THE UNIVERSITY OF MANITOBA.

THE QUANTUM KINETIC ENERGY OPERATOR FOR ARBITRARY MOTION OF A GROUP OF PARTICLES IN TERMS OF GENERALIZED JACOBI VECTORS AND GENERAL NONINERTIAL FRAME.

by

Jean–Pierre Leroy

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE
OF
DOCTOR OF PHILOSOPHY
IN CHEMISTRY

Winnipeg, Manitoba
January 1988

THE QUANTUM KINETIC ENERGY OPERATOR FOR ARBITRARY MOTION OF A GROUP OF PARTICLES IN TERMS OF GENERALIZED JACOBI VECTORS AND GENERAL NONINERTIAL FRAME

BY

JEAN-PIERRE LEROY

A thesis submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
of the degree of

DOCTOR OF PHILOSOPHY

"Qu'on ne dise pas que je n'ai rien dit de nouveau: la disposition des matieres est nouvelle; quand on joue a la paume, c'est une meme balle dont jouent l'un et l'autre, mais l'un la place mieux."

Pascal

To

Genevieve

Andree–Anne

Olivier

Lucie

Contents

Abstract

A form is derived for the quantum kinetic energy operator for the relative motion of a many–body system in a context of large amplitude vibrations with applications to rotational–vibrational spectroscopy in mind. The theory is valid for any noninertial frame. No constraints involving approximations are used. The rotational coordinates are integrated out leaving an expression in terms of the basic rotational invariant (BRI) coordinates of a set of generalized Jacobi vectors (GJV) as precursors of any internal curvilinear coordinates and rotational quantum numbers.

ACKNOWLEDGMENTS

I would like to express my thanks to:

R.Wallace as advisor and friend for his extensive help all along the past five years. Without his confidence and advice, this work would not have been possible

G.Krause as a teacher and friend for the discussions within courses in Mathematics. These have been a rich source of inspiration

Kerry Davie, graduate student, for the discussions and clarifications having helped me to maintain contact with reality

The writing of a thesis can be traumatic to others besides the author. I wish to thank my wife, Lucie, for her "unfailing" support and encouragement in keeping me at my task.

Special thanks are due to the University of Manitoba and the Natural Sciences and Engineering Research Council for the financial support in the form of Graduate Fellowships.

1.Purpose and Organization of the Thesis.

Purpose.

The purpose of this dissertation is to present a new approach to the derivation of a quantum mechanical operator for the vibration–rotation hamiltonian for a many–body system in a context of large amplitude vibration with applications to rotational–vibrational spectroscopy in mind.

The method yields an exact separation of the c.m., rotational, and vibrational motions by proposing a generalization of the concepts of

1) Jacobi vectors (describing the relative motion)

2) noninertial frame (describing the rotational motion of the system).

The point of view adopted here is more formal than physical in the sense that no specific problem is discussed or used in the derivation of the results. It is our view that, in a subject of such importance, a general model has to be set up once and for all in such a way that any application can be easily treated as a particular case of the general result.

The derivation of the kinetic energy operator involves

(1) the specification of a set of "generalized" Jacobi vectors describing the relative motion in such a way that the symmetry of the system can be recovered

(2) the construction of a molecular frame that can be defined in various ways from some or all of the Jacobi vectors according to the behaviour of the molecule under rotational motion.

(3) the parameterization of the internal configuration in coordinates

leading to an acceptable separability of the potential and the internal interactions.

The great advantage of the method, besides conceptual simplicity, is that no constraints involving approximations are used. Given a potential function, the zero–order eigenproblem can be solved by accurate numerical methods. The results involve no approximations whatsoever and are valid for any noninertial frames and any curvilinear internal coordinates.

Organisation

In the present part, the problem is defined and cast in the current scope of molecular spectroscopy, the scheme of the derivation of the hamiltonian is sketched out and the principal results are presented. Part II is concerned with the derivation of the Jacobi vectors by orthonormalization (in label space) of the bond vectors. Part III is concerned with the noninertial frames and the derivation of the kinetic energy operator itself.

The main body of these two chapters are constituted from recent papers (either already published or submitted). Following the presentation of the papers, notes and comments complete the discussion in the form of appendices by elaborating upon some specific points. The theory of angular momentum, the concept of metric tensor and the theory of vector invariant under symmetry groups play a key role all along this work. For this reason, the main results of these theories are presented. In a general conclusion, some immediate applications are presented and further directions of research are suggested.

2. Review.

An attempt to sketch the background of the problem would comprise a short survey of the quantum theory itself and a list of the contributors to the theory would be a Who's–Who in molecular physics for the period beginning in 1925.

The expression for the vibration–rotation hamiltonian for a polyatomic molecule evolved in form from the earliest days of quantum mechanics. The model of a molecule as consisting of nuclei that could execute small vibrations about equilibrium positions (localized potential minima) created by the much faster motions of the electrons had been clearly recognized (Born and Oppenheimer[1]). The use of normal coordinates (Brester[2] and Wigner[3]) for the description of these motions was investigated thoroughly by Wilson[4]. It was, however, only in 1934 and 1935 that Eckart[5,6] considered methods for obtaining a general hamiltonian that would yield an approximate separation of the over–all rotational motion of a molecule (thought of as a rigid body) and the small "internal" displacements of the nuclei away from their equilibrium positions. Actually, the possibility of such a separation had been suggested earlier by Casimir[7,8].

The difficulty in describing the motions of the nuclei in the intuitive model sketched above was one of defining a *moving reference frame* such that the hamiltonian, when referred to the moving frame, would fulfill Casimir's conditions (small interaction between rotational and internal motions). In his first paper, Eckart[5] developed the expression for the

kinetic energy (classical) relative to a frame defined by the *principal moments of inertia at each instant of time* (principal axes frame). The pure rotational energy term in this expression was not, however, of the classical form that was to be expected if it were dominant. This same anomalous rotational energy term appears also in the Schroedinger equation for an N–particle system using cartesian coordinates measured relative to the principal axes frame (Hirschfelder and Wigner[9]). In his second paper, Eckart rejects the principal axes frame as being incompatible with the normal coordinate description of small internal motions although Van Vleck[10] had shown how to correct the anomalous principal axes rotational energy. The evolution of what is now called the Eckart molecular frame ended in 1940 when its modern form was given by Darling and Dennison[11]. A further simplification was proposed later by Watson[12] whereas Louck and Galbraith[13,14] have recently reinterpreted the model.

The principal axes frame and the Eckart molecular frame are equally fundamental; each is an example of a more general kinematic concept: the *body–fixed frames*[15] that is, "global" frames whose instantaneous position and orientation depend only on the instantaneous translationally invariant positions of the particles rotating as a whole.

These methods of treating the vibration–rotation of polyatomic molecules are always formulated in terms of an equilibrium configuration of the nuclei to define the rotating coordinate system. As a result, this formulation is restricted to the description of infinitesimal internal motion (the moments of inertia are expanded in a Taylor series about the

equilibrium configuration and for large amplitude vibration, the series is not necessarily convergent).

In order to treat the problem for molecules undergoing large amplitude vibrations, it is necessary to examine methods which are not tied to any particular equilibrium configuration. This was initiated for the principal axes frame by Van Vleck[10,16] who transformed the hamiltonian to the coordinate system rotating with the *instantaneous* moments of inertia of the molecule. This technique was successfully applied to triatomic molecules by Freed and Lombardi[17] (using valence coordinates) and by Smith and co–workers[18-22] (using hyperspherical coordinates). Lately, Johnson[23-25] reviewed the results for three–body systems and Ohrn[26-28] used hyperspherical coordinates for the description of four–bodies. Buck and co–workers[29] have recently proposed an elegant generalization of the hyperspherical formalism using the principal axes frame as describing the "collective" rotational motion of the system. Their main result furnishes the key to understanding the "moment of inertia problem" posed by non–rigid structures by introducing a *vortex*[30] operator commuting with the total angular momentum.

In situations where some fragment of the system has to be distinguished (from the point of view of its rotational motion), such global frames do not constitute an appropriate description. Part of the system may rotate with a semi–rigid structure whereas the contribution to the rotational motion of the remaining fragment may not be easily recognizable. This inspired Curtiss *et al* [31] to introduce *distinguished particle frames* in a context of scattering problems. In this model, a bond is singled out and the remaining part serves to define completely the

rotating frame (actually, a single bond in the remaining fragment is really needed) of the system rotates "internally" about the direction of the distinguished bond. A frame of this type has been adapted recently with success by Wallace[32] to bound state problems incorporating the (orthogonal) Jacobi vectors description ("mobiles"[33-35]) of the relative motion into the formalism developed by Curtiss. Although simplifying greatly the couplings between the rotational and the internal motions, these frames are constructed in an unsymmetrical fashion (Gram–Schmidt orthogonalization). As well, the mobiles used by Wallace do not reflect any symmetry inherent in the system.

3.Statement of the Problem.

The motivation for the present work comes from molecular spectroscopy and dynamics with applications primarly oriented towards a better understanding of the potential energy surface describing either the movement of atoms within a molecule or atoms in collision with one another. As it turns out, the results presented below can be successfully applied to the interpretation of the vibrational–rotational spectra of polyatomic molecules and in particular, the effects of the rotations on intramolecular energy transfer processes.

Any attempt to improve the knowledge of the potential surface involves the solution of the Schroedinger equation which has to be tractable in a way that the inaccuracies in the calculated spectrum be mainly attribuable to the source potential function itself. Assume that a

potential (source potential) can be set up from spectroscopic data[41-46] for a particular region of the surface, solve the Schroedinger equation for this potential to obtain a spectrum (calculated spectrum), compare with the observed spectrum and make the adjustments to the source potential. Iterate the procedure until the differences between the calculated and the observed spectra are minimized.

The general procedure is illustrated in the following scheme:

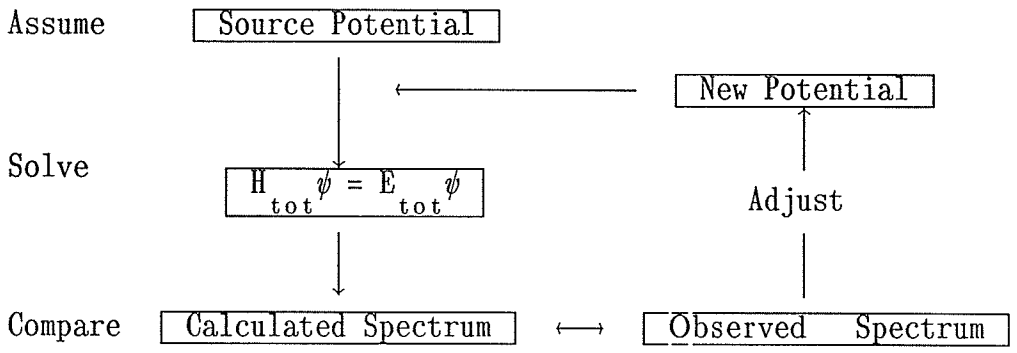


Figure 1

In order to render efficient techniques of perturbation theory, this amounts to minimizing the inevitable couplings between internal motions for arbitrary configurations of nuclei that is, to choosing a set of internal coordinates (internal parameters) which are optimally orthogonal in configuration space (the notion of orthogonal coordinates and the implications relative to the corresponding couplings will be made clear below). As well, the internal coordinates should reflect in some way the symmetry inherent in the system. For instance, if the molecule contains

two or more identical atoms, its potential must be invariant under permutations of identical atoms.

A total decoupling of the internal and external motions being unfeasible, a complete theory would encompass the treatment of couplings between rotational and internal motion. In any event, the derivation of the hamiltonian involves the explicit construction of a rotating frame located at the c.m. This is translated into a choice of three external parameters (for example, three Euler angles) describing the rotational motion of the system with respect to a fixed reference frame. In a context of large amplitude, the choice of a noninertial frame (i.e., the choice of the external parameters) has to be such that the rovibrational interaction in the kinetic energy for arbitrary configurations of the nuclei be minimal. Besides the minimization of the rovibrational couplings, the frame should reflect in some way the symmetry of the system in the sense that the frame be invariant under permutations of identical atoms. It is also important to mention that the choice of the noninertial frame may affect the internal couplings themselves. These considerations motivate the development of a general formalism of construction of noninertial frames.

Otherwise stated, the problem can be formulated in the following way. Given a set of bond vectors $\{\vec{r}_i\}$ and an inertial frame centered at the c.m., what is the most appropriate curvilinear transformation of the 3N–3 components $r^{i\beta}$ such that the above requirements are met. This implies that the notion of external/internal coordinates be clarified. Moreover, it is necessary to be precise in what is meant by orthogonality of coordinates and how this notion is related to the couplings between the linear momenta conjugate to the coordinates. These concepts are largely

used throughout the dissertation, the main results being presented in Appendix I.

In most of the previous approaches, the relative configuration is formulated in terms of a variety of internal coordinates and rotating axis systems reflecting the physical problem under consideration. For instance, the choice of normal coordinates corresponds to restricting the vibrational motion to small amplitudes near the equilibrium configuration, the choice of local modes corresponds to neglecting the angular motion, ... In most of these cases, the configuration is specifically parameterized at the beginning of the derivation of the kinetic energy operator. As a consequence, adapting such a model hamiltonian to slightly different problems becomes an increasingly complicated task. Although some efforts[38-39] have been made in the direction of some "universal" form in the last few years, a systematic discussion is still lacking. This has been the principal motivation for this dissertation: the basic result is an expression for the quantum kinetic energy operator presented in a form valid for any frame and expressed in terms of the basic rotational invariants[40] (lengths Q_i and angles θ_{ij} between the Jacobi vectors encoded in the Gram matrix G) of an appropriate set of Jacobi vectors representing the system. All that is required is the specification of an orthonormalizing matrix O of the bond vectors in label space defining the Jacobi vectors and the specification of a matrix B defining the frame and being related to the tensor of inertia of the Jacobi vectors. The basic rotational invariant (BRI) coordinates constitute an acceptable precursor to other curvilinear internal coordinates.

The radial coordinates Q_i are orthogonal to each other and

orthogonal to the internal angular coordinates which in turn are not orthogonal to each other. A technique of orthogonalization of curvilinear coordinates has to be developed. Actually, this technique is the "infinitesimal" counterpart of the orthonormalization in a euclidean space in the sense that it amounts to orthogonalizing the local basis in the tangent euclidean space at each point of the configuration space (Riemannian space).

It is worth mentioning that for N>5, the angles θ_{ij} are not all independent and a "reduction" technique has to be considered in order to recover the 3N–6 internal coordinates.

PART II

GENERALIZED JACOBI VECTORS DESCRIPTION

OF A N–BODY SYSTEM

Procedures Leading to a Variety of Orthonormal Jacobi–Type Coordinates of Relevance to Large–Amplitude Vibration and Scattering Problems.

Algorithms are developed to produce transformation matrices to convert from scalar bond distance–angle coordinates to scalar coordinates corresponding to a variety of Jacobi–type orthonormal coordinates defined by the usual Gram–Schmidt process, or by alternates taking into account symmetries inherent in the molecular hamiltonian. The transformations have been developed with computer implementation in mind.

1. Introduction.

In the theory of large–amplitude vibration of polyatomic molecules or in molecular scattering problems, considerable current interest aims at obtaining, for any specific molecule, some optimal set of the 3N–3 translationally invariant coordinates. Ideally, such an optimal set would satisfy the following criteria:

(a) Some particular body–fixed frame should be chosen to minimize rovibrational interaction in the kinetic energy operator for arbitrary configurations of the nuclei.

(b) The coordinates should be optimally orthogonal in configuration space since that requirement reduces non–zero cross terms in the internal kinetic energy operator to a minimum.

(c) The coordinates should reflect, in some simple way, any symmetry inherent in the hamiltonian.

(d) The coordinates should be such that the potential energy is approximatively separable when expressed in these coordinates for as large a hypervolume of configuration space as possible.

The first of these requirements has been discussed at great length in the literature[1] and will not be considered here in any detail since our primary concern is with the selection of coordinates which are precursors to the scalar curvilinear coordinates which descibe both rotation of the frame and internal "vibrational" motion.

The second requirement is not met by any kind of bond coordinates but is met by generalized Jacobi coordinates[2–5] or, in the case of the

three–body system, by hyperspherical polar coordinates[6,7]. This requirement is important since it is one logical step in the process of diagonalizing the form of the hamiltonian.

The third criterion is not ordinarly met by generalized Jacobi coordinates but these may be symmetrized as originally suggested by Hirschfelder[5,8] and as developed in the systematic treatment described below. Symmetrization can be carried out in several ways and it must not be thought that the irreducible representation is necessarily optimal.

While it would be nice to claim that some particular sort of coordinates would be appropriate to molecular problems, the contrary appears to be the case, even for the simplest case of triatomic molecules. For the water molecule the most appropriate are the equivalent symmetric coordinates described below, for the HCN–HNC surface a single Jacobi mobile appears best, whereas for ozone the optimal current choice is hyperspherical polar.

The above criteria and the difficulty in fulfilling them suggest the need for some systematic method by which a potential, which is usually expressed in terms of some source coordinates (such as those of Carter et al.[9]) can be studied in a variety of coordinate systems. Just such an approach has been developed in the past few years by one of the present authors[2–4] and this work represents a systematization of an important part of the process not just for three– and four–body problems but for N–body systems.

2. Scalar Coordinates, Configuration Space and Label Space Descriptions.

The source coordinates in which molecular potentials are commonly expressed usually involve bond distances or a mixture of bond distances and angles[9]. While there may be variations, all of these 3N–6 scalar internal coordinates may be viewed as being derived from a set of N–1 interparticle (bond) vectors. Anticipating developments below for a moment, let x_k denote such a bond vector in the lab parallel center–of mass frame, and let $x = (x_1, x_2,..., x_n)$ be a column vector constructed from the set of $n = N–1$ bond vectors. The bilinear form defined by the (symmetric) Gram matrix,

$G = xx^t$

$$= \begin{bmatrix} x_1 \cdot x_1 & x_1 \cdot x_2 & \cdots & x_1 \cdot x_n \\ x_2 \cdot x_1 & x_2 \cdot x_2 & \cdots & x_2 \cdot x_n \\ \cdots & & & \\ x_n \cdot x_1 & x_n \cdot x_2 & \cdots & x_n \cdot x_n \end{bmatrix} \qquad (2.1)$$

is describable in terms of N(N–1)/2 scalars which are the lengths (bond lengths) of the vectors x_k, and their intervector angles (bond angles) $\theta_{ij} = \arccos(x_i \cdot x_j / |x_i||x_j|)$. For three– and four–body systems there are exactly as many such rotationally invariant scalars as linearly independent internal coordinates. For systems comprised of five or more bodies, the number of these invariants is greater than the 3N–6 permissible internal coordinates because not all the angles are linearly independent The following is worthy of note, however. Irrespective of how one defines the

3N–6 scalar coordinates, these are derivable from the invariants which in turn are derived from the bond vectors. One seeks to replace the non–orthogonal 3N–6 scalar invariants above by a system of mutually orthogonal scalar coordinates in the (3N–6)–dimensional subspace. A natural step in this procedure involves the transformation of the non–orthogonal bond vectors x_k into their orthogonal Jacobi counterparts denoted by the symbol Q, i.e. one seeks the transformation matrix O such that

$$Q = Ox \tag{2.2}$$

for variously defined orthonormal systems. Because of the several choices of interparticle vectors and their explicit relationship to the center–of–mass vector, it will be best to begin with the configuration space description of the N–body system.

Let i, j,... denote particle identification labels, and α, β, γ denote cartesian components. An arbitrary configuration in the 3N–dimensional configuration space, Ω_{3N}, can be denoted by a vector

$$X = \sum_{i,\alpha} x^{i\alpha} e_{i\alpha} \tag{2.3}$$

where the $x^{i\alpha}$ represent field components and the $e_{i\alpha}$ a system of orthogonal, but not normal, base vectors. The corresponding covariant metric tensor has block–diagonal form

$$g(\Omega) = \begin{bmatrix} D_N & 0 & 0 \\ 0 & D_N & 0 \\ 0 & 0 & D_N \end{bmatrix} \tag{2.4}$$

where

$$\mathbf{D}_N = \mathrm{diag}(m_1, m_2, \ldots, m_n) \tag{2.5}$$

The trace of $\mathbf{D}_N$ is the total mass M. The configuration space can be regarded as a direct product of a "label space", Λ_N, and a "physical space" E_3:

$$\Omega_{3N} = \Lambda_N \otimes E_3 \tag{2.6}$$

Likewise the base vectors of the configuration space can be expressed

$$\mathbf{e}_{i\alpha} = \mathbf{e}_i \otimes \mathbf{d}_\alpha \tag{2.7}$$

where $\mathbf{e}_i$ are the label space base vectors and $\mathbf{d}_\alpha$ are the "physical" three–dimensional–space base vectors.

