set (ε^t, ε^d, ε^θ) generates all physical internal variables, while the set (ε^t, ε^d, ε^α) generates all kinematic variables.

The metric tensor in these bases reads as (with the notation of section 4)

$$\begin{pmatrix} g(K/P) & 0 \\ 0 & g(E) \end{pmatrix},$$

where $g(E)$ is given by

$$\begin{pmatrix} (\varepsilon^\theta, \varepsilon^\theta) & (\varepsilon^\theta, \varepsilon^\alpha) \\ & (\varepsilon^\alpha, \varepsilon^\alpha) \end{pmatrix},$$

and where $g(K/P)$ is not diagonal. This is overcome by considering an alternate basis for $K \cap I$ provided by the common eigenvalues λ_1 and λ_2 of G and M (eqs. (4)–(12)):

$$2\lambda_1 = t - [t^2 - 4d]^{1/2}, \qquad t = \lambda_1 + \lambda_2\,;$$

$$2\lambda_2 = t + [t^2 - 4d]^{1/2}, \qquad d = \lambda_1 \lambda_2\,,$$

whose generators are ξ^1 and ξ^2. The infinitesimal transformation $\{\varepsilon^t, \varepsilon^d\} \to \{\xi^1, \xi^2\}$ is

$$(\lambda_1 - \lambda_2) Z = \begin{pmatrix} -\lambda_2 & \lambda_1\lambda_2 \\ \lambda_1 & -\lambda_1\lambda_2 \end{pmatrix}.$$

The $K \cap I$ metric sub-tensor $g(t, d)$ transforms as

$$Z g(t, d) Z^t = g(l^1, l^2).$$

A further transformation of $\{\xi^1, \xi^2\}$ into polar coordinates finalizes the diagonalization of the K/P subpace:

$$\varepsilon^r = N(\xi^1 + \xi^2), \quad \varepsilon^p = N(\xi^1 + \xi^2),$$

where $N = [\lambda_1^2 + \lambda_2^2]^{1/2}$. ε^r/N is directly integrable and generates the trace $t = \lambda_1^2 + \lambda_2^2$. ε^p/N is made exact differential by dividing by $\lambda_1\lambda_2$. By integration, ε^p generates the function $F(\lambda_1/\lambda_2)$ whose particular solution can be taken as the polar angle $\Phi = \cos^{-1}(\lambda_1/\lambda_2)$.

6. Summary and conclusions

In this work, we have described a strategy aimed at producing sets of optimally orthogonal internal coordinates by partitioning the internal configuration space according to certain group invariance properties. Integral bases for group invariants serve as defining local bases for the cotangent space in which orthogonalization can be achieved. By this procedure, an orthogonal basis for invariant 1-forms can be produced taking into account the symmetries inherent in the molecular Hamiltonian. The new set of coordinates are obtained by integrating the 1-forms. The latter step is not easily handled due to the difficulty of obtaining analytic integrating factors which are invariant as well with respect to the groups. An alternate approach, involving the method of the characteristics, is currently under study.

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Note: symbols and abbreviations

While there may be some deviation from standard rules, the following guidelines have been used for the symbols in this paper.

(1) The indices i, j, k refer to the label space $\mathbb{R}^n$ and the indices a, b, c refer to physical space $\mathbb{R}^3$.

(2) Upper script indices refer to contravariant components and lower script indices refer to covariant components. A lower script index for a vector indicates contravariance for the components (contravariant base vectors), and an upper script index for a vector refers to covariance for the components (covariant or dual vectors) (see, for example, ref. [23], p. 20).

(3) Coordinates, functions, variables, . . . are represented either by roman or greek letters (angular variables) with upper script indices (q^{ia}, u^r, Θ^s, . . .).

(4) Vectors and vector fields are represented by bold italic roman or greek letters with lower script indices (that is, contravariant components). Examples are $\boldsymbol{f}_a$, $\boldsymbol{\phi}_{ia}$, ... Vectors defined locally (in tangent space) are represented by $\boldsymbol{\phi}_{ia}|_P$.

(5) Generators (vectors in dual space $T_P^*\mathbb{C}$ with covariant components) are also called covariant vectors or 1-forms and are represented by lower case greek

letters with *upper script indices* (ε^{ia}, $\phi^r, \ldots$). Once integrable, the greek letter may be capital (Ξ^u).

(6) Linear transformations are represented by roman capital letters and the matrix notation (two lower case indices for the element of the rotation matrix R_{ab}) is used. This rule applies as well for tensors evaluated locally. Otherwise, the tensor notation is used: tensors are represented by bold roman capital letters **A** and distinction between co- and contravariant indices is made (element G^{ij} of the Gram "matrix" **G**).

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