Separation of the center–of–mass, description of the system topology, and the derivation of Jacobi coordiantes satisfying various criteria all involve linear transformations in the subspace Λ_N and its dual space. For the purpose of describing such transformations, consider a vector X represented in terms of two (covariant) base vector systems $\mathbf{e}$ and $\mathbf{e}'$. Let

$$\mathbf{e}' = \mathbf{A}\mathbf{e}, \qquad \mathbf{e} = \mathbf{A}^{-1}\mathbf{e}' \tag{2.8}$$

where $\mathbf{e}$, $\mathbf{e}'$ denote column vectors, and $\mathbf{A}$ is a matrix describing a linear transformation of basis. The corresponding field quantities x are also denoted by a column vector. Then

$$\mathrm{X} = \mathrm{x}^t\mathbf{e} = \mathrm{x}'^t\mathbf{e}' = \mathrm{x}'^t\mathbf{A}\mathbf{e} \tag{2.9}$$

Hence

$$\mathrm{x}' = (\mathbf{A}^{-1})^t\mathrm{x} \tag{2.10}$$

These relationships also determine the transformation law for the metric tensor,

$$\mathbf{g}' = \mathbf{e}'.\mathbf{e}^t = \mathbf{A}\mathbf{e}.\mathbf{e}^t\mathbf{A}^t = \mathbf{A}\mathbf{g}\mathbf{A}^t \tag{2.11}$$

The center–of–mass coordinate in Λ_N is conventionally defined as follows:

$$x'^{N} = M^{-1}\Sigma_i m_i x^i \qquad (2.12)$$

Interparticle bond vectors likewise have the usual form

$$x'^{k} = -x^i + x^j$$

$$(i \neq j,\ k = 1,2,\ldots,N-1) \qquad (2.13)$$

where in both equations (2.12) and (2.13) reference is made to the field components. In terms of equation (2.10) the matrix $(A^{-1})^t$ has the form

$$\begin{array}{c} \\ (k) \\ \\ (N) \end{array} \begin{array}{c} \begin{array}{ccccccc} & & (i) & & (j) & & \end{array} \\ \begin{bmatrix} \cdots & & & & & & \\ 0 & \cdots & -1 & \cdots & 1 & \cdots & 0 \\ \cdots & & & & & & \\ m_1/M & \cdots & m_i/M & \cdots & m_j/M & \cdots & m_n/M \end{bmatrix} \end{array} \qquad (2.14)$$

The first N–1 rows of this matrix determine the N–1 interparticle vectors in a unique fashion. The last row describes the center–of–mass coordiante. The matrix A^{-1} may be inverted analytically to generate the matrix A describing the transformation of base vectors:

$$A = \begin{bmatrix} \mu_1{}^{-1} & \mu_1 & \mu_1 & \cdots \\ \mu_{12}{}^{-1} & \mu_{12}{}^{-1} & \mu_{12} & \cdots \\ \mu_{123}{}^{-1} & \mu_{123}{}^{-1} & \mu_{123}{}^{-1} & \cdots \\ \cdots & & & \\ 1 & 1 & 1 & \cdots \end{bmatrix} \qquad (2.15)$$

where $\mu_i = m_i/M$ and $\mu_{ijk\ldots} = \mu_i + \mu_j + \mu_k + \ldots$

From equation(2.14) one easily demonstrates that

$$g'_{kN} = 0 \quad (\text{all } k \neq N) \tag{2.16}$$

This shows that the (N–1)–dimensional subspace spanned by the e'_k is orthogonal to the one–dimensional subspace spanned by e'_N. Thus the one–dimensional label space is a direct sum,

$$\Lambda_N = \Lambda_{rel} \oplus \Lambda_G \tag{2.17}$$

One may also verify that the various base vectors e'_k are not in general orthogonal among themselves, i.e.

$$g'_{jk} = e'_j . e'_k \neq 0 \quad (j \neq k) \tag{2.18}$$

One seeks those linear transformations, O, in the space Λ_{rel} which will diagonalize g'. All such transformations define orthogonal coordiantes in Λ_{rel}.

3. Orthonormalization procedures in Λ_{rel}.

Orthonormalization in the (n = N–1)–dimensional space Λ_{rel} can be carried out such as to satisfy several different criteria. An arbitrary basis transformation,

$$\mathbf{E'} = \mathbf{Oe} \tag{3.1}$$

is specified by the n^2 parameters constituting O. If $\mathbf{E'}$ is to represent an orthonormal set,

$$\mathbf{E'E'}^t = 1 \tag{3.2}$$

this specifies (n+1)n/2 conditions on the n^2 parameters and leaves n(n–1)/2 conditions which can be determined by choice. Several such choices will be implemented below.

The traditional method of achieving orthonormalization is that of

Gram–Schmidt. This produces the conventional N–body "mobiles" usually associated with Jacobi coordinates[5]. The procedure suffers from the disadvantage that it does not treat all of the bond vectors on an equal footing and, as a result, does not produce coordinates which reflect any symmetry inherent in the hamiltonian of a molecule which possesses sets of identical nuclei, such as H_2O, SO_3, etc. That deficiency can be rectified by a second choice which we shall call equivalent symmetric (ES) or by a transformation of these coordinates which produce coordinates transforming as the irreducible representations of the molecular PI group.

3.1. Gram–Schmidt.

Two separate aspects of the GS procedure are worthy of description, these being that we seek a matrix representation of the procedure and the second being that in order to obtain the field components in the orthonormal space in the desired form,

$$\begin{aligned} Q^1 &= \alpha x^1, \\ Q^2 &= \beta x^1 + \gamma x^2, \\ &\text{etc,} \end{aligned} \tag{3.3}$$

the GS procedure must be carried out on the base vectors of the dual space in inverse order.

Matrix representation of the Gram–Schmidt procedure has already been approached in the literature. Letting $e_1,...,e_n$ be linearly independent but not orthogonal base vectors, then a set $E_1,...,E_n$ of orthonormal base vectors may be derived from these as follows:

$$E_1 = N_1^{-1} e_1,$$
$$E_2 = N_2^{-1}[e_2 - (E_1.e_2)E_1]$$
...
$$E_k = N_k^{-1}[e_k - \sum_{r=1}^{k-1} (E_r.e_k)E_r] \tag{3.4}$$

where N_k is the norm of the vector e_k minus its projection on the span of $E_1,...,E_{k-1}$. This system of equations can be cast in the following form[12]

$$E_1 = D_1^{-1/2} e_1$$
$$E_2 = \Delta_2 \, (D_1 D_2)^{-1/2}$$

$$= \begin{vmatrix} e_1 \cdot e_1 & e_1 \cdot e_2 \\ e_1 & e_2 \end{vmatrix} (D_1 D_2)^{-1/2} \tag{3.5}$$

$$E_k = \Delta_k \, (D_{k-1} D_k)^{-1/2}$$

$$\begin{vmatrix} e_1 \cdot e_1 & e_1 \cdot e_2 & \cdots & e_1 \cdot e_k \\ \cdots & & & \\ e_1 \cdot e_{k-1} & e_2 \cdot e_{k-1} & \cdots & e_{k-1} \cdot e_{k-1} \\ e_1 & e_2 & & e_k \end{vmatrix} (D_{k-1} D_k)^{-1/2}$$

where D_k denotes the Gram determinant formed from $e_1,...,e_k$. Expanding the various determinants Δ_k in terms of the co–factors of the last row,

$$\Delta_k = \sum_{i}^{k} c_{ki} e_i \tag{3.6}$$

where $c_{ki} = (-1)^{k+i} |M_{ki}|$, it can be shown that

$$E_k = (D_{k-1} D_k)^{-1/2} \sum_{i=1}^{k} c_{ki} e_i \tag{3.7}$$

which gives explicit form to the required matrix transformation O_{GS},

$$E = O_{GS}e \tag{3.8}$$

By construction, it is evident that O_{GS} is a lower triangular matrix.

Our second requirement of Gram–Schmidt can be achieved by direct application of tensor algebra. If $e_0 = e_1,e_2,...,e_n$ is defined as the covariant basis in standard order, and $e_P = e_n,...,e_2,e_1 = Pe_0$ is the basis which results from an inversion of this order, and if e^P is the corresponding contravariant basis, then the transformation of the field components under the GS matrix which orthonormalizes the contravariant basis is given by

$$Q = (O^P)^{-1}x = P(O_0)^tPx \tag{3.9}$$

where O_0 is the GS matrix which orthonormalizes the standard covariant basis e_0. Since O_0 is a lower triangular matrix, its transpose is an upper triangular matrix. Pre– and post–multiplication by P recover the form of a lower triangular matrix, hence the field components have the desired form (3.3). It can be seen that the various bond coordinate vectors are not treated in an evenhanded fashion in the definition of the set of Jacobi coordiantes.

3.2. Equivalent symmetric (ES) coordinates.

In the transformation $E' = Oe$ in which E' represents an orthonormal set, let us require that

$$E'e^t = eE'^t \tag{3.10}$$

It follows that

$$Og = gO^t = g^tO^t = (Og)^t \tag{3.11}$$

i.e. Og is a symmetric matrix (g itself is by definition symmetric). Hence

$$g' = 1 = OgO^t = O^2 g$$

(3.12)

and

$$O = g^{-1/2} \tag{3.13}$$

The properties of g determine O uniquely. Since g is positive definite, so also is g^{-1} and there exists a unique positive square root given by[10]

$$O_s = \lim_{n\to\infty} O_n \tag{3.14}$$

where $O_0 = 0$ and

$$O_{n+1} = O_n + (g^{-1} - O_n^2)/2$$

(3.15)

Since O_s is a polynomial in g^{-1}, which is symmetric, all O_n are symmetric and O_s is a symmetric matrix.

In any molecule possessing a set of identical nuclei, if one chooses as bond vectors equivalent bonds (as for the three N–H bonds of NH_3), then the resultant set of ES Jacobi coordinates Q_1, Q_2 and Q_3 are merely interchanged by the operations of the molecular permutation–inversion group. In other words, these coordinates can be regarded as orthonormal (in the configuration space) analogues of the non–orthogonal bond vectors.

In the specific case of molecules of the form AX_n the various coordiantes of the ES representation are closely related to Radau coordinates[11]. The matrix O defining Radau coordiantes is inverse to that defining ES coordiantes, the difference deriving from orthogonalization in the configuration space and dual space respectively. Quite apart from this technical difference it should be noted, as described in section 3.4 below, that ES coordinates can be defined for systems such as AX_nY_m (e.g.,

CH_2X_2 and CH_2O) for which Radau coordinates have not been defined.

3.3 Irreducible symmetric (IS) coordinates.

With regard to the above example of NH_3, one may regard the set Q_1, Q_2, Q_3 as equivalent group generators of the PI group. In the conventional manner one can derive coordinates, R_n, which transform as the various irreducible representations of the group

$$R_\alpha = \sum_P \chi^\alpha(P)\ PQ_i \qquad (3.15)$$

where the $\chi^\alpha(P)$ are the characters for the various operators P for irreducible representation α.

3.4. Intermediate coordinates.

From the ES coordinates of section 3.2 above one can generate a variety of "intermediate" orthonormal coordinate systems. Consider each of the N–1 vectors Q_k as the position vector of a fictitious unit mass particle. Apply the same procedure as in equations (2.12) and (2.13) to separate the center–of–mass. The last row of the matrix corresponding to equation (2.14) has matrix elements given by 1/(N–1) while the upper rows are characterized by the same kind of choice before. This procedure defines a vector which is the "polysector" of the Q–vectors and an (N–2)–dimensional subspace which is orthogonal to the polysector but whose base vectors are not orthogonal to each other. It may be orthonormalized by any one of the above procedures to produce yet another orthonormal set of coordiantes. If one chooses ES coordinates for

the (N–2)–dimensional subspace and continues the procedure from the beginning of this section until the (N–2)–dimensional subspace is reduced to one dimension, the resulting coordinates coincide with the irreducible coordinates described in section 3.3.

4. Implementation.

Specification of particle masses and identification of a particular set of bond vectors are the only imput required to implement any of the orthonormalization schemes of the previous section. The resulting set of 3N–3 coordiantes Q^i are field components defined with respect to a (3N–3)–dimensional cartesian basis ($g_{ij} = \delta_{ij}$, i,j = 1,2,...,3N). This is exactly the required form from which to define 3N–3 curvilinear scalar coordinates which somehow identify the molecular frame (three coordinates) and 3N–6 rotationally invariant coordinates usually associated with "vibration". The work reported in this paper has been preparative to the choice of curvilinear coordinates. We have shown how to generate a variety of orthonormal precursors of scalar curvilinear coordiantes. The actual choice of a specific molecular frame (Hirschfelder, Eckart, etc)[1] is a quite separate issue, as is the definition of internal coordinates. While it is not our wish to address these topics here, it is perhaps appropriate to indicate how the above theory is to be employed. If we adopt the molecular frame described by Hirschfelder, for example, and choose as scalar internal coordinates the lengths of the vectors **Q** in physical space, together with the corresponding intervector angles, then the transformation between the sets

$$x^1, x^2, ..., x^{N(N-1)/2} \leftrightarrow Q^1, Q^2, ..., Q^{N(N-1)/2}$$

(where the x and Q refer to the scalars) is accomplished by means of the transformation

$$G(Q) = OG(x)O^t$$

(4.1)

where G(x) is defined in equation (2.1). For any number of particles the N–1 length coordiantes are orthogonal in the configuration space[2,3]. In systems having fewer than five nuclei, the angles either are orthogonal or may readily be orthogonalized, thereby leading to a relatively simple kinetic energy operator. The transformation (4.1) permits multidimensional plots[2–4] of the potential to be constructed with a view to choosing that set of coordinates (both by choice of scalars and by choice of section 3) which is optimal.

References.

1. L.C. Biedenharn and J.D. Louck, Angular momentum in Quantum Physics. Encyclopedia of Mathematics and its Applications (Addison–Wesley, Reading, 1981) Ch.7.
2. R. Wallace, Chem. Phys. 88 (1984) 247
3. R. Wallace, Chem. Phys. 98 (1985) 197
4. R. Wallace, Chem. Phys. 71 (1982) 173; 74 (1983) 339; 76 (1983) 421.
5. J.O Hirschfelder and J.S. Dahler, Physics 42 (1956) 363;
   D.W. Jepsen and J.O Hirschfelder, Physics 45 (1959) 249;
   J.O Hirschfelder, Intern. J. Quantum Chem. 3S (1969) 17.
6. B.R. Johnson, J. Chem. Phys. 73 (1980) 5051; 79 (1983) 1906, 1916
   M. Mishra and J. Linderberg, Mol. Phys. 50 (1983) 91.
   J. Linderberg and Y. Ohrn, Intern. J. Quantum Chem. 27 (1985) 273
7. Y. Ohrn an J. Linderberg, Mol. Phys. 49 (1983) 53
8. J.O Hirschfelder and E.P. Wigner, Physics 21 (1935) 113
9. S. Carter, I.M. Mills, J.N. Murrell and A.J.C. Varandas, Mol. Phys. 45 (1982) 1053
10. G. Bachman and L. Narici, Functional Analysis (Academic Press, New York, 1966)
11. F.T. Smith, Phys. Rev. Letters 45 (1980) 1157
12. In ref.1 notice that in the equations (7.10.32) and (7.10.38) the term $(D_1D_2D_3)^{-1/2}$ should be $(D_2D_3)^{-1/2}$.

The determination of Generalized Jacobi Vectors (GJV)
for common types of small molecules.

Methods previously described [1] to define generalized Jacobi vectors for N–body systems are elaborated for common types of small molecules to define a variety of orthonormal coordinates describing relative motion.

1.Introduction.

Configuration Space description of the N–body system.

The work presented in this paper is a direct elaboration of general methods previously described [1](and references therein) to define and derive (in algorithmic form) generalized Jacobi vectors (GJV) for N–body systems. Here the methods will be explicitly applied to generate orthonormal coordinates satisfying a variety of chosen symmetry constraints for typical small molecules AB_n, AB_2C_2, ABC_3. The resultant coordinates, as n–dimensional cartesian coordinates, are not immediately applicable to the analysis of molecular dynamics (except in the "trivial" case of infinitesimal amplitude motion) but are necessary intermediates in the construction of any kind of curvilinear relative coordinates. The most evident curvilinear coordinates would be basic rotational invariant coordinates (lengths of GJV and angles between them) which would be defined in exactly the same way for **any** choice of GJV. Definition of the GJV for any system therefore appears as a distinct problem in its own right and for that reason is all that is considered here.

Let i,j,... denote particle identification labels, and α,β,γ denote physical space cartesian components. An arbitrary configuration in the 3N–dimensional configuration space, Ω_{3N}, can be described by a vector

$$\vec{X} = \Sigma_i x^{i\alpha} e_{i\alpha} \qquad (1.1)$$

where the $x^{i\alpha}$ represent field components and the $e_{i\alpha}$ a system of orthogonal, but not normal, base vectors. The corresponding covariant metric tensor has block–diagonal form

$$g(\Omega) = \begin{bmatrix} D_N & 0 & 0 \\ 0 & D_N & 0 \\ 0 & 0 & D_N \end{bmatrix} \qquad (1.2)$$

where

$$D(N) = \mathrm{diag}(m_1, m_2, \ldots m_N). \qquad (1.3)$$

The trace of D(N) is the total mass M. The configuration space can be regarded as a direct product of a "label" space, Λ_N, and a "physical space", E_3:

$$\Omega_{3N} = \Lambda_N \otimes E_3. \qquad (1.4)$$

Likewise the base vectors of the configuration space can be expressed

$$\mathbf{e}_{i\alpha} = \mathbf{e}_i \otimes \mathbf{d}_3, \qquad (1.5)$$

where $\mathbf{e}_i$ are the label space base vectors and $\mathbf{d}_3$ are the "physical space" base vectors.

The set of cartesian coordinates, $\{x^{i\alpha}\}$ does not provide a particularly useful description of the system and it is conventional to perform an initial transformation from these coordinates to centre of mass – relative coordinates which lead to a more separable Hamiltonian. Such a coordinate transformation is accompanied by a transformation of base vectors, it being easily demonstrated (as in the examples below) that the base vectors of the relative subspace are not orthogonal. Since we must carry out transformations with respect to nonorthogonal bases, it is advantageous to make use of co– and contravariant bases, denoted (as column vectors) by $\mathbf{e}$ and $\tilde{\mathbf{e}}$ respectively. If $\mathbf{g}$ denotes the metric tensor for the covariant basis (square symmetric matrix), then the contravariant basis and contravariant metric tensor are expressed by the

matrix equations

$$\tilde{e} = \tilde{g}\, e \qquad\qquad \tilde{g} = g^{-1}. \qquad (1.6)$$

The value of the contravariant basis derives from a well known theorem which is simple to prove.

Linear transformations

Let e be a column vector denoting some covariant basis, $\tilde{e}$ a column vector denoting the corresponding contravariant basis.

Let x be a column vector denoting the contravariant field components, $\tilde{x}$ a column vector denoting the corresponding covariant field components.

Consider an arbitrary linear transformation of the covariant basis

$$e' = A\, e \qquad\qquad x' = (A^{-1})^t x \qquad (1.7)$$

The corresponding transformations of contravariant basis and covariant field components are as follows. Since $e = g\, \tilde{e}$

$$e' = g'\tilde{e}' = A\, e = A\, g\, \tilde{e}$$

Thus $$\tilde{e}' = (g')^{-1} A\, g\, \tilde{e} = \tilde{A}\, \tilde{e}$$

where $\tilde{A}$ denotes the appropriate transformation of the contravariant basis. Noting that $g' = A\, g\, A^t$

$$\tilde{e}' = (A^{-1})^t \tilde{e}$$

whence $$\tilde{A} = (A^{-1})^t \qquad (1.8)$$

Thus

> A linear transformation of the field components in the covariant basis is equivalent to the same transformation performed on the contravariant basis itself.

While transformations of field components appear as algebraic manipulations alone, transformations of bases are subject to a geometric

as well as an algebraic interpretation. It is this geometric interpretation which lends itself to the conception of alternate orthonormalization strategies.

As an example, consider the transformation to centre of mass and relative coordinates where, for simplicity, we restrict attention to the label space. Definition of the centre of mass coordinate

$$x'^N = \Sigma_i m_i x^i \tag{1.9}$$

and of (N–1) independent relative coordinates

$$x'^k = -x^i + x^j \tag{1.10}$$

correspond to a transformation of the field quantities (in the notation of the theorem above)

$$\mathbf{x}' = (\mathbf{A}^{-1})^t \mathbf{x} \tag{1.11}$$

to which there is a corresponding transformation of the contravariant base vectors $\tilde{e}$

$$\tilde{e}' = \tilde{A}\,\tilde{e}. \qquad (A^{-1})^t = \tilde{A} \tag{1.12}$$

It is readily verified from the metric tensor $\tilde{g}'$ that $\tilde{e}'^N$ is orthogonal to all of the relative base vectors $\tilde{e}'^k$ but that the latter are not orthogonal to each other. The implication is that the field component of the centre of mass x'^N will be separable in the Laplacian (KE operator). On the other hand, since the relative base vectors e'^i are not orthogonal, the corresponding covariant field components of the Laplacian will be coupled. Any stratagem to decouple such field components is none other than a way of generating an orthonormal contravariant basis. Reciprocally, any technique which orthogonalizes the contravariant basis will lead to a separable Laplacian.

If $\tilde{O}$ denotes an orthonormalizing transformation of the

contravariant basis, then

$$\tilde{E} = \tilde{O}\ \tilde{e}' \tag{1.13}$$

Since the base vectors $\tilde{E}$ are orthonormal

$$\tilde{E}\ \tilde{E}^t = 1 = \tilde{O}\ \tilde{g}'\ \tilde{O}^t \tag{1.14}$$

whence

$$\tilde{O}^{-1}(\tilde{O}^{-1})^t = \tilde{g}' \tag{1.15}$$

This equation can be interpreted as a condition to be satisfied by any orthonormalizing transformation.

While general computational procedures were previously described [1] to generate orthonormal GJV satisfying a variety of criteria, the procedures suitable to specific types of molecule and the interpretation and value of the resulting GJV were not discussed. A great many molecules of interest possess certain symmetry with respect to exchange within subsets of identical particles and it is important to generate GJV reflecting this symmetry. Such GJV cannot be generated by Gram Schmidt (GS) orthonormalization, but require for their definition some combination of at least two other orthonormalization procedures. The first is by generating equivalent symmetric (ES) GJV which are the orthogonal analogue of equivalent interparticle vectors (equivalent bonds). These are defined by the requirement $\tilde{O}^t = \tilde{O}$, i.e. $\tilde{O}$ is a symmetric matrix. In that case

$$\tilde{O}^{-2} = \tilde{g}' \qquad\qquad \tilde{O} = \tilde{g}'^{-1/2} \tag{1.16}$$

Irreducible symmetric (IS) coordinates are defined as the eigenvectors of g' (or $\tilde{g}'$, these being identical).

$$g'\ T = T\ \Lambda \qquad\qquad T^{-1} g'\ T = \Lambda \tag{1.17}$$

where Λ is the diagonal matrix of eigenvalues of g'. If the transformation to diagonal form is considered as resulting from a transformation M of basis, then

$$M\, g'\, M^t = \Lambda \qquad \text{whence} \qquad M^t = M^{-1} \tag{1.18}$$

i.e. M is an orthogonal matrix. The transformation M produces an orthogonal but not orthonormal basis. A second transformation by $\Lambda^{-1/2}$ leads to orthonormality. Since the eigenvalues Λ_i are usually nondegenerate, the eigenvectors T are usually unique. If certain Λ_i are degenerate, the nonuniqueness of the eigenvectors T may be removed by requiring that the T be simultaneous eigenvectors of g' and the matrix representatives of those symmetry operators which commute with g'. The eigenvectors T belong to one or other of the various irreducible representations of the group.

Irreducible symmetric coordinates possess a unique property. If $\vec{X} = \Sigma_i x^i e'_i$ is the relative configuration vector, then

$$\vec{X}.\vec{X} = \Sigma_{i,j} x^i x^j (e'_i . e'_j) = \Sigma_{i,j} G^{ij} g'_{ij} \tag{1.19}$$

where $G^{ij} = x^i x^j$ is the Gram matrix. Because g_{ij} is symmetric

$$\vec{X}.\vec{X} = \Sigma_i (\Sigma_j G^{ij} g_{ji}) = \Sigma_i\ G\ g' = \mathrm{Tr}\ (G\ g')$$

Since the trace is invariant to a similarity transformation T

$$\mathrm{Tr}\ (G\ g') = \mathrm{Tr}[(T^{-1} G\ T)(T^{-1} g' T)] = \mathrm{Tr}\ (G''\ g'')$$

If T corresponds to the eigenvectors of g' then

$$\mathrm{Tr}\ (G\ g') = \mathrm{Tr}\ (G''\ \Lambda) \tag{1.20}$$

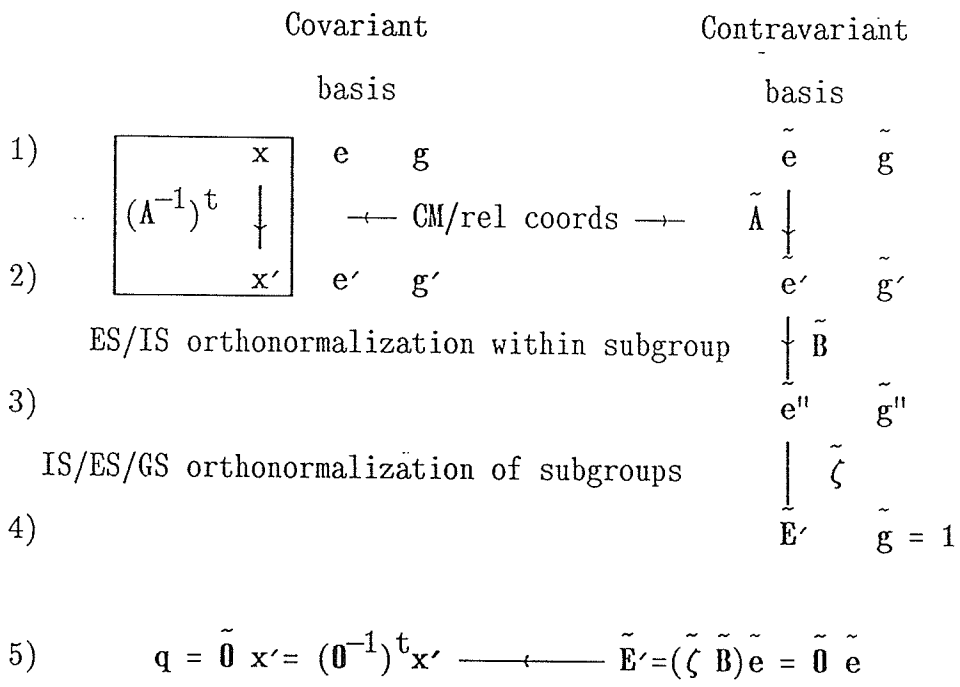
which is a function of the diagonal elements G''_{ii} alone. The importance of this result is that any quadratic function

$$V = \Sigma_{ij} k_{ij} x^i x^j \tag{1.21}$$

can be reduced to diagonal form in irreducible symmetric coordinates.

Because the kinetic energy operator is invariant to any fixed displacement of coordinate origin, it follows that, if the origin is shifted to the equilibrium configuration (in configuration space) and if the x^i are displacements therefrom, the irreducible symmetric coordinates above, with a potential of the form (1.21) become the conventional "normal coordinates" of the system. Conversely, the "normal coordinates" are seen to be a particular realization of one of many orthonormal coordinate sets describing the system.

Molecules often possess different types of identical particles as for example in molecules of the type AB_nC_m. In such cases orthonormalization may first be performed on each identifiable subgroup of equivalent interparticle vectors, the resultant GJV being orthogonalized with respect to each other at the end. The procedure applied in the examples is explained schematically below.



2. Orthonormalization procedures for AB_n molecules.

In the case of the AB_n systems let particle 1 have mass m, the remaining particles being given mass m′(m +nm′ = M).

$$\tilde{g}_{ij} = (1/mm')^{1/2}\delta_{ij} \tag{2.1}$$

Corresponding to the choice of field components x^{12}, x^{13}, ...x^{1n}, the matrix $\tilde{A} = (A^{-1})^t$is given by

$$\tilde{A} = \begin{bmatrix} -1 & 1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 1 & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \frac{m'}{M} & \frac{m}{M} & \frac{m}{M} & \frac{m}{M} & \frac{m}{M} & \frac{m}{M} \end{bmatrix} \qquad (2.2)$$

The new metric tensor is $\tilde{g}' = \tilde{A}\,\tilde{g}\,\tilde{A}^t$ where

$$\tilde{g}' = \begin{bmatrix} \mu' & 1/m & 1/m & 1/m & \cdots & 0 \\ 1/m & \mu' & 1/m & 1/m & \cdots & 0 \\ 1/m & 1/m & \mu' & 1/m & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & 0 & \cdots & 1/M \end{bmatrix} \qquad (2.3)$$

with $\mu' = (m+m')/mm'$. Setting $\cos\phi = 1/m\mu' = m'/(m+m')$ and restricting consideration to the relative subspace

$$\tilde{g}' = \mu' \begin{bmatrix} 1 & \cos\phi & \cos\phi & \cos\phi & \cdots \\ \cos\phi & 1 & \cos\phi & \cos\phi & \cdots \\ \cos\phi & \cos\phi & 1 & \cos\phi & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cos\phi & \cos\phi & \cdots & \cdots & 1 \end{bmatrix} \qquad (2.4)$$

If we introduce an orthonormal basis

$$\tilde{E} = \tilde{O}\ \tilde{e}' \tag{2.5}$$

then, as before $\tilde{g}' = \tilde{O}^{-1}(\tilde{O}^{-1})^t$. If, in addition, $\tilde{O}^{-1}$ is symmetric corresponding to the choice of ES coordinates, then $\tilde{g}' = \tilde{O}^{-2}$ or $\tilde{O} = \tilde{g}'^{-1/2}$. From a practical standpoint, the matrix $\tilde{O}$ is in this case more easily computed from $\tilde{O}^{\,2} = \tilde{g}'^{-1} = g'$ where $g' = A\ g\ A^t$. The matrix A can be analytically obtained by inversion of A^{-1}

$$\Lambda = \begin{bmatrix} -\mu & 1-\mu & -\mu & & -\mu \\ -\mu & -\mu & 1-\mu & & -\mu \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 1 & 1 & 1 & & 1 \end{bmatrix} \tag{2.6}$$

where $\mu = m/M$. Thus

$$g' = M\begin{bmatrix} \mu(1-\mu) & -\mu^2 & -\mu^2 & -\mu^2 & 0 \\ -\mu^2 & \mu(1-\mu) & -\mu^2 & -\mu^2 & 0 \\ \cdots & \cdots & \cdots & \cdots & 0 \\ -\mu^2 & -\mu^2 & -\mu^2 & \mu(1-\mu)^2 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \qquad (2.7)$$

Restricting attention once more to the relative subspace and setting

$$\alpha = [M\mu/(1-\mu)]^{1/2} \quad \cos\phi = -\mu/(1-\mu) \qquad (2.8)$$

it follows that

$$g'_{rel} = \alpha^2 \begin{bmatrix} 1 & \cos\phi & \cos\phi & \cos\phi \\ \cos\phi & 1 & \cos\phi & \cos\phi \\ \cdots & \cdots & \cdots & \cdots \\ \cos\phi & \cos\phi & \cos\phi & 1 \end{bmatrix} \qquad (2.9)$$

g'_{rel} is a positive matrix since $(1-\cos\phi)$, $1 + (n-1)\cos\phi \geq 0$. Since g'_{rel} is a circulant matrix then $\tilde{O} = g'^{1/2}_{rel}$ can also be shown (appendix 1) to be a circulant

$$\tilde{O} = \begin{bmatrix} a & b & b & b \ldots \\ b & a & b & b \ldots \\ \cdots & \cdots & \cdots & \cdots \\ b & b & b & b \ldots a \end{bmatrix} \qquad (2.10)$$

It follows that

$$a = (\alpha/n)\{\tfrac{1}{2}[1 + (n-1)\cos\phi] + (n-1)\tfrac{1}{2}(1-\cos\phi)\}$$

$$b = (\alpha/n)\{\tfrac{1}{2}[1 + (n-1)\cos\phi] - \tfrac{1}{2}(1-\cos\phi)\} \qquad (2.11)$$

Noting that $a - b = \alpha\tfrac{1}{2}(1-\cos\phi) = \beta$

then $$a = b + \beta \qquad (2.12)$$

Without further elaboration, the ES coordinates are seen to be of the form

$$q^1 = (b+\beta)x^{12} + bx^{13} + bx^{14} + \ldots\ldots bx^{1n}$$

$$q^2 = bx^{12} + (b+\beta)x^{13} + bx^{14} + \ldots\ldots bx^{1n}$$

etc. (2.13)

It is easy to see that these are converted into each other under the operations of the molecular group. In this sense the q^i are equivalent symmetric coordinates. The various coordinates Q^i, which result by using the projection relation for the group of equivalent bonds with one of the above as a group generator, transform as the various irreducible representations of the group.

3. Generalized Jacobi Vectors for AB_2C_2 systems.

Let $m_A = m$, $m_B = m'$, $m_C = m''$ and the total mass be M. Assign to A the label (1), to particles B the labels (2) and (3) and to particles C the labels (4) and (5). The contravariant metric tensor is:

$$\tilde{g} = \begin{bmatrix} \frac{1}{m} & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{m'} & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{m'} & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{m''} & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{m''} \end{bmatrix} \qquad (3.1)$$

Once more the coordinate choice from which to generate orthonormal coordinates is $x^{12}, x^{13}, x^{14}, x^{15}$.

The matrix $\tilde{A}$ representing the transformation into the CM/relative contravariant basis is:

$$\tilde{A} = \begin{bmatrix} -1 & 1 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 1 & 0 \\ -1 & 0 & 0 & 0 & 1 \\ \frac{m}{M} & \frac{m'}{M} & \frac{m'}{M} & \frac{m''}{M} & \frac{m''}{M} \end{bmatrix} \qquad (3.2)$$

The new metric tensor is $\tilde{g}' = \tilde{A}\,\tilde{g}\,\tilde{A}^t$:

$$\tilde{g}' = \begin{bmatrix} \mu' & \frac{1}{m} & \frac{1}{m} & \frac{1}{m} & 0 \\ \frac{1}{m} & \mu' & \frac{1}{m} & \frac{1}{m} & 0 \\ \frac{1}{m} & \frac{1}{m} & \mu'' & \frac{1}{m} & 0 \\ \frac{1}{m} & \frac{1}{m} & \frac{1}{m} & \mu'' & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{M} \end{bmatrix} \qquad (3.3)$$

where $\mu' = \frac{m'+m}{m'm}$ and $\mu'' = \frac{m''+m}{m''m}$

The contravariant basis $\{e^1, e^2, \ldots e^4\}$ is not orthonormal:

$$(e^1,e^1) = (e^2,e^2) = \mu'^{1/2}$$
$$(e^3,e^3) = (e^4,e^4) = \mu''^{1/2}$$
$$\cos\phi_{23} = \frac{m'}{m+m'} = \cos\phi'; \quad \cos\phi_{45} = \frac{m''}{m+m''} = \cos\phi''$$
$$\cos\phi_{24} = \left[\frac{m'm''}{(m+m')(m+m'')}\right]^{1/2} = \cos\zeta \qquad (3.4)$$

$$\tilde{g}' = \begin{bmatrix} \mu' & \mu'\cos\phi' & (\mu'\mu'')^{1/2}\cos\zeta & (\mu'\mu'')^{1/2}\cos\zeta \\ \mu'\cos\phi' & \mu' & (\mu'\mu'')^{1/2}\cos\zeta & (\mu'\mu'')^{1/2}\cos\zeta \\ (\mu'\mu'')^{1/2}\cos\zeta & (\mu'\mu'')^{1/2}\cos\zeta & \mu'' & \mu''\cos\phi'' \\ (\mu'\mu'')^{1/2}\cos\zeta & (\mu'\mu'')^{1/2}\cos\zeta & \mu''\cos\phi'' & \mu'' \end{bmatrix}$$

(3.5)

Orthonormalization Procedures.

Three distinct orthonormalization procedures will be considered as examples, the resultant coordinates being, respectively, orthonormal arbitrary amplitude analogues of local mode, mixed mode, and normal mode coordinates. In each of these the AB_2 and AC_2 fragments will first be orthonormalized either by ES or IS orthonormalization. In all of the following attention will be focussed on the structure of the various matrices, the actual values of the matrix components being suppressed to give emphasis to this structure. The values themselves follow automatically from the various operations.

a) ES orthonormalization of AB_2 and AC_2 fragments.

Following from appendices 2 and 3, a matrix of the form

$$\tilde{B} = \begin{bmatrix} \Lambda'_+ & -\Lambda'_- & 0 & 0 \\ -\Lambda'_- & \Lambda'_+ & 0 & 0 \\ 0 & 0 & \Lambda''_+ & -\Lambda''_- \\ 0 & 0 & -\Lambda''_- & \Lambda''_+ \end{bmatrix} \qquad (3.6)$$

will, under the transformation $\tilde{B}\,\tilde{g}'\tilde{B}^t$, transform $\tilde{g}'$ to the form

$$\tilde{g}'' = \begin{bmatrix} 1 & 0 & A & A \\ 0 & 1 & A & A \\ A & A & 1 & 0 \\ A & A & 0 & 1 \end{bmatrix} \qquad (3.7)$$

which is seen to separately orthonormalize the AB_2 and AC_2 subspaces. The matrix $g''^{-1/2}$ (Appendix $\bar{4}$) will, by the ES procedure, orthonormalize these subspaces with respect to each other, thus the complete orthonormalization matrix $\tilde{O}_{es} = \tilde{g}''^{-1/2}\,\tilde{B}$ is of the form

$$\tilde{O}_{es} = \begin{bmatrix} \alpha' & \beta' & \gamma'' & \gamma'' \\ \beta' & \alpha' & \gamma'' & \gamma'' \\ \gamma' & \gamma' & \alpha'' & \beta'' \\ \gamma' & \gamma' & \beta'' & \alpha'' \end{bmatrix} \tag{3.8}$$

whence

$$\begin{aligned} q^1 &= \alpha' x^{12} + \beta' x^{13} + \gamma'' x^{14} + \gamma'' x^{15} \\ q^2 &= \beta' x^{12} + \alpha' x^{13} + \gamma'' x^{14} + \gamma'' x^{15} \\ q^3 &= \gamma' x^{12} + \gamma' x^{13} + \alpha'' x^{14} + \beta'' x^{15} \\ q^4 &= \gamma' x^{12} + \gamma' x^{13} + \beta'' x^{14} + \alpha'' x^{15} \end{aligned} \tag{3.9}$$

These represent four orthonormal internal coordinates such that

$$\begin{aligned} &(23)q^1 = q^2 \quad (23)q^2 = q^1 \quad (23)q^3 = q^3 \quad (23)q^4 = q^4 \\ &(45)q^1 = q^1 \quad (45)q^2 = q^2 \quad (45)q^3 = q^4 \quad (45)q^4 = q^3 \end{aligned} \tag{3.10}$$

b) Mixed mode orthonormalization.

In a molecule such as CH_2Cl_2 it may be desirable to treat the CH_2 fragment in "local mode" fashion and the CCl_2 fragment in "normal mode" fashion. The matrix

$$\tilde{B} = \begin{bmatrix} \Lambda_+ & -\Lambda_- & 0 & 0 \\ -\Lambda_- & \Lambda_+ & 0 & 0 \\ 0 & 0 & \epsilon & \epsilon \\ 0 & 0 & \gamma & -\gamma \end{bmatrix} \tag{3.11}$$

transforms $\tilde{g}'$ to the form

$$\tilde{g}'' = \begin{bmatrix} 1 & 0 & C & 0 \\ 0 & 1 & C & 0 \\ C & C & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \tag{3.12}$$

As before the AB_2 and AC_2 subspaces are separately orthonormal but in this case the antisymmetric AC_2 vector is orthogonal to all others. To maintain the integrity of the AB_2 fragment coordinates a Gram–Schmidt orthogonalization is called for. If the base vectors underlying $\tilde{g}''$ are denoted $e^1,...e^4$ and the corresponding orthonormal vectors are $E^1.....E^4$ then define

$$\begin{bmatrix} E^1 \\ E^2 \\ E^3 \\ E^4 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ \alpha & \alpha & \beta & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} e^1 \\ e^2 \\ e^3 \\ e^4 \end{bmatrix} = \tilde{\zeta}\ \tilde{e} \tag{3.13}$$

Thus the complete orthonormalizing transformation is $\tilde{O}_{mx} = \tilde{\zeta}\ \tilde{B}$ where $\tilde{O}_{mx}$ has the form

$$\tilde{O}_{mx} = \begin{bmatrix} \Lambda_+ & -\Lambda_- & 0 & 0 \\ -\Lambda_- & \Lambda_+ & 0 & 0 \\ \alpha(\Lambda_+ - \Lambda_-) & \alpha(\Lambda_+ - \Lambda_-) & \beta\epsilon & \beta\epsilon \\ 0 & 0 & \gamma & -\gamma \end{bmatrix} \tag{3.14}$$

As in the previous procedure $q = \tilde{O}_{mx}\, x$ and

$$(23)q^1 = q^2 \quad (23)q^2 = q^1 \quad (23)q^3 = q^3 \quad (23)q^4 = q^4$$
$$(45)q^1 = q^1 \quad (45)q^2 = q^2 \quad (45)q^3 = q^3 \quad (45)q^4 = -q^4 \qquad (3.15)$$

c) Irreducible orthonormalization of both fragments.

The matrix

$$\tilde{B} = \begin{bmatrix} \epsilon & \epsilon & 0 & 0 \\ \delta & -\delta & 0 & 0 \\ 0 & 0 & \epsilon' & \epsilon' \\ 0 & 0 & \delta' & -\delta' \end{bmatrix} \qquad (3.16)$$

transforms $\tilde{g}'$ to the form

$$\tilde{g}'' = \begin{bmatrix} 1 & 0 & A & 0 \\ 0 & 1 & 0 & 0 \\ A & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \qquad (3.17)$$

By inspection it can be seen solution of the eigenproblem for $\tilde{g}''$ yields two degenerate eigenvalues (base vectors e_2 and e_4 being already orthonormal) Solution of the eigenproblem for the pair e_1, e_3 permits us to define new orthonormal base vectors by multiplying those underlying $\tilde{g}''$ by the matrix

$$\tilde{\zeta} = 2^{-1/2} \begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & -1 & 0 \\ 0 & -1 & 0 & 1 \end{bmatrix} \qquad (3.18)$$

Thus $\tilde{O}_{IS} = \tilde{\zeta}\,\tilde{B}$ is of the form

$$\tilde{O}_{IS} = \begin{bmatrix} A & A & A' & A' \\ B & -B & B' & -B' \\ C & C & -C' & -C' \\ D & -D & -D' & D' \end{bmatrix} \tag{3.19}$$

and from $q = \tilde{O}_{IS}\, x$, we derive

$$\begin{aligned} &(23)q^1 = q^1 \quad (23)q^2 = -q^2 \quad (23)q^3 = q^3 \quad (23)q^4 = -q^4 \\ &(45)q^1 = q^1 \quad (45)q^2 = -q^2 \quad (45)q^3 = q^3 \quad (45)q^4 = -q^4 \end{aligned} \tag{3.20}$$

4. Generalized Jacobi vectors for AB_3C systems.

Let $m_A = m$, $m_B = m'$, $m_C = m''$ and the total mass be M. Assign to A the label (1), to particles B the labels (2), (3) and (4) and to particle C the label (5). The metric tensor for the contravariant basis $\{e^1, e^2, e^3, e^4, e^5\}$ is:

$$\tilde{g} = \begin{bmatrix} \frac{1}{m} & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{m'} & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{m'} & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{m'} & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{m''} \end{bmatrix} \tag{4.1}$$

The source coordinates as before are chosen to be $x^{12},x^{13},x^{14},x^{15}$.

The matrix $\tilde{A}$ representing the transformation into the CM/relative contravariant basis is:

$$\tilde{A} = \begin{bmatrix} -1 & 1 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 1 & 0 \\ -1 & 0 & 0 & 0 & 1 \\ \frac{m}{M} & \frac{m'}{M} & \frac{m'}{M} & \frac{m'}{M} & \frac{m''}{M} \end{bmatrix} \qquad (4.2)$$

The new metric tensor is $\tilde{g}' = \tilde{A}\,\tilde{g}\,\tilde{A}^t$:

$$\tilde{g}' = \begin{bmatrix} \mu' & \frac{1}{m} & \frac{1}{m} & \frac{1}{m} & 0 \\ \frac{1}{m} & \mu' & \frac{1}{m} & \frac{1}{m} & 0 \\ \frac{1}{m} & \frac{1}{m} & \mu' & \frac{1}{m} & 0 \\ \frac{1}{m} & \frac{1}{m} & \frac{1}{m} & \mu'' & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{M} \end{bmatrix} \qquad (4.3)$$

where $\mu' = \frac{m'+m}{m'm}$ and $\mu'' = \frac{m''+m}{m''m}$.

In the relative label subspace, the contravariant basis $\{e'^1,e'^2,e'^3,e'^4\}$ is not orthonormal:

$$\tilde{g}'_{11} = \tilde{g}'_{22} = \tilde{g}'_{33} = \mu'^{1/2}$$
$$\tilde{g}'_{44} = \mu''^{1/2}$$
$$\cos\phi_{23} = \cos\phi_{24} = \cos\phi_{34} = \frac{m'}{m+m'} = \cos\phi$$
$$\cos\phi_{25} = \cos\phi_{35} = \cos\phi_{45} = \left[\frac{m'm''}{(m+m')(m+m'')}\right]^{1/2} = \cos\zeta \tag{4.4}$$

$$\tilde{g}' = \begin{bmatrix} \mu' & \mu'\cos\phi & \mu'\cos\phi & \eta \\ \mu'\cos\phi & \mu' & \mu'\cos\phi & \eta \\ \mu'\cos\phi & \mu'\cos\phi & \mu' & \eta \\ \eta & \eta & \eta & \mu'' \end{bmatrix} \tag{4.5}$$

where $\eta = (\mu'\mu'')^{1/2}\cos\zeta$.

Orthonormalization procedures.

In order to conserve the symmetry of AB_3, we may orthonormalize the sub–basis $\{e'^1, e'^2, e'^3\}$ by either ES or IS procedure:

In either case the extension in relative label space is:

$$\tilde{B} = \begin{bmatrix} \tilde{B}' & 0 \\ 0 & 1 \end{bmatrix} \tag{4.6}$$

where $\tilde{B}'$ is the 3×3 matrix:

$$\tilde{B}' = \begin{bmatrix} a & b & b \\ b & a & b \\ b & b & a \end{bmatrix} \quad \text{ES} \qquad \text{or} \qquad \begin{bmatrix} \alpha & \alpha & \alpha \\ \beta & -\beta & 0 \\ -\gamma & -\gamma & 2\gamma \end{bmatrix} \quad \text{IS} \qquad (4.7)$$

with:

$$a = \frac{(2\sqrt{M} + \sqrt{m})\sqrt{m'}}{3\sqrt{M}}$$

$$b = \frac{(\sqrt{m} - \sqrt{M})\sqrt{m'}}{3\sqrt{M}}$$

Under this transformation the new metric tensor is $\tilde{g}'' = \tilde{B}\,\tilde{g}'\tilde{B}^t$:

$$\tilde{g}'' = \begin{bmatrix} 1 & 0 & 0 & A \\ 0 & 1 & 0 & A \\ 0 & 0 & 1 & A \\ A & A & A & \mu'' \end{bmatrix} \quad \text{ES} \qquad \text{or} \qquad \begin{bmatrix} 1 & 0 & 0 & C \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ C & 0 & 0 & \mu'' \end{bmatrix} \quad \text{IS} \qquad (4.8)$$

where:

$$A = \left[\frac{m'}{mM}\right]^{1/2}$$

Either of the new bases could be orthonormalized by GS, ES, or IS procedures yielding a total of six distinct orthonormal coordinate systems, all of which should now be derivable by the reader. A priori, one cannot say which of these would be best suited to a particular molecule or application. Nevertheless, if , as in the previous example, one wishes to maintain an orthonormal "local mode" description of the CH_3 fragment,

and if one is interested primarily in observables related to the CH_3 fragment, then GS orthonormalization of the first of the above bases will be the favoured choice, the above basis being orthonormalized in the order (1,2,3,4). Since the three first vectors are already orthonormalized, the GS procedure does not affect them (integrity of fragment coordinates maintained). We find:

$$\tilde{\zeta}_{GS} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ c & c & c & d \end{bmatrix} \qquad (4.9)$$

where:

$$c = -\left[\frac{mm''}{(m+m'')^2+3mm''}\right]^{1/2} \qquad d = \left[\frac{Mmm''}{(m+m'')^2+3mm''}\right]^{1/2}$$

The overall transformation is the matrix $\tilde{O} = \tilde{\zeta}_{GS}\tilde{B}$:

$$\tilde{O}_{GS} = \begin{bmatrix} a & b & b & 0 \\ b & a & b & 0 \\ b & b & a & 0 \\ c(a+2b) & c(a+2b) & c(a+2b) & d \end{bmatrix} \qquad (4.10)$$

Appendix 1.

Positive square root of a circulant.

Let A be a matrix

$$A = \begin{bmatrix} a & b & b & b & \ldots\ldots \\ b & a & b & b & \ldots\ldots \\ b & b & a & b & \ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{bmatrix}$$

Then

1) A is positive iff $a-b,\ a+(n-1)b \geq 0$.

Suppose A is positive, then

2) The positive square root of A has the form

$$B = \begin{bmatrix} a' & b' & b' & b' & \ldots\ldots \\ b' & a' & b' & b' & \ldots\ldots \\ b' & b' & a' & b' & \ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{bmatrix}$$

where

$$a' = \frac{1}{n}\{\sqrt{}[a+(n-1)b] + (n-1)\sqrt{}(a-b)\}$$
$$b' = \frac{1}{n}\{\sqrt{}[a+(n-1)b] - \sqrt{}(a-b)\}$$

.....

Proof:

Fact 1: $A \in L(\mathbb{R}^n,\mathbb{R}^n)$, A is positive, then A has a unique positive square root [2].

Definition: A circulant is defined as a matrix

$$\text{circ } (a_1,.....a_n) = \begin{bmatrix} a_1 & a_2 & a_3 & & a_n \\ a_n & a_1 & a_2 & & a_{n-1} \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{bmatrix}$$

Fact 2: $A \in M_{nn}(\mathbb{C})$

1) A is a circulant iff A commutes with π

where

π = circ (0,1,0,0,0,0,0...)

2) If A is a circulant it can be diagonalized. All circulants are diagonalized by a matrix X

$$X = \begin{bmatrix} 1 & 1 & 1 & 1 & & 1 \\ 1 & \omega & \omega^2 & \omega^3 & & \omega^{n-1} \\ 1 & \omega^2 & (\omega^2)^2 & \cdots\cdots\cdots & & (\omega^{n-1})^2 \\ 1 & & & & & \end{bmatrix}$$

where $\omega = \exp(2\pi\iota/n)$.

3) A is a circulant

$$\det A = \prod_{j=1}^{n} [a_1 + \sum_{k=1}^{n-1} (\omega^j)^k a_{k+1}]$$

In our case

$$\det A = (a-b)^{n-1} \cdot [a+(n-1)b]$$

i) The eigenvalues of A are $(a-b)$, $[a+(n-1)b] \geq 0$.

ii) $A = B^2$. $[\pi, A] = 0$. Thus

$$\pi^{-1}A\pi = A = (\pi^{-1}B\pi)^2 = B^2$$

and $\pi^{-1}B\pi = B$ or $[\pi, B] = 0$

whence B is a circulant.

Then $X^{-1}AX = (X^{-1}BX)^2$

in which case B has the eigenvalues $\pm(a-b)$, $\pm(a+(n-1)b)$.

Denoting the eigenvalues of B by a column vector $\Lambda = (\lambda_1, \ldots \lambda_n)$, we can write, since B is a circulant defined by n quantities $a = (a_1, a_2 \ldots a_n)$

$$\Lambda = X\,a \qquad\qquad a = X^{-1}\Lambda$$

where

$$X^{-1} = \begin{bmatrix} 1 & 1 & 1 & & 1 \\ 1 & \omega^{n-1} & \cdots\cdots\cdots\cdots & & \omega \\ 1 & (\omega^{n-1})^2 & \cdots\cdots\cdots & & \omega^2 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 1 & (\omega^{n-1})^{n-1} & & & \omega^{n-1} \end{bmatrix}$$

whence in our case where a = (a′,b′,b′.....)

$$a' = \frac{1}{n}\{\sqrt{}[a+(n-1)b] + (n-1)\sqrt{}(a-b)\}$$
$$b' = \frac{1}{n}\{\sqrt{}[a+(n-1)b] - \sqrt{}(a-b)\}$$

Appendix 2.

$\tilde{g}^{1/2}$ and $\tilde{g}^{-1/2}$ for the 2 x 2 case.

Let

$$\tilde{g} = \begin{bmatrix} a & b \\ b & a \end{bmatrix}$$

Then from Appendix 1

$$\tilde{g}^{1/2} = \begin{bmatrix} \lambda_+ & \lambda_- \\ \lambda_- & \lambda_+ \end{bmatrix}$$

where

$$\lambda_+ = \frac{1}{2}[\sqrt{}(a+b) + \sqrt{}(a-b)]$$
$$\lambda_- = \frac{1}{2}[\sqrt{}(a+b) - \sqrt{}(a-b)]$$

With $\Delta = \lambda_+^2 - \lambda_-^2$, $\Lambda_+ = \lambda_+/\Delta$, and $\Lambda_- = \lambda_-/\Delta$

$$\tilde{0} = \tilde{g}^{-1/2} = \begin{bmatrix} \Lambda_+ & -\Lambda_- \\ -\Lambda_- & \Lambda_+ \end{bmatrix}$$

where $\tilde{O}$ is an orthonormalizing matrix, i.e. $\tilde{O}\ \tilde{g}\ \tilde{O}^t = 1$

Appendix 3:

Irreducible orthonormalization of a 2 x 2 matrix.

The eigenvalues of the matrix $\tilde{g}$ are $\gamma = a \pm b$. If we express the eigenvalues as a matrix

$$\Gamma = \begin{bmatrix} (a+b) & 0 \\ 0 & (a-b) \end{bmatrix}$$

the corresponding eigenvectors are

$$\Gamma = 2^{-1/2} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$$

and $\Gamma = \zeta\ \tilde{g}\ \zeta^t$. Orthonormalization of $\tilde{g}$ is therefore achieved by a matrix

$$\tilde{0} = \Gamma^{-1/2}\zeta = 2^{-1/2} \begin{bmatrix} (a+b)^{-1/2} & (a+b)^{-1/2} \\ (a-b)^{-1/2} & -(a-b)^{-1/2} \end{bmatrix}$$

which is of the form

$$\tilde{O} = \begin{bmatrix} \epsilon & \epsilon \\ \tau & -\tau \end{bmatrix}$$

with

$$\epsilon = [2(a+b)]^{-1/2} \qquad \tau = [2(a-b)]^{-1/2}$$

Appendix 4.

AB_2C_2 model: positive square root of $\tilde{g}''^{-1/2}$.

Let A ($\tilde{g}''$) be of the form:

$$A = \begin{bmatrix} 1 & 0 & a & a \\ 0 & 1 & a & a \\ a & a & 1 & 0 \\ a & a & 0 & 1 \end{bmatrix}$$

To evaluate the **positive** square root $A^{-1/2}$, let us consider (in the fashion of Appendix 1) :

$$A^{-1/2} = \rho^t \Lambda^{-1/2} \rho \tag{A4.1}$$

where ρ diagonalizes the symmetric, positive definite matrix A:

$$\rho\ A\ \rho^t = \Lambda = \mathrm{diag}(\lambda_1,\lambda_2,\lambda_3,\lambda_4). \tag{A4.2}$$

The determinant of A is factorized in the following way

$$|A| = (\lambda-1)^2(\lambda-1-2a)(\lambda-1+2a) \tag{A4.3}$$

The eigenvalues of A are

$$\lambda_1 = 1+2a \qquad \lambda_2 = 1-2a \qquad \lambda_3 = \lambda_4 = 1 \tag{A4.4}$$

Thus

$$\Lambda^{-1/2} = \mathrm{diag}([1+2a]^{-1/2},[1-2a]^{-1/2},1,1) \tag{A4.5}$$

ρ is defined up to a 2–d. rotation of the subspace spanned by the vectors corresponding to λ_3 and λ_4.

$\vec{\rho}_1$ is the eigenvector corresponding to λ_1:

$$(\rho_{11},\rho_{12},\rho_{13},\rho_{14})\mathrm{A} = (1+2a)(\rho_{11},\rho_{12},\rho_{13},\rho_{14})$$

Therefore

$$\vec{\rho}_1 = \tfrac{1}{2}(1,1,1,1) \qquad \text{(A4.6)}$$

Similarly,

$$\vec{\rho}_2 = \tfrac{1}{2}(1,1,-1,-1)$$

Substitute in (A4.1) and use the orthogonality relations:

for k=1,2,3,4: $\quad \rho_{3k}^2 + \rho_{4k}^2 = 1/2$

for $k \neq k' = 1,2,3,4$ $\quad \rho_{3k}\rho_{3k'} + \rho_{4k}\rho_{4k'} = -1/2$

Finally, the positive solution of $\mathrm{A}^{-1/2}$ is given by:

$$\mathrm{A}^{-1/2} = \frac{1}{4}\begin{bmatrix} \alpha & \beta & \gamma & \gamma \\ \beta & \alpha & \gamma & \gamma \\ \gamma & \gamma & \alpha & \beta \\ \gamma & \gamma & \beta & \alpha \end{bmatrix} \qquad \text{(A4.8)}$$

where:

$$\alpha = (1+2a)^{-1/2} + (1-2a)^{-1/2} + 2$$
$$\beta = (1+2a)^{-1/2} + (1-2a)^{-1/2} - 2$$
$$\gamma = (1+2a)^{-1/2} - (1-2a)^{-1/2} - 2$$

Acknowledgement:

Thanks is due to George Adel Aziz for the proof of Appendix 1.

References.

1. J.P.Leroy, R.Wallace, Chemical Physics, 111 (1987) 11–16.

2. "Functional Analysis", G.Bachman, L.Narici, Academic Press (1966).

PART III

QUANTUM KINETIC ENERGY OPERATOR IN A GENERAL NONINERTIAL REFERENCE FRAME

Form of the quantum kinetic energy operator for relative motion of a group of particles in a general noninertial reference frame.

Abstract: A form is derived for the quantum kinetic energy operator for relative motion of a group of particles in a general noninertial reference frame. Rotational coordinates are integrated out leaving an expression in terms of internal cartesian coordinates and rotational quantum numbers. The operator reduces to standard forms for conventional choices of reference frames (such as instantaneous principal axes of inertia) and serves as a general starting point for internal curvilinear coordinates describing large amplitude internal motion.

1. Introduction.

The reduction of the description of the motion of a quantum N–body system in which large amplitude relative motion may occur follows a fairly well defined pathway. The first step involves the separation of the motion of the centre of mass, this leaving the relative motion described by n = N–1 Jacobi vectors. Shortcomings in the original definition of the Jacobi vectors (notably their lack of symmetry upon exchange of identical particles) have recently been overcome [1].

One proceeds to describe the relative motion with some optimal set of n generalized Jacobi vectors (GJV). At this point it is usual (at least for small amplitude motion) to define a noninertial (body fixed) frame which is in some way tied to the configuration of the Jacobi vectors. For infinitesimal amplitudes of motion the Eckart frame is the conventional choice. For large amplitude motion, on the other hand, the frames employed appear to be those of Hirschfelder and Wigner[2], and Curtiss, Hirschfelder and Adler[3] (CHA). One of these is the instantaneous principal axes of inertia frame which underlies recent work on hyperspherical polar coordinates[4] while the other (CHA frame) might be referred to as a "distinguished particle" frame in the sense that it is directly tied to the configuration of a subset of two Jacobi vectors. Again, as with the choice of the Jacobi vectors themselves, distinguished particle frames may be such that Hamiltonian symmetry is not maximal, the reason being that the frame is derived from the Jacobi vectors by a Gram–Schmidt orthogonalization process as opposed to a symmetric orthogonalization process[1]. The choice of CHA frame underlies recent

work by one of the present authors[5] in which a Hamiltonian was derived for arbitrary amplitude motion in a molecular context.

In situations with one or more large amplitude degrees of freedom the term "body fixed frame" is something of a misnomer since the nuclear configuration may bear no simple or obvious relationship to the noninertial frame. Depending upon the system under study one might wish to identify frames satisfying a variety of conditions. It is therefore of considerable interest to derive the form of the Hamiltonian (really the KE operator) in the general frame, that in specific frames being derivable therefrom.

Any choice of noninertial frame defines three angular coordinates (the three Euler angles), leaving a maximum of 3n–3 rotationally invariant independent internal coordinates. Here we shall be content with the transformation of the cartesian coordinates, momenta, and kinetic energy operator from the inertial frame to the noninertial reference frame. The resultant set of cartesian internal coordinates, momenta, etc., are invariant to rotations of the frame and are valuable precursors to any choice of curvilinear internal coordinates.

Section 2 of the paper is devoted to a general definition of noninertial reference frames. In Section 3 the transformation law for angular and linear momentum operators is derived, this leading to a set of matrices $I^{(i)}$ characterizing the frame. The resultant KE operator is obtained in Section 4 and, in the manner of CHA, is integrated over rotational coordinates to a form dependent only upon internal coordinates and rotational quantum numbers. Specific realizations and comparison to standard frames is the subject of Section 5.

The paper develops in parallel with the treatment by Curtiss, Hirschfelder and Adler[3] but with the more general terminology of Biedenharn and Louck[6].

2.Reference Frames

a). Rotation Matrices.

With respect to the inertial frame $\{\vec{\ell}_\alpha\}$ (lab.parallel frame (LPF)), the cartesian coordinates of the generalized Jacobi vectors $\vec{q}(i)$ are given by:

$$q^{i\alpha} = (\vec{q}(i),\vec{\ell}_\alpha) \tag{2.1}$$

Under a rotation $\mathcal{R}$, the vector $\vec{q}(i)$ transforms into $\mathcal{R}\vec{q}(i)$. $\mathcal{R}$ is represented in the basis $\{\vec{\ell}_\alpha\}$ by the orthogonal matrix R such that the most general orthogonal transformation in the physical space on the 3(N–1) cartesian coordinates $q^{i\alpha}$ is given by:

$$q^{i\lambda} = \Sigma_\alpha R_{\lambda\alpha}\, y^{i\alpha} \qquad (\alpha,\lambda = 1,2,3) \tag{2.2}$$

The action of the matrix R may equally be viewed as an orthogonal transformation of the LPF into a new frame $(\vec{f}_\alpha;\alpha=1,2,3)$ such that:

$$\vec{f}_\alpha = \Sigma_\lambda R_{\lambda\alpha}\vec{\ell}_\lambda \tag{2.3}$$

where $R_{\lambda\alpha} = (\vec{\ell}_\lambda,\vec{f}_\alpha)$ is the direction cosine of $\vec{f}_\alpha$ with respect to $\vec{\ell}_\lambda$.

The matrices R are conventionally parameterized by a set of Euler angles θ_s (s=1,2,3).

The new cartesian coordinates are obtained by inverting (2.2) taking into account the orthogonality properties of R:

$$y^{i\alpha} = (\vec{q}(i),\vec{f}_\alpha) = \Sigma_\lambda R_{\lambda\alpha} q^{i\lambda} \tag{2.4}$$

b) Noninertial frames: definition.

The new frame is in some way "attached" to the molecular configuration if the $\vec{f}_\alpha$ depend upon some or all of the GJV $\vec{q}(i)$, the precise form of attachment being determined by the specific linear combination of the GJV involved in the frame construction :

$$\vec{f}_\alpha = \Sigma_k B_{\alpha k} \vec{q}(k) \qquad (2.5)$$

Let $\{\vec{q}_o(i)\}$ be the set of the GJV used in the construction of the "attached" frame and $\{\vec{q}'(i)\}$ be the set of the remaining vectors. The frame is considered "global" if all the vectors $\vec{q}(i)$ define the frame, or "local" if some subset define it.

The distinction between "global" and "local" frames can be expressed mathematically in the following manner. Non–inertial frames satisfy the relationship:

$$\left[\frac{\partial \vec{f}_\alpha}{\partial q^{i1}}, \frac{\partial \vec{f}_\alpha}{\partial q^{i2}}, \frac{\partial \vec{f}_\alpha}{\partial q^{i3}} \right] \neq (\vec{0},\vec{0},\vec{0}) \qquad (2.6)$$

for at least one α and all i=1,...,n in the case of a global frame or for at least one α and a subset $\{\vec{q}_o(i)\}$ of the i=1,...,n in the case of a locally defined frame. Condition (2.6) assures that the orientation of a "global" frame depends on the instantaneous position of each particle in the molecule.

To proceed with the construction of non–inertial frames, define the Gram matrices of the sets of vectors $\{\vec{q}(i)\}$, $\{\vec{q}_o(i)\}$ and $\{\vec{q}'(i)\}$ respectively by G, G_o and G′ such that

$$G_{ij} = (\vec{q}(i),\vec{q}(j)) = \Sigma_\alpha q^{i\alpha} q^{j\alpha} \qquad (2.7)$$

In terms of its components G is partitioned as follows:

$$G = \begin{bmatrix} G_o & C^t \\ C & G' \end{bmatrix}$$

where C is a rectangular matrix linking the sets $\{\vec{q}_o)$ and $(\vec{q}')$; its dimension is $n_o \times \eta$, where n_o is the number of GJV of the set $\{\vec{q}_o)$ and η is the number of GJV $\{\vec{q}'(i)\}$ not involved in the definition of the non–inertial frame.

Since the new frame is orthonormal, B is a $(3\times n_o)$ dimensional matrix satisfying :

$$(\vec{f}_\alpha, \vec{f}_\beta) = \delta_{\alpha\beta} \tag{2.8}$$

Substitution of (2.5) into (2.8) leads to the fundamental relation linking the matrix B to the matrix G_o:

$$BG_oB^t = I_{n_o} \tag{2.9}$$

This corresponds to a customary orthonormalization of 2 or 3 GJV (i.e. for 3 or 4–body systems), since B is a square matrix (respectively 2×2 and 3×3). In the general case, the corresponding orthonormalization is best approached by a two step process involving:

(1) a **reduction** A of the n_o GJV into a preliminary set of 3 (nonorthogonal) vectors $\vec{F}_\gamma$ (γ=1,2,3):

$$\vec{F}_\gamma = \Sigma_k A_{\gamma k} \vec{q}_o(k) \tag{2.10}$$

followed by (2) an **orthonormalization** O:

$$\vec{f}_\alpha = \Sigma_\gamma O_{\alpha\gamma} \vec{F}_\gamma \tag{2.11}$$

hence

$$B_{\alpha k} = \Sigma_\gamma O_{\alpha\gamma} A_{\gamma k} \tag{2.12}$$

The reduction A is represented by some prescribed $(3\times n_o)$ matrix whose elements $A_{\gamma k}$ are invariant under any rotation of the frame. Actually, if $\mathcal{R}$ is a collective rotation of the set $\{\vec{q}_o\}$, by definition, the set $\{\vec{F}_\gamma\}$ (actually a non–orthonormal attached frame) is invariant and:

$$A_{\gamma k}[\mathcal{R}\vec{q}_o(1),...,\mathcal{R}\vec{q}_o(n)] = A_{\gamma k}[\vec{q}_o(1),...,\vec{q}_o(n)] \qquad (2.13)$$

According to the Weyl theorem[7], every rotational invariant depending on n_o vectors $\{\vec{q}_o(i)\}$ is expressible in terms of the n_o^2 scalar products $(\vec{q}_o(i),\vec{q}_o(j)) = (G_o)_{ij}$. The coefficients $A_{\gamma k}$ are therefore functions of the $n_o(n_o-1)/2$ distinct elements of G_o:

$$A_{\gamma k} = A_{\gamma k}[(G_o)_{ij}] \qquad (2.14)$$

Since G_o is rotationally invariant, $(G_o)_{ij}$ may be expresssed as well by $\Sigma_\alpha y_o^{i\alpha} y_o^{j\alpha}$ so that $A_{\gamma k} = A_{\gamma k}(y_o^{i\alpha})$.

Construction of the noninertial frame is reduced to an orthonormalization O of the three 3–d vectors $\vec{F}_\alpha$ which can be carried out by any standard method[1]. If G_F denotes the Gram matrix of the vectors $\vec{F}_\alpha$, i.e., $(G_F)_{\alpha\beta} = (\vec{F}_\alpha,\vec{F}_\beta)$ which is a function of the components $y_o^{i\gamma}$,then, since O is such that $OG_FO^t = I_3$, the choice of a particular frame imposes three conditions on the components $y_o^{i\alpha}$. Conversely, imposing three constraints on the cartesian components of n_o GJV and satisfying the above requirement defines uniquely a non–inertial frame attached to the n_o vectors $\vec{q}_o(i)$.

The $3n_o$ rotationally invariant coordinates $y_o^{i\alpha}$ together with the three constraints may be parameterized by $3n_o-3$ internal coordinates ζ_o^ν (ν=1,...,$3n_o$–3). The cartesian components of the remaining vectors with respect to the frame $\{\vec{f}_\alpha\}$ are obtained by forming the scalar products:

$$y'^{k\alpha} = (\vec{q}'(k),\vec{f}_\alpha) = \Sigma_i B_{\alpha i}(\vec{q}'(k),\vec{q}_o(i)) = \Sigma_i B_{\alpha i} C_{ik} \qquad (2.15)$$

The set of 3η coordinates $\{y'^{k\alpha}\}$ constitute a set of independent internal coordinates (i.e., invariant under a rotation of the non–inertial frame (Appendix 2)) which, taken together with the set $\{\zeta_o^\nu\}$, recover the (3n–3) independent internal coordinates.

The separation of the rotational and internal degrees of freedom is formally expressed by the relationship:

$$q^{i\lambda} = \Sigma_\alpha R_{\lambda\alpha}(\theta_s) y^{i\alpha}(\zeta^\nu) \qquad (2.16)$$

where R is now the rotation matrix describing the relative motion of the non–inertial frame $\{\vec{f}_\alpha\}$ with respect to the LPF. The three parameters θ_s (external coordinates) are functions of the $q_o^{i\lambda}$ involved in the definition of the frame. The 3n cartesian coordinates are rotationally invariant and their motion in configuration space is restricted by the imposition of three constraints defining the new frame.

There exist of course many ways to define such non–inertial frames depending upon the physical problem one has in mind. In any case, one should expect the frame to reflect in some way the symmetry of the system (for instance, invariance under permutation of identical constituants).

3. Momentum Operators.

a) Angular momentum.

Let $\vec{L}$ be the total orbital angular momentum of the system; the components $L_\alpha = (\vec{L},\vec{\ell}_\alpha)$ are defined by:

$$L_\alpha = -i\sum_k \left[q^{k\beta} \frac{\partial}{\partial q^{k\gamma}} - q^{k\gamma} \frac{\partial}{\partial q^{k\beta}} \right] \qquad (2.17)$$

where k=1,..,n and α,β,γ are cyclic permutations of 1,2,3.(c.p.)

Define also component angular momenta L°_{α} and L'_{α} relative to the sets $\{\vec{q}_o(i)\}$ and $\{\vec{q}'(i)\}$. Of course,

$$L_{\alpha} = L^{\circ}_{\alpha} + L'_{\alpha} \tag{2.18}$$

$\vec{L}^{\circ}$ is the generator of the rotations of the vectors $\{\vec{q}_o(i)\}$ and thus each $\vec{q}_o(i)$ as well as each $\vec{f}_{\alpha}$ are vector operators with respect to $\vec{L}^{\circ}$. It follows (Appendix 1, A1.9) that:

$$[L^{\circ}_{\alpha}, \vec{f}_{\beta}] = i(\vec{f}_{\beta} \times \vec{\ell}_{\alpha}) \tag{2.19}$$

$$[L^{\circ}_{\alpha}, R_{\beta\lambda}] = i\epsilon_{\alpha\beta\gamma} R_{\gamma\lambda} \tag{2.20}$$

where R is parameterized by the angles θ_s (functions of $q_o^{i\alpha} = (\vec{q}_o(i), \vec{\ell}_{\alpha})$). Furthermore, each $y_o^{i\alpha}$ is an invariant with respect to the rotation described by R, hence:

$$[L^{\circ}_{\alpha}, y_o^{i\beta}] = 0 \tag{2.21}$$

Let us evaluate the derivatives appearing in the definition of L°_{α} in terms of the derivatives with repect to $R_{\lambda\mu}$ and $y_o^{k\lambda}$ using the transformation:

$$q_o^{i\alpha} = \Sigma_{\beta} R_{\alpha\beta} y_o^{i\beta} \tag{2.22}$$

The chain rule yields :

$$\frac{\partial}{\partial q_o^{i\alpha}} = \sum_{\lambda,\mu} \left[\frac{\partial R_{\lambda\mu}}{\partial q_o^{i\alpha}} \right] \frac{\partial}{\partial R_{\lambda\mu}} + \sum_{k,\lambda} \left[\frac{\partial y_o^{k\lambda}}{\partial q_o^{i\alpha}} \right] \frac{\partial}{\partial y_o^{k\lambda}} \tag{2.23}$$

Substitute (2.23) into (2.17) and use the derivation property for any function F:

$$q_o^{i\beta} \frac{\partial F}{\partial q_o^{i\gamma}} \left[\frac{\partial}{\partial F} \right] = [q_o^{i\beta} \frac{\partial}{\partial q_o^{i\gamma}}, F] \frac{\partial}{\partial F} \tag{2.24}$$

therefore,

$$L^{\circ}_{\alpha} = -i \left\{ \sum_{\lambda,\mu} [L^{\circ}_{\alpha}, R_{\lambda\mu}] \frac{\partial}{\partial R_{\lambda\mu}} + \sum_{k,\lambda} [L^{\circ}_{\alpha}, y_o^{k\lambda}] \frac{\partial}{\partial y_o^{k\lambda}} \right\} \tag{2.25}$$

Use the commutation relations (2.20) and (2.21) to get the

expression for the component angular momentum L°_{α}:

$$L^{\circ}_{\alpha} = -i\Sigma_{\lambda}\left[R_{\beta\lambda} \frac{\partial}{\partial R_{\gamma\lambda}} - R_{\gamma\lambda} \frac{\partial}{\partial R_{\beta\lambda}} \right]; \ \alpha,\beta,\gamma \text{ are c.p} \quad (2.26)$$

This justifies the statement that the component angular momentum $\vec{L}^{\circ}$ is the generator of the rotations of the noninertial frame.

L'_{α} is evaluated by noting that the $R_{\lambda\mu}$ do not depend upon the $q'^{i\alpha}$, therefore,

$$L'_{\alpha} = -i\sum_{k'}\left[q^{k'\beta} \frac{\partial}{\partial q^{k'\gamma}} - q^{k'\gamma} \frac{\partial}{\partial q^{k'\beta}} \right]$$

$$= \Sigma_{\lambda} P'_{\lambda}[R_{\beta\mu}R_{\gamma\nu} - R_{\beta\nu}R_{\gamma\mu}] \quad (\lambda,\mu,\nu \text{ are c.p})$$

where:

$$P'_{\alpha} = -i\sum_{k'}\left[q^{k'\beta} \frac{\partial}{\partial q^{k'\overline{\gamma}}} - q^{k'\gamma} \frac{\partial}{\partial q^{k'\overline{\beta}}} \right] \quad (2.27)$$

Employing the properties of the orthogonal matrices, we finally obtain:

$$L'_{\alpha} = \Sigma_{\lambda} R_{\alpha\lambda} P'_{\lambda} \quad (2.28)$$

The L°_{α} are the differential operators $\mathcal{J}_{\alpha}$ defined in Appendix 1 (Eq A1.4). The set of operators $\{L^{\circ}_{\alpha}\}$ are the generators of the rotations of the frame $\{\vec{f}_{\alpha}\}$, while the set $\{L'_{\alpha}\}$ generates the rotations of the "complement" ***with respect to the inertial frame***. One can evaluate the components of the operators $\vec{L}^{\circ}$ and $\vec{L}'$ with respect to the noninertial frame:

$$K_{\alpha} = \Sigma_{\lambda} R_{\lambda\alpha}(L^{\circ}_{\lambda} + L'_{\lambda}) = K^{\circ}_{\alpha} + P'_{\alpha} \quad (2.29)$$

where K°_{α} is:

$$K^{\circ}_{\alpha} = i\sum_{\mu=1}^{\mu=3}\left\{ R_{\mu\beta} \frac{\partial}{\partial R_{\mu\gamma}} - R_{\mu\gamma} \frac{\partial}{\partial R_{\mu\beta}} \right\} \quad (2.30)$$

where α,β,γ are c.p. This expresses that the α^{th} component of the total angular momentum with respect to the noninertial frame is the sum of

the α^{th} component of the partial angular momentum K°_{α} and the operator P'_{α}, component along the noninertial frame of the generator of the rotations of the set $\{\vec{q}'(i)\}$ with respect to the inertial frame. Therefore, $\vec{P}'$ is to be identified as an internal angular momentum generating the rotations of the set $\{\vec{q}'(i)\}$ with respect to the noninertial frame $\{\vec{f}_{\alpha}\}$.

b) Linear momentum operators.

To obtain the hamiltonian for relative motion of a molecule whose configuration is represented by the N–1 generalized Jacobi vectors $\vec{q}(i)$ and in which the motions are referred to a noninertial frame, we seek to transform the kinetic energy operator from inertial to noninertial frame:

$$T = -\frac{1}{2}\sum_{i,\alpha}\{\frac{\partial}{\partial q^{i\alpha}}\}^2 \qquad (3.1)$$

To achieve this transformation, the linear momentum operators $p_{i\alpha} = -i\frac{\partial}{\partial q^{i\alpha}}$ are first transformed to the coordinates $\{R_{\lambda\mu}(\theta_s)\}$ and $y^{i\gamma}$. Let us rewrite Eq.(2.23) in the form:

$$\frac{\partial}{\partial q^{i\alpha}} = \sum_{\beta,\gamma}[I]\frac{\partial}{\partial R_{\beta\gamma}} + \sum_{j,\gamma}[II]\frac{\partial}{\partial y^{j\gamma}} \qquad (3.2)$$

where:

$$[I] = \frac{\partial R_{\beta\gamma}}{\partial q^{i\alpha}} \quad ; \quad [II] = \frac{\partial y^{j\gamma}}{\partial q^{i\alpha}} \qquad (3.3)$$

Evaluation of the derivative [I].

$$[I] = \frac{\partial}{\partial q^{i\alpha}}(\vec{\ell}_{\alpha'}\vec{f}_{\gamma}) = (\vec{\ell}_{\alpha'}\frac{\partial\vec{f}_{\gamma}}{\partial q^{i\alpha}})$$

One needs the derivative of the vector $\vec{f}_\gamma$ with respect to $q^{i\alpha}$. From the orthonormality relation $(\vec{f}_\alpha,\vec{f}_b) = \delta_{\alpha\beta}$, we deduce:

$$\frac{\partial}{\partial q^{i\sigma}}(\vec{f}_\alpha,\vec{f}_\beta) = (\vec{f}_\alpha,\frac{\partial \vec{f}_\beta}{\partial q^{i\sigma}}) + (\frac{\partial \vec{f}_\alpha}{\partial q^{i\sigma}},\vec{f}_\beta) = 0$$

Therefore,

$$(\vec{f}_\alpha,\frac{\partial \vec{f}_\beta}{\partial q^{i\sigma}}) = -(\frac{\partial \vec{f}_\alpha}{\partial q^{i\sigma}},\vec{f}_\beta)$$

Taking $\alpha = \beta$ we conclude that the derivative of the base vector $\vec{f}_\alpha$ with respect to the $q^{i\sigma}$ is orthogonal to $\vec{f}_\alpha$:

$$(\vec{f}_\alpha,\frac{\partial \vec{f}_\alpha}{\partial q^{i\sigma}}) = 0 \tag{3.4}$$

Accordingly[6], the vector $\frac{\partial \vec{f}_\alpha}{\partial q^{i\sigma}}$ may be expressed as the vector product of $\vec{f}_\alpha$ with some vector $\vec{\Omega}^i_\sigma$ which depends upon the functional form of $\vec{f}_\alpha$ with respect to the $q^{i\alpha}$:

$$\frac{\partial \vec{f}_\gamma}{\partial q^{i\sigma}} = \vec{f}_\gamma \times \vec{\Omega}^i_\sigma \tag{3.5}$$

Using this result, [I] becomes, after replacing $\vec{\ell}_\beta$ by $\Sigma_\lambda R_{\beta\lambda}\vec{f}_\lambda$:

$$\begin{aligned}[I] &= (\vec{\ell}_\beta,\vec{f}_\gamma \times \vec{\Omega}^i_\alpha) = (\vec{\Omega}^i_\alpha,\vec{\ell}_\beta \times \vec{f}_\gamma) = \Sigma_\lambda R_{\beta\lambda}(\vec{\Omega}^i_\alpha,\vec{f}_\lambda \times \vec{f}_\gamma) \\ &= \sum_{\lambda\neq\gamma} R_{\beta\lambda}(\vec{\Omega}^i_\alpha,\vec{f}_\sigma) = \sum_{\lambda\neq\gamma} R_{\beta\lambda}\Omega^i_{\alpha\sigma}\end{aligned} \tag{3.6}$$

where λ,γ,σ are c.p. of 1,2.3.

The 3×3 quantities $\Omega^i_{\alpha\sigma}$ (i fixed) can be considered as elements of a 3×3 matrix Ω^i. They are easily determined from eq.(3.5) and the property of the triple product:

$$\Omega^i_{\alpha\gamma} = (\frac{\partial \vec{f}_\sigma}{\partial q^{i\alpha}},\vec{f}_\delta) \tag{3.7}$$

where γ,δ,σ are c.p. of 1,2,3. In practical calculations, we will need the obvious result:

$$\Omega^{i}_{\alpha\gamma} = -\left(\frac{\partial \vec{f}_{\delta}}{\partial q^{i\alpha}}, \vec{f}_{\sigma} \right) \tag{3.8}$$

With the definition of the frame given by eq.(2.41), we obtain the explicit expression for the matrix elements $\Omega^{i}_{\alpha\gamma}$:

$$\Omega^{i}_{\alpha\gamma} = \Sigma_k \left(\frac{\partial B_{\sigma k}}{\partial q^{i\alpha}} \vec{q}(k) + B_{\sigma k} \frac{\partial \vec{q}(k)}{\partial q^{i\alpha}}, \vec{f}_{\delta} \right)$$

Substituting $\vec{q}(k) = \Sigma_\tau q^{i\tau} \vec{\ell}_\tau = \Sigma_\tau y^{k\tau} \vec{f}_\tau$:

$$\Omega^{i}_{\alpha\gamma} = \Sigma_k \frac{\partial B_{\sigma k}}{\partial q^{i\alpha}} y^{k\delta} + B_{\sigma i} R_{\alpha\delta} \tag{3.9}$$

Of course, if $\vec{q}(i)$ is not involved in the construction of the frame, the matrix Ω^{i} is the null matrix.

Evaluation of the derivative [II].

$$[II] = \frac{\partial y^{j\gamma}}{\partial q^{i\alpha}} = \frac{\partial}{\partial q^{i\alpha}} (\vec{q}(j), \vec{f}_\gamma) = \left(\frac{\partial \vec{q}(j)}{\partial q^{i\alpha}}, \vec{f}_\gamma \right) + \left(\vec{q}(j), \frac{\partial \vec{f}_\gamma}{\partial q^{i\alpha}} \right)$$
$$= \delta_{ij} R_{\alpha\gamma} + (\vec{\Omega}^{i}_{\alpha}, \vec{q}(j) \times \vec{f}_\gamma) \tag{3.10}$$

This result can be expressed in terms of the matrix elements $\Omega^{i}_{\alpha\sigma}$ (using $\vec{q}(k)$ expanded in the moving frame):

$$[II] = \delta_{ij} R_{\alpha\gamma} + \sum_{\lambda \neq \gamma} y^{j\lambda} \Omega^{i}_{\alpha\sigma} \tag{3.11}$$

where λ,γ,σ are c.p. Substitute [I] and [II] into (3.2) and evaluate the summations.

$$[S_1] \equiv \sum_{\beta,\gamma} \frac{\partial R_{\beta\gamma}}{\partial q^{i\alpha}} \frac{\partial}{\partial R_{\beta\gamma}} = \sum_{\beta,\gamma} (\vec{\Omega}^{i}_{\alpha}, \vec{\ell}_\beta \times \vec{f}_\gamma) \frac{\partial}{\partial R_{\beta\gamma}} \tag{3.12}$$

With (3.6):

$$[S_1] = \sum_{\beta,\gamma} [\sum_{\lambda \neq \gamma} R_{\beta\lambda}\ \Omega^{i}_{\alpha\sigma}] \frac{\partial}{\partial R_{\beta\gamma}} \qquad (\lambda,\gamma,\sigma \text{ are c.p.})$$

Introducing the vector $\vec{K}^{\circ}$ defined in (2.30), it follows that

$$[S_1] = \not{\iota}(\vec{\Omega}^{i}_{\alpha}, \vec{K}^{\circ}) \tag{3.13}$$

$$[S_2] \equiv \sum_{j,\gamma} \frac{\partial y^{j\gamma}}{\partial q^{i\alpha}} \frac{\partial}{\partial y^{j\gamma}} = \sum_{j,\gamma} \left[\delta_{ij} (\vec{\ell}_{\alpha}, \vec{f}_{\gamma} \frac{\partial}{\partial y^{j\gamma}}) + (\vec{\Omega}^{i}_{\alpha}, \vec{q}(j) \times \vec{f}_{\gamma} \frac{\partial}{\partial y^{j\gamma}}) \right] \tag{3.14}$$

The summation over j kills all $j \neq i$ in the first term, so that:

$$[S_2] = \Sigma_{\gamma} (\vec{\ell}_{\alpha}, \vec{f}_{\gamma} \frac{\partial}{\partial y^{i\gamma}}) + \sum_{j,\gamma} (\vec{\Omega}^{i}_{\alpha}, \vec{q}(j) \times \vec{f}_{\gamma} \frac{\partial}{\partial y^{j\gamma}})$$

Defining the vector operator $\vec{\pi}_i$:

$$\vec{\pi}_i = -\not{\iota} \Sigma_{\alpha} \vec{f}_{\alpha} \frac{\partial}{\partial y^{i\alpha}} \tag{3.15}$$

we obtain:

$$[S_2] = \not{\iota} \left\{ (\vec{\pi}_i, \vec{\ell}_{\alpha}) + \Sigma_j (\vec{\Omega}^{i}_{\alpha}, \vec{q}(j) \times \vec{\pi}_j) \right\}$$

$$= \not{\iota} \left\{ (\vec{\pi}_i, \vec{\ell}_{\alpha}) + (\vec{\Omega}^{i}_{\alpha}, \Sigma_j \vec{q}(j) \times \vec{\pi}_j) \right\}$$

$$= \not{\iota} \left\{ (\vec{\pi}_i, \vec{\ell}_{\alpha}) + (\vec{\Omega}^{i}_{\alpha}, \vec{P}) \right\} \tag{3.16}$$

where

$$\vec{P} = \Sigma_{\alpha} P_{\alpha} \vec{f}_{\alpha} = \Sigma_j \vec{q}(j) \times \vec{\pi}_j \tag{3.17}$$

Expanding $\vec{P}$ along $\{\vec{f}_{\alpha}\}$ gives:

$$P_{\alpha} = -\not{\iota} \Sigma_j \left\{ y^{j\beta} \frac{\partial}{\partial y^{j\gamma}} - y^{j\gamma} \frac{\partial}{\partial y^{j\beta}} \right\} \tag{3.18}$$

where α,β,γ are c.p. The P_α are intrinsic operators (see appendix 2). P_α is the sum of two terms P°_α and P'_α respectively the vortex[9] angular momentum (with respect to the frame) and the internal angular momentum, generators of the rotations of the set $\{\vec{q}'(i)\}$ in the non–inertial frame.

Combining $[S_1]$ and $[S_2]$ gives the expression for the linear momentum $p_{i\alpha}$:

$$p_{i\alpha} \equiv -i\frac{\partial}{\partial q^{i\alpha}} = (\vec{\pi}_i, \vec{l}_\alpha) + (\vec{\Omega}^i_\alpha, \vec{K}^\circ + \vec{P}) \tag{3.19}$$

or, in component form:

$$p_{i\alpha} = \Sigma_\lambda \left\{ R_{\alpha\lambda}\pi_{i\lambda} + \Omega^i_{\alpha\lambda}(K^\circ_\lambda + P_\lambda) \right\} \tag{3.20}$$

where $\pi_{i\alpha}$ is the linear momentum conjugate to the internal cartesian coordinate $y^{i\alpha}$:

$$\pi_{i\alpha} = -i\frac{\partial}{\partial y^{i\alpha}} \tag{3.21}$$

We now employ the Cartan decomposition[10] of the matrices Ω^i:

$$\Omega^i = \mathcal{O}^i \mathscr{S}^i$$

where $\mathcal{O}^i$ is orthogonal and $\mathscr{S}^i$ is a positive semi–definite symmetric matrix. From the group properties of orthogonal matrices, the equation $\mathcal{O} = R\mathcal{R}^i$ is solvable, hence there exists a unique matrix I^i such that:

$$\Omega^i = RI^i \tag{3.22}$$

with $I^i = \mathcal{R}^i \mathscr{S}^i$. It follows that we can express the elements $\Omega^i_{\alpha\lambda}$ in the form:

$$\Omega^i_{\alpha\lambda} = \Sigma_\beta R_{\alpha\beta} I^i_{\beta\lambda} \tag{3.23}$$

where the matrices I^i are invariant under rotations of the frame, i.e. the $I^i_{\beta\lambda}$ are functions of the internal coordinates only.

Substituting (3.23) into the linear momentum relation:

$$p_{i\alpha} = \Sigma_\beta R_{\alpha\beta}[\pi_{i\beta} + \Sigma_\gamma I^i_{\beta\gamma} P_\gamma] + \Sigma_\beta R_{\alpha\beta}[\Sigma_\gamma I^i_{\beta\gamma} K^\circ_\gamma] \qquad (3.24)$$

$$= \Sigma_\beta R_{\alpha\beta}\, \mathcal{J}_{i\beta} + \Sigma_\beta R_{\alpha\beta}\, \mathcal{E}_{i\gamma} = \Sigma_\beta R_{\alpha\beta} \mathcal{Q}_{i\beta} \qquad (3.25)$$

In the first term, the operator $\mathcal{J}_{i\alpha}$ acts only on internal coordinates (since $\pi_{i\alpha}$ and P_α are intrinsic) while in the second term $\mathcal{E}_{i\alpha}$ acts only on the external coordinates. The operators K°_γ are identified with the operators $-\mathcal{P}_\gamma$ defined in Appendix 1, (A1.6): $K^\circ_\gamma = -\mathcal{P}_\gamma$. The action of K°_γ on the rotation matrices give (A1.12):

$$\begin{aligned} K^\circ_1 D^{(J)*}_{MK} &= -\frac{1}{2}\left\{ l_+(J,K) D^{(J)*}_{M,K+1} + l_-(J,K) D^{(J)*}_{M,K-1} \right\} \\ K^\circ_2 D^{(J)*}_{MK} &= -\frac{i}{2}\left\{ l_+(J,K) D^{(J)*}_{M,K+1} - l_-(J,K) D^{(J)*}_{M,K-1} \right\} \\ K^\circ_3 D^{(J)*}_{MK} &= -K D^{(J)*}_{M,K} \end{aligned} \qquad (3.26)$$

where

$$l_\pm(J,K) = [(J \mp K)(J \pm K + 1)]^{1/2} \qquad (3.27)$$

4: The Kinetic Energy Operator.

To evaluate the kinetic operator given in eq.(2.1), we proceed directly by squaring the $p_{i\alpha}$ and adding over i and α .

Squaring eq.(3.25):

$$(p_{i\alpha})^2 = (\Sigma_\beta R_{\alpha\beta} \mathcal{Q}_{i\beta})^2 \qquad (4.1)$$

where

$$\mathcal{Q}_{i\beta} = \pi_{i\beta} + \Sigma_\gamma I^i_{\beta\gamma}(K^\circ_\gamma + P_\gamma) \qquad (4.2)$$

The operator $\mathcal{Q}_{i\beta}$ possesses the property of a derivative since it is a linear expression in linear and angular momenta:

$$\partial_{i\beta}(FG) = (\partial_{i\beta}F)G + F(\partial_{i\beta}G) \qquad (4.3)$$

Eq.(4.1) becomes after summing over α and using the orthogonality of the elements $R_{\alpha\beta}$:

$$\Sigma_\alpha(p_{i\alpha})^2 = \Sigma_\lambda(\partial_{i\lambda})^2 + \sum_{\alpha,\lambda}[R_{\alpha\mu}(\partial_{i\mu}R_{\alpha\lambda}) + R_{\alpha\nu}(\partial_{i\nu}R_{\alpha\lambda})]\partial_{i\lambda} \qquad (4.4)$$

$$= \quad (I) \qquad + \qquad (II)$$

Evaluation of expression (I).

The operators $\pi_{i\beta}$ and P_β as well as the coefficients $I^i_{\alpha\beta}$ are all invariant under rotations of the frame (see Appendix 2) :

$$[K^\circ_\lambda,\pi_{i\beta}] = [K^\circ_\lambda,P_\beta] = [K^\circ_\lambda,I^i_{\alpha\beta}] = 0 \qquad (4.5)$$

Using these results, it is straightforward to calculate (I). The result is as follows:

$$\begin{aligned}(I) = &\sum_{i,\lambda}\pi^2_{i\lambda} \\ &+ \sum_\gamma A_\gamma(K^\circ_\gamma)^2 + \sum_\gamma B_\gamma\{K^\circ_\alpha,K^\circ_\beta\} \\ &+ \sum_\gamma (C_\gamma + \mathcal{D}_\gamma)K^\circ_\gamma \\ &+ \sum_\gamma A_\gamma(P_\gamma)^2 + \sum_\gamma B_\gamma\{P_\alpha,P_\beta\} \\ &+ \sum_\gamma C_\gamma P_\gamma \\ &+ \sum_{i,\lambda,\gamma} I^i_{\lambda\gamma}\{\pi_{i\lambda},P_\gamma\}\end{aligned} \qquad (4.6)$$

where $\{A,B\}$ stands for $AB + BA$ and

$$A_\gamma = \sum_{i,\lambda} (I^i_{\lambda\gamma})^2$$

$$B_\gamma = \sum_{i} I^i_{\gamma\alpha} I^i_{\gamma\beta}$$

$$C_\gamma = \sum_{i,\lambda} [\pi_{i\lambda} I^i_{\lambda\gamma} + I^i_{\lambda\gamma} P_\gamma I^i_{\lambda\gamma}] + I^i_{\alpha\beta} P_\beta I^i_{\alpha\gamma} + I^i_{\beta\alpha} P_\alpha I^i_{\beta\gamma}$$

$$\mathscr{D}_\gamma = \sum_{i,\lambda} [2I^i_{\lambda\gamma}\pi_{i\lambda} + 2I^i_{\lambda\gamma} P_\gamma + I^i_{\lambda\gamma} I^i_{\lambda\alpha}(P_\alpha + P_\beta)] \qquad (4.7)$$

Evaluation of the expression (II)

The $R_{\alpha\beta}$ all commute with P_γ and $\pi_{i\lambda}$ (see Appendix 2):

$$[\pi_{i\lambda}, R_{\alpha\gamma}] = [P_\gamma, R_{\alpha\gamma}] = 0 \qquad (4.8)$$

and the action of the angular momenta K°_γ on the matrix elements $R_{\alpha\beta}$ can be deduced from relations (3.26) by taking j=1. From the orthogonality of the elements $R_{\alpha\beta}$, the following expression for (II) is obtained:

$$(II) = \mathscr{i} \sum_{i,\beta} \left\{ \Delta_{i\beta}\pi_{i\beta} + \Sigma_\gamma \Delta_{i\beta} I^i_{\beta\gamma} (K^\circ_\gamma + P_\gamma) \right\} \qquad (4.9)$$

where:

$$\Delta_{i\beta} = (I^i_{\gamma\delta} - I^i_{\delta\gamma}) \qquad (\beta,\gamma,\delta \text{ are c.p}) \qquad (4.10)$$

Combine now (I) and (II) and regroup the terms as follows:

1. Internal operators.

KE(int) =

$$\sum_{i,\lambda} [\pi^2_{i\lambda} + (\mathscr{i}\Delta_{i\lambda}\pi_{i\lambda}] \qquad \text{(linear momenta)}$$

$$+\sum_{\gamma} A_{\gamma}(P_{\gamma})^2 + \sum_{\gamma} B_{\gamma}\{P_{\alpha},P_{\beta}\} + \sum_{\gamma} (C_{\gamma} + \mathcal{i}\Sigma_{i,\beta}\Delta_{i\beta}I^{i}_{\beta\gamma})P_{\gamma}$$

(vortex momenta)

$$+\sum_{i,\lambda,\gamma} I^{i}_{\lambda\gamma}\{\pi_{i\lambda},P_{\gamma}\}$$ (coupling linear/vortex momenta)

(4.11)

2. External operators.

$$KE(ext) = \sum_{\gamma} A_{\gamma}(K^{\circ}_{\gamma})^2 + \sum_{\gamma} B_{\gamma}\{K^{\circ}_{\alpha},K^{\circ}_{\beta}\} + \sum_{\gamma} (C_{\gamma} + \mathcal{i}\Sigma_{i,\beta}\Delta_{i\beta}I^{i}_{\beta\gamma})K^{\circ}_{\gamma} \qquad (4.12)$$

3. Coupling operators.

$$KE(coup) = \sum_{\gamma} \mathcal{D}_{\gamma}K^{\circ}_{\gamma} \qquad (4.13)$$

To obtain an internal kinetic energy operator, we apply the operator KE to the components (wave functions) of the state vectors of "sharp" angular momentum $|(n)JM>$ in the representation $|y^{i\alpha};\theta_s>$:

$$<y^{i\alpha};\theta_s|(n)JM> = \Sigma_K D^{(J)*}_{MK}(\theta_s)\chi^{(J)}_{n,K}(y^{i\alpha}) \qquad (4.14)$$

The elements of the rotation matrices $D^{(J)*}_{MK}$ are functions of the external variables (θ_s) alone while the functions $\chi^{(J)}_{n,K}$ have internal arguments $y^{i\alpha}$ only. Accordingly,

$$KE(\Sigma_K D^{(J)*}_{MK}\chi^{(J)}_{n,K}) = \Sigma_K D^{(J)*}_{MK}KE(int)\chi^{(J)}_{n,K}$$

$$+ \Sigma_K\left[\{KE(ext) + KE(coup)\}D^{(J)*}_{MK}\right]\chi^{(J)}_{n,K} \qquad (4.15)$$

The action of the operators K°_{γ} is given by (3.26). Introduce the operators Γ_{α} defined by:

$$\begin{aligned}\Gamma_1 &= \tfrac{1}{2}[l_+(J,K)\sigma_+ + l_-(J,K)\sigma_-] \\ \Gamma_2 &= \tfrac{i}{2}[l_+(J,K)\sigma_+ - l_-(J,K)\sigma_-] \\ \Gamma_3 &= K\end{aligned} \tag{4.16}$$

where the operators $\sigma_{\pm}$ are defined by:

$$\sigma_{\pm}\chi^{(J)}_{n,K} = \chi^{(J)}_{n,K\pm1} \tag{4.17}$$

Substituting into eq.(4.15), we obtain the following expression for the kinetic energy acting on the wave function:

$$KE(\Sigma_K D^{(J)*}_{MK}\chi^{(J)}_{n,K}) = \Sigma_K D^{(J)*}_{MK}\{KE(int) + KE'\}\chi^{(J)}_{n,K} \tag{4.18}$$

where now KE′ is given by (using the commutativity of the operators Γ_{α}):

$$KE' = \sum_{\gamma}\left[A_{\gamma}(\Gamma_{\gamma})^2 + 2B_{\gamma}\Gamma_{\alpha}\Gamma_{\beta} + (C_{\gamma} + i\Sigma_{i,\beta}\Delta_{i\beta}I^{i}_{\beta\gamma})\Gamma_{\gamma}\right] \tag{4.19}$$

$$+\sum_{\gamma}\mathcal{D}_{\gamma}\Gamma_{\gamma} \tag{4.20}$$

After integration over all the rotational coordinates following the procedure used by CHA[3], the internal kinetic energy operator can be partitioned in the following way[5]:

$$KE = T_0 + T_1 + T_2 \tag{4.21}$$

where T_0 (given by eq.4.11) represents the s–state of the system, T_1 (given by eq.4.19) mixing of rotational states alone and T_2 (given by eq.4.20) represents coupling of internal motions with rotations.

The removal of the rotational coordinates (being replaced by rotational quantum numbers) from the rovib kinetic energy operator given by eqs.(4.11), (4.12) and (4.13) (that is the derivation of a kinetic energy operator involving internal coordinates alone) is obtained simply by replacing the external operators K°_{α} by the quantities Γ_{α}.

5.Examples.

a) The Instantaneous Principal Axes of Inertia (PAI) Frame

This is a typical "global" noninertial frame in the sense that its definition involves all GJV. The PAI frame is particularly suited to systems described by a set of equivalent symmetric Jacobi vectors[1], since it is invariant under permutation of identical particles.

The most natural way to define the PAI frame is as follows. Consider the mass quadrupole M in the inertial frame:

$$M_{\alpha\beta} = \Sigma_i q^{i\alpha} q^{i\beta} \tag{5.1}$$

M is a real, positive definite, symmetric matrix hence can be diagonalized by a real proper orthogonal matrix R:

$$R^t M R = \Lambda = \mathrm{diag}(\lambda_1,\lambda_2,\lambda_3) \tag{5.2}$$

where the λ_γ denote the three eigenvalues (real, positive) of M.

The three eigenvectors $\vec{j}_\gamma$ corresponding to each of the λ_γ constitute a set of orthonormal vectors:

$$M\vec{j}_\gamma = \lambda_\gamma \vec{j}_\gamma \tag{5.3}$$

In this new frame, the components of the $\vec{q}(i)$ are:

$$y^{i\alpha} = (\vec{q}(i),\vec{j}_\alpha) \tag{5.4}$$

and they satisfy:

$$\Sigma_i y^{i\alpha} y^{i\beta} = M^{(pa)}_{\alpha\beta} = \Lambda_{\alpha\beta} = \lambda_\alpha \delta_{\alpha\beta} \tag{5.5}$$

The matrix R in (5.2) is identified with the matrix R of eqn. (2.16) defining the orientation of the noninertial frame with rsepect to the LPF.

To complete the construction in terms of the reduction A and the orthonormalization O of Section 2, express the mass quadrupole M as the matrix product $M = Q^t Q$ where Q is the n x 3 matrix of the components $q^{i\alpha}$. Under a rotation, M transforms as follows

$$M' = R^t M R.$$

It follows that $M' = BG^2B^t$. The diagonalization of M' is achieved by taking $B = \Lambda^{-1}Q^t = OA$. Therefore,

$$A_{\alpha k} = \Sigma_\nu R_{\nu\alpha} q^{k\nu} = y^{k\alpha} \tag{5.6}$$

and, by ES orthonormalization

$$O_{\gamma\nu} = (G_F^{-1/2})_{\gamma\nu} = \lambda_\gamma^{-1} \delta_{\gamma\nu} \tag{5.7}$$

so that the orthonormal vectors of the frame are:

$$\vec{j}_\alpha = \lambda_\alpha^{-1} \Sigma_k y^{k\alpha} \vec{q}(k) \tag{5.8}$$

Each vector $\vec{j}_\alpha$ is expressible as a linear combination of all the GJV with rotation invariant coefficients so that the frame $(\vec{j}_\alpha)$ constitutes a noninertial frame rotating with the particles under a simultaneous rotation of all particles. This justifies the denomination of "global" frame.

The 3n rotationally invariant coordinates $y^{i\alpha}$ together with the conditions (5.5) imposed by the definition of the frame may be parameterized by some set of 3n–3 independent internal coordinates. The most familiar way to do this consists of taking the three eigenvalues λ_α as three of the internal coordinates.

Define now in the customary manner[6]:

$$z^{i\alpha} = \lambda_{\alpha}^{-1/2}\, y^{i\alpha} \tag{5.9}$$

The three n–dimensional label space[1] vectors $\vec{z}^{\cdot\alpha}$ whose components are $z^{i\alpha}$ wrt the orthonormal label space basis $\{\vec{c}_i\}$ are orthonormal, that is:

$$(\vec{z}^{\cdot\alpha}, \vec{z}^{\cdot\beta}) = \delta_{\alpha\beta} \tag{5.10}$$

This imposes six conditions on the $z^{i\alpha}$ which may be parameterized by 3n–6 angles ϕ_s:

$$z^{i\alpha} = z^{i\alpha}(\phi_1,\ldots,\phi_{3n-6}) \tag{5.11}$$

By setting $\mu_\alpha = \lambda_\alpha^{1/2}$, one obtains the transformation:

$$q^{i\alpha} = \Sigma_\gamma R_{\alpha\gamma}(\theta_s)\mu_\gamma z^{i\gamma}(\phi_s) \tag{5.12}$$

The inversion of (5.12) is given by:

$$\begin{aligned} \vec{j}_\alpha &= \Sigma_\gamma R_{\gamma\alpha}\vec{\ell}_\gamma' \qquad R^t Q R = \mathrm{diag}(\lambda_\alpha) \\ \mu_\alpha &= \left\{\Sigma_i (y^{i\alpha})^2\right\}^{1/2} \\ z^{i\alpha} &= \mu_\alpha^{-1}\, y^{i\alpha} \end{aligned} \tag{5.13}$$

The axes $\vec{j}_\alpha$ are finally expressed by:

$$\vec{j}_\alpha = \mu_\alpha^{-1}\Sigma_k z^{k\alpha}(\phi_s)\vec{q}(k) \tag{5.14}$$

To define a set of internal coordinates derived from the basic rotational invariants (Gram matrix elements G_{ij}), we need to express $\{\mu_\alpha\}$ and $\{z^{i\alpha}\}$ in terms of the G_{ij} as well as the inverse transformation. This transformation is far from being trivial and will be treated elsewhere.

The matrices I^i can be obtained from the defining equations (3.7) and (3.23) by using the principal axes unit vectors $\vec{j}_\alpha$ given by (5.8) or

(5.14). The result (in cartesian coordinates) is as follows:

$$I^i = \begin{bmatrix} 0 & \frac{y^{i3}}{\lambda_3-\lambda_1} & \frac{y^{i2}}{\lambda_1-\lambda_2} \\ \frac{y^{i3}}{\lambda_2-\lambda_3} & 0 & \frac{y^{i1}}{\lambda_1-\lambda_2} \\ \frac{y^{i2}}{\lambda_2-\lambda_3} & \frac{y^{i1}}{\lambda_3-\lambda_1} & 0 \end{bmatrix} \qquad (5.15)$$

Substitute now the $I^i_{\alpha\beta}$ into eqs.(4.6) and (4.10) to obtain the coefficients for the KE operator.

Observe that:

$$\sum_i I^i_{\lambda\alpha} I^i_{\lambda\beta} = (D_\alpha D_\beta)^{-1} \sum_i y^{i\alpha} y^{i\beta}$$

where $D_\alpha = \lambda_\beta - \lambda_\gamma$. Set also $S_\alpha = \lambda_\beta + \lambda_\gamma$. Therefore the coefficients for the KE operator are:

$$\Delta_{i\alpha} = y^{i\alpha}\left(\frac{D_\beta - D_\gamma}{D_\beta D_\gamma}\right)$$

$$A_\alpha = S_\alpha / D_\alpha$$

$$B_\alpha = C_\alpha = 0$$

Actually, the final result in cartesian coordinates is quite cumbersome and, as such, not very useful. It is more convenient at this point to express the various terms in more appropriate curvilinear internal coordinates.

By using the internal coordinates given in eqs.(5.13), we recover the usual rovib kinetic energy operator[8] or its vibrational counterpart following the prescription discussed at the end of the section 4.

b) Locally defined frames

As a second example, consider the case of two "distinguished" vectors $\vec{Q}(i)$ which are linearly independent combinations from within a subset of GJV:

$$\vec{Q}(i) = \sum_k A_{ik}\vec{q}(k) \qquad (i=1,2) \qquad (5.16)$$

The two vectors $\vec{Q}(i)$ can be transformed by some orthonormalization procedure[1] O into two unit orthogonal vectors $\vec{d}_1$ and $\vec{d}_2$. The vector product $\vec{d}_1 \times \vec{d}_2 = \vec{d}_3$ is uniquely defined and the set $\{\vec{d}_\alpha\}$ forms a non–inertial frame. The particular non–inertial frame one has in mind translates into a particular choice of the reduction matrix A together with a particular orthonormalization procedure.

For the seek of simplicity, we proceed with two GJV $\vec{q}(1)$ and $\vec{q}(2)$; the generalization to linear combinations (5.16) can be deduced trivially by extension.

Following the usual conventions of the theory of angular momentum, we identify:

$$\vec{d}_1 \to O\vec{x} \qquad \vec{d}_2 \to O\vec{y} \qquad \vec{d}_3 \to O\vec{z}$$

The frame $\{\vec{d}_\alpha\}$ is defined by:

$$\begin{aligned} \vec{d}_3 &= O_{31}\vec{q}(1) + O_{32}\vec{q}(2) \\ \vec{d}_1 &= O_{11}\vec{q}(1) + O_{12}\vec{q}(2) \\ \vec{d}_2 &= \vec{d}_3 \times \vec{d}_1 \end{aligned} \qquad (5.17)$$

where the 2×2 matrix $O = (O_{\alpha i})$ obeys the fundamental relation (2.9): $OGO^t = I_2$.

The matrices I^i are obtained by employing eq.(3.9).

For $i>2$, all the I^i are zero since:

$$\Omega^{i}_{\alpha 1} = (\vec{d}_2, \frac{\partial \vec{d}_3}{\partial q^{i\alpha}}) = 0,\ \Omega^{i}_{\alpha 2} = -(\vec{d}_1, \frac{\partial \vec{d}_3}{\partial q^{i\alpha}}) = 0,\ \Omega^{i}_{\alpha 3} = -(\vec{d}_2, \frac{\partial \vec{d}_1}{\partial q^{i\alpha}}) = 0$$

For i = 1, 2, we obtain the result:

$$\Omega^{i}_{\alpha 1} = (\vec{d}_2, \frac{\partial \vec{d}_3}{\partial q^{i\alpha}}) = O_{3i} R_{\alpha 2}$$

$$\Omega^{i}_{\alpha 2} = -(\vec{d}_1, \frac{\partial \vec{d}_3}{\partial q^{i\alpha}}) = (\vec{d}_3, \frac{\partial \vec{d}_1}{\partial q^{i\alpha}}) = -O_{3i} R_{\alpha 1} + O_{1i} R_{\alpha 3}$$

$$\Omega^{i}_{\alpha 3} = -(\vec{d}_2, \frac{\partial \vec{d}_1}{\partial q^{i\alpha}}) = -O_{1i} R_{\alpha 2}$$

With (3.23), the matrices I^i (i=1,2) become:

$$I^{i} = \begin{bmatrix} 0 & -0_{3i} & 0 \\ 0_{3i} & 0 & -0_{1i} \\ 0 & 0_{1i} & 0 \end{bmatrix} \qquad (5.18)$$

From eq.(2.9), one can deduce that the matrix O is the inverse of the matrix $Y = (y^{i\alpha})$ of the cartesian components:

$$\begin{bmatrix} 0_{31} & 0_{32} \\ 0_{11} & 0_{12} \end{bmatrix} = \begin{bmatrix} y^{13} & y^{11} \\ y^{23} & y^{21} \end{bmatrix}^{-1}$$

Therefore, by setting $\delta = y^{13}y^{21} - y^{11}y^{23}$, (5.18) becomes

$$I^1 = \frac{1}{\delta}\begin{bmatrix} 0 & -y^{21} & 0 \\ y^{21} & 0 & y^{23} \\ 0 & -y^{23} & 0 \end{bmatrix}$$

$$I^2 = \frac{1}{\delta}\begin{bmatrix} 0 & y^{11} & 0 \\ -y^{11} & 0 & -y^{13} \\ 0 & y^{13} & 0 \end{bmatrix} \qquad (5.19)$$

The coefficients A_α, B_α, C_α, $\Delta_{i\alpha}$ and the operator $\mathscr{D}_\alpha$ can be evaluated in terms of the cartesian coordinates $y^{i\alpha}$.

The KE operator follows immediately from the transformation law into internal coordinates (ζ^ν; ν=1,2,3).

Consider the three following particular cases.

a) CHA Frame.

This corresponds to the frame obtained by a Gram–Schmidt orthonormalization[1] of the two vectors $\vec{q}(1)$ and $\vec{q}(2)$. Here

$$O_{31} = Q_1^{-1} \qquad O_{32} = 0$$
$$O_{11} = -\cot\theta Q_1^{-1} \qquad O_{12} = \sin^{-1}\theta\, Q_2^{-1} \qquad (5.20)$$

where $Q_i = |\vec{q}(i)|^2$ and $\cos\theta = (\vec{q}(1),\vec{q}(2))/Q_1Q_2$. By substitution of these expressions into the KE operator of the previous section, the hamiltonian of reference (5) is recovered.

b) Equivalent Symmetric (ES) Frames (planar case).

Impose the condition that $y^{11} = y^{23}$ (that is, $O_{11} = O_{32}$) corresponding to an ES orthonormalization[1] in the plane of the vectors $\vec{q}(i)$. The matrix O is symmetric and according to the fundamental relation (2.9), $O = G^{-1/2}$, where G is the Gram matrix of the vectors $\vec{q}(i)$. The analytic expression of $G^{-1/2}$ is:

$$0 = N\begin{bmatrix} \gamma_2 & -\gamma_3 \\ -\gamma_3 & \gamma_1 \end{bmatrix} \tag{5.21}$$

where:

$$\gamma_1 = Q_1(Q_1 + Q_2\sin\theta)$$
$$\gamma_2 = Q_2(Q_2 + Q_1\sin\theta) \tag{5.22}$$
$$\gamma_3 = Q_1Q_2\cos\theta$$

$$N = [Q_1^2 + Q_2^2 + 2Q_1Q_2\sin\theta]^{-1/2}[Q_1Q_2\sin\theta]^{-1} \tag{5.23}$$

It is interesting to notice that any frame can be generated from the ES frame (or the CHA–frame) by an in–plane rotation R′. The matrix O transforms into O′[1]:

$$R'O = O' \tag{5.24}$$

For instance, we can consider a frame such that $\vec{d}_3$ be along the bisector of the vectors $\vec{q}(1)$ and $\vec{q}(2)$. This corresponds to a $\pi/4$ in–plane rotation R′ of the ES frame.

c) Equivalent Symmetric Frames (3 vectors)

In this third example the ES orthonormalization of three vectors $\vec{q}(i)$ is considered. The matrices I^i are obtained in a way similar to that in the previous section. The equivalent of eq.(5.18) for an arbitrary orthonormalization O involving three vectors is:

$$I^i = \begin{bmatrix} 0 & -0_{3i} & 0_{2i} \\ 0_{3i} & 0 & -0_{1i} \\ -0_{2i} & 0_{1i} & 0 \end{bmatrix} \tag{5.25}$$

Once expressed in catesian coordinates, one has:

$$I^1 = \frac{1}{\delta} \begin{bmatrix} 0 & y^{31}y^{22} - y^{21}y^{32} & y^{23}y^{31} - y^{33}y^{21} \\ y^{21}y^{32} - y^{31}y^{22} & 0 & y^{33}y^{22} - y^{23}y^{32} \\ y^{21}y^{33} - y^{23}y^{31} & y^{32}y^{23} - y^{33}y^{22} & 0 \end{bmatrix}$$

$$I^2 = \frac{1}{\delta} \begin{bmatrix} 0 & y^{31}y^{12} - y^{11}y^{32} & y^{33}y^{11} - y^{13}y^{31} \\ y^{11}y^{32} - y^{31}y^{12} & 0 & y^{33}y^{12} - y^{13}y^{32} \\ y^{13}y^{31} - y^{11}y^{33} & y^{13}y^{32} - y^{33}y^{12} & 0 \end{bmatrix} \tag{5.26}$$

$$I^3 = \frac{1}{\delta} \begin{bmatrix} 0 & y^{12}y^{21} - y^{11}y^{22} & y^{13}y^{21} - y^{23}y^{11} \\ y^{11}y^{22} - y^{21}y^{12} & 0 & y^{13}y^{22} - y^{23}y^{12} \\ y^{23}y^{11} - y^{13}y^{21} & y^{23}y^{12} - y^{13}y^{22} & 0 \end{bmatrix}$$

where δ is the determinant of the matrix Y:

$$Y = \begin{bmatrix} y^{13} & y^{11} & y^{12} \\ y^{23} & y^{21} & y^{22} \\ y^{33} & y^{31} & y^{32} \end{bmatrix} \tag{5.27}$$

The ES frame is obtained by prescribing the following three conditions on the cartesian coordinates:

$$y^{11} = y^{23}; \quad y^{12} = y^{33}; \quad y^{22} = y^{31} \tag{5.28}$$

As in the in–plane ES frame, "derived" frames may be of greater interest. For instance, consider the normalized "polysector" of $\vec{q}(1)$, $\vec{q}(2)$ and $\vec{q}(3)$ as one axis together with two linearly independent combinations of the axes orthogonalized in some way with respect to the polysector. This corresponds to a 3–d rotation of the ES frame. Using eq.(5.24), one deduces the new orthonormalization matrix O', hence a new set of matrices I^i and finally the KE operator in the new frame.

6. SUMMARY AND CONCLUSIONS

We have derived in this work a decomposition of the relative kinetic energy operator for N particles described by N–1 generalized Jacobi vectors into rotational (eq.4.12) and intrinsic (eq.4.11) components . The coupling between the two is expressed by eq.(4.13) or (4.20). The result is expressed in cartesian coordinates with respect to an abritrary noninertial

frame characterized by a set of 3×3 intrinsic matrices . The great advantage of this method, besides simplicity, is that no approximations and no constraints are assumed. The KE operator can be employed in any physical problem provided suitable choices have been made for the GJV, the noninertial frame and the set of curvilinear coordinates.

APPENDIX 1

ROTATION MATRICES, ANGULAR MOMENTUM OPERATORS

We review in this appendix some standard results of the theory of angular momentum.[6]

Under a physical rotation $\mathcal{R}$, the state $|\psi>$ transforms into a new state $|\psi'> \equiv \mathcal{R}[|\psi>] \equiv \mathcal{U}|\psi>$ while conserving the physical properties of the system: $\mathcal{U}$ is called the *rotation operator*. The usual representations of the rotation operator are obtained by choosing the standard bases $|kJM>$ (common eigenkets of the hamiltonian operator $\mathcal{H}$, J^2 and J_3). With respect to these bases, the components J_α of the total angular momentum operator are represented by the (2J+1)×(2J+1) matrices $J_\alpha^{(J)}$ acting in the invariant subspaces $\mathcal{E}_J$ (irreducible with respect to the rotation operator).

The rotation operator (parameterized by the Euler angles θ_s) is represented in the same irreducible (2J+1) dimensional spaces $\mathcal{E}_J$ by the ***rotation matrices*** $D^{(J)}(\theta_s)$:

$$D^{(J)}(\theta_s) = \exp(-i\theta_1 J_3^{(J)})\exp(-i\theta_2 J_2^{(J)})\exp(-i\theta_3 J_3^{(J)}) \qquad (A1.1)$$

with matrix elements:

$$D^{(J)}_{M'M} = \langle JM' | \mathcal{U}(\theta_S) | JM \rangle \qquad \text{(A1.2)}$$

It is the matrix elements $\bar{D}^{(J)*}_{MM'}$, as opposed to $D^{(J)}_{MM'}$, that transform properly as ***state vectors*** carrying angular momentum labels (J,M), this result being true for each $M'=J,\ldots,-J$.

Differentiation of $D^{(J)}(\theta_S)$ (given in equation A1.1) with respect to θ_S yields the following results:

$$\begin{aligned}
\frac{\partial}{\partial\theta_1} D^{(J)}(\theta_S) &= -i J_3^{(J)} D^{(J)}(\theta_S) \\
\frac{\partial}{\partial\theta_2} D^{(J)}(\theta_S) &= -i(-J_1^{(J)}\sin\theta_1 + J_2^{(J)}\cos\theta_1) D^{(J)}(\theta_S) \\
\frac{\partial}{\partial\theta_3} D^{(J)}(\theta_S) &= -i(J_1^{(J)}\cos\theta_1\sin\theta_2 + J_2^{(J)}\sin\theta_1\sin\theta_2 \\
&\qquad + J_3^{(J)}\cos\theta_2) D^{(J)}(\theta_S)
\end{aligned} \qquad \text{(A1.3)}$$

One can invert these results to obtain the action (realization) of the matrix operators $J^{(J)}_\alpha$ on the matrices $D^{(J)}$ as ***differential operators*** $\mathcal{J}_\alpha$:

$$J^{(J)}_\alpha D^{(J)}(\theta_S) = -\mathcal{J}_\alpha D^{(J)}(\theta_S) \qquad \text{(A1.4)}$$

The differential operators $\mathcal{J}_\alpha$ are:

$$\begin{aligned}
\mathcal{J}_1 &= i\left[\cos\theta_1\cot\theta_2 \frac{\partial}{\partial\theta_1} + \sin\theta_1 \frac{\partial}{\partial\theta_2} - \frac{\cos\theta_1}{\sin\theta_2}\frac{\partial}{\partial\theta_3}\right] \\
\mathcal{J}_2 &= i\left[\sin\theta_1\cot\theta_2 \frac{\partial}{\partial\theta_1} - \cos\theta_1 \frac{\partial}{\partial\theta_2} - \frac{\sin\theta_1}{\sin\theta_2}\frac{\partial}{\partial\theta_3}\right] \\
\mathcal{J}_3 &= -i\frac{\partial}{\partial\theta_1}
\end{aligned} \qquad \text{(A1.5)}$$

The standard action of the differential operators $\mathcal{J}_\alpha$ is given by:

$$\mathcal{J}_\pm D^{(J)*}_{M'M}(\theta_S) = [(J\mp M')(J\pm M'+1)]^{1/2} D^{(J)*}_{M'\pm1,M}(\theta_S)$$

$$\mathcal{J}_3 D^{(J)*}_{M'M}(\theta_s) = M' D^{(J)*}_{M'M}(\theta_s) \qquad \text{(A1.6a)}$$

$\vec{\mathcal{J}}$ is the physical total angular momentum operator of the system (differential operator acting in the space of the angular momentum wave functions $D^{(J)*}_{M'M}$).

Let us introduce the operators $\mathcal{P}_\beta$:

$$\mathcal{P}_\beta = \Sigma_\alpha R_{\alpha\beta}(\theta_s)\mathcal{J}_\alpha \qquad \text{(A1.6b)}$$

The following commutation relations are easily obtained:

$$[\mathcal{P}_\alpha, \mathcal{P}_\beta] = -i\mathcal{P}_\gamma \qquad (\alpha,\beta,\gamma \text{ are cyclic}) \qquad \text{(A1.7)}$$

$$[\mathcal{P}_\alpha, \mathcal{J}_\beta] = 0 \qquad (\alpha,\beta=1,2,3) \qquad \text{(A1.8)}$$

With respect to an inertial frame $\{\vec{\ell}_\alpha\}$, the total angular momentum $\vec{\mathcal{J}}$ is expressed by $\vec{\mathcal{J}} = \vec{\ell}_1\mathcal{J}_1 + \vec{\ell}_2\mathcal{J}_2 + \vec{\ell}_3\mathcal{J}_3$. It is therefore correct that $\vec{\mathcal{P}}$ is defined by $\vec{\mathcal{P}} = \vec{f}_1\mathcal{P}_1 + \vec{f}_2\mathcal{P}_2 + \vec{f}_3\mathcal{P}_3$ where $\{\vec{f}_\alpha\}$ is a new frame (non–inertial) obtained from $\{\vec{\ell}_\alpha\}$ by the rotation $R(\theta_s)$. $\mathcal{P}_\alpha$ is the component of the total angular momentum referred to the moving frame $\{\vec{\ell}_\alpha\}$.

The commutation relations of the $\mathcal{J}_\gamma$ with the $R_{\alpha\beta}(\theta_s)$ are easily found:

$$[\mathcal{J}_\alpha, R_{\beta\lambda}] = i\epsilon_{\alpha\beta\gamma}R_{\gamma\lambda} \qquad \text{(A1.9)}$$

where $\{\alpha,\beta,\gamma\}$ are cyclic and λ=1,2,3.

The total angular momentum operator $\vec{\mathcal{J}}$ is the generator of the rotations of the moving frame $(\vec{f}_\alpha)$ and may be identified with the total angular momentum of a rigid body whose instantaneous orientation is specified by the frame $(\vec{f}_\alpha)$ which is itself fixed (no relative motion) in the system defining the frame.

In eq.(A1.7), that is the set of operators $-\mathcal{P}_\alpha$ that satisfy the usual commutation relations of angular momentum. This is a direct consequence of the fact that the $\mathcal{J}_\alpha$ do not commute with the rotated axes $\vec{f}_\beta$. Observe also that the $\mathcal{P}_\alpha$ are invariants with repect to the rotations generated by $\vec{\mathcal{J}}$ a result that follows geometrically from the fact that the rotations generated by $\vec{\mathcal{J}}$ rotate both $\vec{\mathcal{J}}$ and $\vec{f}_\alpha$ simultaneously, thereby leaving their scalar product invariant.

In order to obtain the action of the $\mathcal{P}_\alpha$ on the rotation matrices, transpose eq.(A1.4) using the symmetric and antisymmetric properties of $J_\alpha^{(J)}$:

$$J_1^{t(J)} = J_1^{(J)} \qquad J_3^{t(J)} = J_3^{(J)}$$
$$J_2^{t(J)} = -J_2^{(J)}$$

and

$$D^{t(J)}(\theta_3,-\theta_2,\theta_1) = D^{(J)}(\theta_1,\theta_2,\theta_3)$$

Therefore,

$$D^{(J)}(\theta_s)J_\alpha^{(J)} = -\mathcal{P}_\alpha D^{(J)}(\theta_s) \qquad \text{(A1.10)}$$

The operators $\mathcal{P}_\alpha$ take now the explicit form:

$$\mathcal{P}_- = \mathcal{P}_1 + i\mathcal{P}_2 = \exp(-i\theta_3)\left[-i\cot\theta_2 \frac{\partial}{\partial\theta_3} + \frac{\partial}{\partial\theta_2} + \frac{i}{\sin\theta_2}\frac{\partial}{\partial\theta_1}\right]$$
$$\mathcal{P}_+ = \mathcal{P}_1 - i\mathcal{P}_2 = \exp(i\theta_3)\left[-i\cot\theta_2 \frac{\partial}{\partial\theta_3} - \frac{\partial}{\partial\theta_2} + \frac{i}{\sin\theta_2}\frac{\partial}{\partial\theta_1}\right]$$
$$\mathcal{P}_3 = -i\frac{\partial}{\partial\theta_3} \qquad \text{(A1.11)}$$

The action of the body–referred angular momentum operators $\mathcal{P}_\alpha$ are obtained in conplex conjugating (A1.10) and in taking the matrix elements:

$$\mathcal{P}_{-}D^{(J)*}_{M'M}(\theta_S) = [(J-M)(J+M+1)]^{1/2}D^{(J)*}_{M',M+1}(\theta_S)$$
$$\mathcal{P}_{+}D^{(J)*}_{M'M}(\theta_S) = [(J+M)(J-M+1)]^{1/2}D^{(J)*}_{M',M-1}(\theta_S) \qquad \text{(A1.12)}$$
$$\mathcal{P}_3 D^{(J)*}_{M'M}(\theta_S) = MD^{(J*}_{M'M}(\theta_S)$$

It is important to notice that *it is $\mathcal{P}_{-}$ and $\mathcal{P}_{+}$ that act as step–up and step–down operators respectively.*

Physically, the wave functions $D^{(J)*}_{M'M}$ are the wave functions of a solid body with center of mass fixed in space; $\mathcal{J}_3$ is the z–component of the angular momentum referred to space–fixed axes, while $\mathcal{P}_3$ is the component of the angular momentum referred to the noninertial z–axis.

APPENDIX 2.

This is an attempt to prove that all the linear momentum operator components $\pi_{i\alpha} = -i\frac{\partial}{\partial y^{i\alpha}}$ (in a non–inertial frame attached to the system) are intrinsic operators, i.e., that $\pi_{i\alpha}D^{(J)*}_{MK}(\theta_S) = 0.$ (for any i) where the set of Euler angles $\{\theta_S\}$ parameterize the rotation transforming the inertial frame into the noninertial frame.

Let k_o label the particles entering into the definition of the frame and k' be the remaining particles. Therefore, $\pi_{k_o\alpha}$ are intrinsic operators and $\pi_{k_o\alpha}D^{(J)*}_{MK} = 0$. We want to prove that this is true for $\pi_{k'\alpha}$ as well.

We first show that, for any k', $\pi_{k'\alpha}$ commutes with a particular L^o_λ, i.e.,that $\pi_{k'\alpha}$ is invariant under any rotation along the axis of

quantization $\vec{f}_{\alpha'}$. An analogous proof follows for $y^{k'\alpha}$ and consequently for the $P'_{\alpha'}$.

Since $p_{k'\alpha}$ is invariant under any rotation of the frame, we have:

$$[L^{\circ}_{\alpha'}, p_{k'\beta}] = 0 \tag{A2.1}$$

$p_{k'\beta}$ is given by (see footnote):

$$p_{k'\beta} = \Sigma_{\lambda} R_{\beta\lambda} \pi_{k'\lambda} \tag{A2.2}$$

Using the property of commutators:

$$[A,BC] = [A,B]C + B[A,C] \tag{A2.3}$$

and the fact that the $R_{\alpha\beta}$ are vector operators with respect to $\vec{L}^{\circ}$:

$$[L^{\circ}_{\alpha'}, R_{\beta\lambda}] = (i)R_{\gamma\lambda} \qquad (\alpha,\beta,\gamma \text{ are c.p.}) \tag{A2.4}$$

we deduce that:

$$\Sigma_{\lambda} R_{\beta\lambda} [L^{\circ}_{\alpha'}, \pi_{k'\lambda}] + i p^{k'\gamma} = 0 \tag{A2.5}$$

Similarly, we have:

$$\Sigma_{\lambda} R_{\gamma\lambda} [L^{\circ}_{\alpha'}, \pi_{k'\lambda}] - i p^{k'\beta} = 0 \tag{A2.6}$$

and

$$\Sigma_{\lambda} R_{\alpha\lambda} [L^{\circ}_{\alpha'}, \pi_{k'\lambda}] = 0 \tag{A2.7}$$

Solving the system of three equations (5,6,7) in the three unknowns $[L^{\circ}_{\alpha'}, \pi_{k'\lambda}]$ gives the solution:

$$[L^{\circ}_{\alpha'}, \pi_{k'\lambda}] = i\{R_{\lambda\mu}\pi_{k'\nu} - R_{\lambda\nu}\pi_{k'\nu}\} \tag{A2.8}$$

where λ,μ,ν are c.p.

This means that $\pi_{k'\lambda}$ are not invariant under an arbitrary rotation of the non–inertial frame. Consider now the rotations about $\vec{f}_{\alpha'}$ axis of quantization, i.e., rotations of the plane $\{\vec{f}_{\beta'}, \vec{f}_{\gamma}\}$. The rotation matrix elements appearing in (8) are zero and $[L^{\circ}_{\alpha'}, \pi_{k'\lambda}] = 0$.

Consider now the action of the commutator $[L^{\circ}_{\alpha'}, \pi_{k'\lambda}]$ on the

$D^{(J)*}_{MK}$:

$$L^{\circ}_{\alpha}\pi_{k'\lambda}D^{(J)*}_{MK} = \pi_{k'\lambda}L^{\circ}_{\alpha}D^{(J)*}_{MK} \qquad (A2.9)$$

In particular for L°_{3},

$$L^{\circ}_{3}\pi_{k'\lambda}D^{(J)*}_{MK} = M\pi_{k'\lambda}D^{(J)*}_{MK} \qquad (A2.10)$$

Therefore, $D^{(J)*}_{MK}$ are eigenfunctions of $\pi_{k'\lambda}$:

$$\pi_{k'\lambda}D^{(J)*}_{MK} = aD^{(J)*}_{MK} \qquad (A2.11)$$

This is true for any i, in particular for $i = k_o$, we have:

$$\pi_{k_o\lambda}D^{(J)*}_{MK} = 0 \qquad (A2.12)$$

Since $[\pi_{k_o\lambda},\pi_{k'\lambda}] = 0$, we have:

$$\pi_{k_o\lambda}\pi_{k'\lambda}D^{(J)*}_{MK} = \pi_{k'\lambda}\pi_{k_o\lambda}D^{(J)*}_{MK} = 0 \qquad (A2.13)$$

and $\pi_{k'\lambda}D^{(J)*}_{MK} = 0$.

In particular, for J=1, one deduces that:

$$\pi_{k\lambda}R_{\alpha\beta} = 0 \qquad (A2.14)$$

The same argument can be used for the operators P'_{α}

NOTE:

$$\frac{\partial}{\partial q^{k'\alpha}} = \sum_{j,\lambda} \frac{\partial y^{j\lambda}}{\partial q^{k'\gamma}} \frac{\partial}{\partial y^{j\lambda}} \qquad \text{(summation over all j)}$$

But:

$$y^{j\lambda} = \Sigma_{\rho}R_{\rho\lambda}q^{j\rho} \qquad (N.1)$$

so that:

$$\frac{\partial y^{j\lambda}}{\partial q^{k'\gamma}} = \frac{\partial}{\partial q^{k'\gamma}}\{\Sigma_{\rho}R_{\rho\lambda}q^{j\rho}\}$$

$$= \Sigma_{\rho}R_{\rho\lambda}\frac{\partial q^{j\rho}}{\partial q^{k'\gamma}}$$

since the $R_{\rho\lambda}$ are independent of the $q^{k'\gamma}$ ($R_{\rho\lambda} = \Sigma_{k_o}B_{\lambda k_o}q^{k_o\gamma}$)

$$\Rightarrow \quad \frac{\partial y^{j\lambda}}{\partial q^{k'\gamma}} = R_{\gamma\lambda}\delta_{jk'}$$

$$\Rightarrow \quad \frac{\partial}{\partial q^{k'\gamma}} = \Sigma_\lambda R_{\gamma\lambda}\frac{\partial}{\partial y^{k'\lambda}}$$

$$\Rightarrow p_{k'\gamma} = \Sigma_\lambda R_{\gamma\lambda}\pi_{k'\lambda} \qquad (N.2)$$

Compare the inverse transformation of (N.1) with (N.2) => the cartesian components transform in the same way as the linear momenta for the $\vec{q}(k')$. This is true also for the internal angular momenta:

$$L'_\alpha = \Sigma_\lambda R_{\alpha\lambda}P'_\lambda \qquad (N.3)$$

References.

1. J.P.Leroy, R.Wallace, Chemical Physics, 111 (1987) 11.

2. J.O.Hirschfelder, E.P. Wigner, Physics 21 (1935) 113.

3. C.F.Curtiss, J.O.Hirschfelder, F.T.Adler, J.Chem.Phys. 18 (1950) 1638.

4. B.R. Johnson, J.Chem.Phys. 73 (1980) 5051; 79 (1983) 1906,1916.

M.Mishra, J.Linderberg, Mol. Phys. 50 (1983) 91.

J.Linderberg, Y.Ohrn, Intern. J. Quantum Chem 27 (1985) 273.

5. R. Wallace, Chemical Physics 88 (1984) 247. and references therein.

6."Encyclopedia of Mathematics: Angular Momentum in Quantum Physics", L.C.Biedenharn, J.D.Louck, Addison–Wesley 1981. Section 7.10.

7. "The Classical Groups", H.Weyl, Princeton University Press, Princeton, 1946.

8. B.Buck,L.Biedenharn, R.Y.Cusson, Nucl.Phys. A317(1979) 205.

P.Gulshani, D.J.Rowe, Can. J. Phys. 54 (1976) 970.

9. O.L.Weaver, R.Y.Cusson, L.C.Biedenharn, Ann. of Phys. 102 (1976) 493.

10)"The Theory of Matrices", Vol 1, F.R.Gantmacher, Chelsea, N.Y.1959.

The quantum kinetic energy operator for a group of particles in terms of scalar basic rotational invariant coordinates derived from a generalized Jacobi vectors (GJV) description. I. Frames derived from two GJV.

Abstract: Previous work[1] defining the quantum kinetic energy operator for relative motion of a group of particles in terms of cartesian components of generalized Jacobi vectors (GJV) is logically extended. The first such extension examines alternate definitions of the noninertial reference frame which follow from the minimum specification by two GJV, the second invokes the simplest scalar internal coordinates which are the basic rotational invariants of the GJV. KE operators are explicitly evaluated and compared to assess the relative value (in terms of separability) of alternate approaches.

1.Introduction.

In a previous paper[1], the quantum kinetic energy operator for relative motion of a system of N particles described by N–1 "generalized Jacobi vectors"[2,3] (GJV) was decomposed into rotational and intrinsic components. The resulting KE operator was expressed in terms of cartesian components with respect to a noninertial frame characterized by a set of η intrinsic (3×3) matrices I^i, η being the number of Jacobi vectors involved in the construction of the noninertial frame.

The present study applies the foregoing general theory to systems of N particles described by local noninertial frames tied to the instantaneous configuration of two GJVs. The kinetic energy operator is re–expressed in terms of the "basic rotational invariant" coordinates (BRI) of the N–1 Jacobi vectors (lengths of GJV and angles between them). These coordinates constitute precursors for any set of independent coordinates since any internal coordinate is expressible as a polynomial of the BRI[4]. Unfortunately, for $N > 4$, they are not independent and a further step must be taken to obtain an appropriate parameterization.

Section 2 reviews the concept of noninertial frames and presents examples for typical 2GJV frames. The matrices I^i are evaluated in section 3. In section 4, the kinetic energy operator derived in ref.(1) is re–expressed in simplified form. In local two and three GJV frames the three components P^0_α of the vortex angular momentum cancel. This is expected since $\vec{P}^0$ is an angular momentum acting in label space and we are currently considering a fixed Jacobi vectors description. Section 5 is devoted to the expression of the KE operator in terms of the BRI

coordinates and their conjugate momenta for typical frames constructed independently of the lengths of the Jacobi vectors (norm independent frames). In section 6, the KE operator is derived for the norm dependent equivalent symmetric frame and for the principal axes of inertia frame. One result is to demonstrate the invariance of the intrinsic part of the 3 body hamiltonian to alternate choices of noninertial frame i.e., the projection of the hamiltonian on the sub–manifold (S=0;L=0) is independent of the way the frame is defined. The hamiltonian for the general N–body system behaves differently: whereas the intrinsic hamiltonian is invariant to the choice of alternate **global frames** as demonstrated by H.M. Pickett[5], it does differ from that for locally defined frames (which in turn differ from one another). Finally, in section 7, detailed application to 3–body AB_2 and 4–body $(AB_2)X$ systems is carried out for different internal curvilinear coordinates. In particular the coupling terms between the internal coordinates are discussed in regard to the choice of the rotating frame used in the description.

2. Non–inertial frames.

Generalized Jacobi Vectors (GJV) were recently described[2] by the present authors. They constitute an important intermediate step in the derivation of a hamiltonian for intrinsic (vibrational) motion since the relative kinetic energy operator is diagonal when expressed in cartesian components of the GJV. The transformation of (non–orthogonal) interparticle vectors into (orthonormal) GJV is actually generated by an orthonormalization **O** in label space[2]. As a result, the Gram matrix G(r)

of the interparticle vectors transforms into the Gram matrix G(q) of the GJV according to:

$$G(q) = O\ G(r)\ O^t \tag{2.1}$$

where the matrix elements are given by:

$$G(q)_{ij} = (\vec{q}_i,\vec{q}_j) = Q_iQ_j\cos\theta_{ij}. \tag{2.2}$$

Q_i is the length of the vector $\vec{q}_i$ and θ_{ij} is the angle between vectors $\vec{q}_i$ and $\vec{q}_j$ with the convention that θ is measured positive on going from $\vec{q}_i$ to $\vec{q}_j$. The $n \equiv N-1$ quantities Q_i together with the $\frac{n(n-1)}{2}$ different quantities $Q_iQ_j\cos\theta_{ij}$ are referred to as the **Basic Rotational Invariants (BRI)**. For $n > 3$, they are not independent since the rank of the determinant of G is 3.

Once the configuration has been expressed in terms of n GJV, the relative kinetic energy operator is "diagonal":

$$T_{rel} = \frac{1}{2}\sum_{k,\alpha} p_{k\alpha}^2 \tag{2.3}$$

where $p_{k\alpha} = -i\frac{\partial}{\partial q^{k\alpha}}$ is the linear momentum operator conjugate to the cartesian component $q^{k\alpha}$ of the GJV $\vec{q}_k$ with respect to the lab. parallel base vector $\vec{\ell}_\alpha$ i.e.:

$$q^{i\alpha} = (\vec{q}_k,\vec{\ell}_\alpha) \tag{2.4}$$

The inertial LPF (lab. parallel frame) $\{\vec{\ell}_\alpha\}$ is obtained from the LFF (lab. fixed frame) by translation of the latter accompanying restriction of the label space to the relative label space.

Under a rotation (represented by the matrix R), the LPF transforms into a new frame $(\vec{f}_\alpha)$ such that:

$$\vec{f}_\alpha = \Sigma_\lambda R_{\lambda\alpha}\vec{\ell}_\lambda \tag{2.5}$$

where $R_{\lambda\alpha}$ is the direction cosine of $\vec{f}_\alpha$ with respect to $\vec{\ell}_\alpha$. The new components of the Jacobi vector $\vec{q}_i$ are given by:

$$(\vec{q}_i,\vec{f}_\alpha) = y^{i\alpha} = \Sigma_\lambda R_{\lambda\alpha} q^{i\lambda} \qquad (2.6)$$

The new frame is in some way "attached" to the molecular configuration if the $\vec{f}_\alpha$ depend upon some or all of the GJV, the precise form of attachment being determined by the specific linear combination of the GJV involved in the frame construction.

Formally, the construction is achieved in two steps. Let $\{\vec{q}^0_k\}$ be the set of n_o Jacobi vectors involved in the definition of the frame. For $n_o = n$, the frame is global, otherwise, it is local.

1. Define three independent linear combinations $\vec{F}_\lambda$ of the vectors $\vec{q}^0_k$:

$$\vec{F}_\lambda = \Sigma_k A_{\lambda k} \vec{q}^0_k \qquad (2.7)$$

where A is a $3\times n_o$ matrix whose elements are some prescribed (rotational invariant) functions of the $q^{i\alpha}$. The Gram matrix G(F) is given by:

$$G(F) = A\ G(q^0)\ A^t \qquad (2.8)$$

2. Orthonormalize the vectors $\vec{F}_\lambda$ in one of the standard ways[2] (a review of these is contained in appendix I):

$$\vec{f}_\mu = \Sigma_\lambda O_{\mu\lambda} \vec{F}_\lambda \qquad (2.9)$$

The overall transformation is represented by the $3\times n_o$ matrix $B = OA$ whose rotationally invariant elements $B_{\mu k}$ are functions of the cartesian coordinates $q^{i\alpha}$. Equation (2.9) becomes:

$$\vec{f}_\mu = \Sigma_k B_{\mu k} \vec{q}^0_k \qquad (2.10)$$

On account of orthonormality of the frame, matrix B obeys the fundamental relation:

$$B\ G(q^0)\ B^t = I_{n^0} \qquad (2.11)$$

The equations defined by (2.11) are not independent; there exist three arbitrary relations among the elements $B_{\mu k}$ which uniquely define the

frame.

The Jacobi vectors $\vec{q}_k^{\,0}$ are expressible in a unique way in terms of the base vectors $\vec{f}_\mu$:

$$\vec{q}_k = \Sigma_\mu \, y_o^{k\mu} \, \vec{f}_\mu \tag{2.12}$$

Forming the scalar product of equation (2.10) with $\vec{f}_\mu$ (and employing (2.12)) the following matrix equation is obtained:

$$\mathbf{B} \; \mathbf{Y}_o = \mathbf{I}_3 \tag{2.13}$$

where $\mathbf{Y}_o$ is the $n_o \times 3$ matrix of the components $y_o^{k\mu}$. From the uniqueness of the expansion (2.12), it follows that $\mathbf{Y}_o$ is the unique pseudo–inverse of the matrix B:

$$\mathbf{Y}_o = \mathbf{B}^\dagger \tag{2.14}$$

The three relations among the elements of B become three conditions on the cartesian components $y_o^{k\mu}$; that is the set of $3n_o$ dependent variables can be parameterized by $3n_o$–3 independent internal parameters (curvilinear coordinates) ζ^ν.

Alternatively, form the scalar product of equation (2.10) with $\vec{\ell}_a$ to obtain the matrix equation:

$$\mathbf{R} = \mathbf{B} \; \mathbf{Q}_o \tag{2.15}$$

where R is the orthogonal matrix whose elements are the direction cosines of the $\vec{f}_\mu$ with respect to the $\vec{\ell}_\alpha$ hence the matrix representing the rotation transforming the inertial frame into the noninertial frame defined uniquely by B. $\mathbf{Q}_o$ is the $n_o \times 3$ matrix of the components of the $\vec{q}_k$ in the inertial frame. It follows (dot equation 2.12 with $\vec{\ell}_\alpha$) that the separation of the variables is formally expressed by:

$$\mathbf{Q}_o = \mathbf{Y}_o(\zeta^\nu)\mathbf{R}^t(\phi_s) \tag{2.16}$$

where ϕ_s are the three Euler angles parameterizing the orthogonal matrix R.

It is worthwhile mentioning that the same frame can be generated by different procedures: the matrix B can be expressed as different products OA. Let A and A′ be two independent linear combinations. There exists a (3×3) non singular matrix T such that A′ = T A. It follows that B can be expressed as O′A′ where O′ = T^{-1}. In particular, provided an appropriate choice for A is made, any frame can be constructed using two vectors $\vec{F}_\lambda$ and a two dimensional orthonormalization, the third vector being uniquely defined by their vector product.

Corresponding to the above, the same frame can be interpreted either as:

(1) derived from a fixed set of Jacobi vectors (the matrix A in equation (2.7) is constant)

(2) derived from varying Jacobi vectors (the matrix A has elements which are functions of $y^{i\alpha}$).

In the former case, the BRI coordinates are the natural choice for the internal coordinates. In the latter case, it is usual to take as internal coordinates the principal moments of inertia together with the parameters of the label rotation matrix. The angular hyperspherical coordinates[6] are typical examples of label internal coordinates. Formally, the matrix B of equation (2.10) defines in label space a set of three linearly independent vectors $\vec{z}_\alpha$:

$$\vec{z}_\alpha = \Sigma_k B_{\alpha k} \vec{c}_k \qquad (2.17)$$

The Gram matrix (3×3) of the label vectors $\vec{z}_\alpha$ is:

$$G(z) = BB^t = \mathscr{M}^{-1} \tag{2.18}$$

that is the inverse of the mass quadrupole of the Jacobi vectors defining the frame. The six independent parameters of G(z) are the inverses of the elements of the inertia tensor and they may be taken as internal coordinates together with some angles defining the orientation of $\{\vec{z}_\alpha\}$ with respect to the basis $\{\vec{c}_k\}$.

3. Description of N body systems with non inertial frames defined by a triatomic fragment.

In accordance with standard convention, the axis of quantization is identified with $\vec{f}_3$ (z–axis) in the plane of the triatomic fragment. Axis $\vec{f}_1$ (x–axis) is defined to lie in the same plane, therefore $\vec{f}_2$ is uniquely defined by the vector product $\vec{f}_3 \times \vec{f}_1$ and is perpendicular to the plane of the fragment.

BRI Coordinates.

In any (2GJV) noninertial frame (with the above conventions), the BRI coordinates of the Jacobi vectors $\vec{q}_1$ and $\vec{q}_2$ are expressed in terms of their cartesian components ($y^{i\alpha}$) by the relations:

$$\begin{aligned} Q_1 &= \{(y^{11})^2 + (y^{13})^2\}^{1/2} \\ Q_2 &= \{(y^{21})^2 + (y^{23})^2\}^{1/2} \end{aligned} \tag{3.1}$$

$$\theta = \cos^{-1}\left\{ \frac{y^{11}y^{21} + y^{13}y^{23}}{Q_1 Q_2} \right\}$$

where θ is taken positive on going from $\vec{q}(1)$ to $\vec{q}(2)$.

The BRI coordinates of the remaining Jacobi vectors $\vec{q}_k'$ are:

$$Q_k' = \{\Sigma_\alpha (y'^{k\alpha})^2\}^{1/2}$$

$$\theta_{jk}' = \cos^{-1}\left\{ \frac{\Sigma_\alpha y'^{j\alpha} y'^{k\alpha}}{Q_j' Q_k'} \right\} \qquad (3.2)$$

Let Y be the (2×2) matrix of the cartesian components $(y^{i\alpha})$:

$$Y = \begin{bmatrix} y^{13} & y^{11} \\ y^{23} & y^{21} \end{bmatrix} \qquad (3.3)$$

Let δ be the determinant of Y:

$$\delta = y^{13}y^{21} - y^{11}y^{23} = Q_1 Q_2 \sin\theta \qquad (3.4)$$

The noninertial frame is defined by:

$$\begin{aligned} \vec{f}_3 &= B_{31}\vec{q}(1) + B_{32}\vec{q}(2) \\ \vec{f}_1 &= B_{11}\vec{q}(1) + B_{12}\vec{q}(2) \\ \vec{f}_2 &= \vec{f}_3 \times \vec{f}_1 \end{aligned} \qquad (3.5)$$

Since $B = Y^{-1}$, we obtain

$$\begin{aligned} \vec{f}_3 &= \frac{1}{\delta}[\, y^{21}\vec{q}(1) - y^{11}\vec{q}(2)] \\ \vec{f}_1 &= \frac{1}{\delta}[-y^{23}\vec{q}(1) + y^{13}\vec{q}(2)] \end{aligned} \qquad (3.6)$$

The cartesian components can be expressed as:

$$y^{i\alpha} = (\vec{q}(i), \vec{f}_\alpha) = Q_i \cos\lambda_{i\alpha} \qquad (3.7)$$

where $\cos\lambda_{i\alpha}$ is the direction cosine of $\vec{q}(i)$ with respect to $\vec{f}_\alpha$. Let $\lambda_{13} = \zeta$ and $\lambda_{23} = \zeta'$. The cartesian components in terms of the BRI coordinates and the independent parameter ζ (or ζ') are:

$$y^{13} = Q_1 \cos\zeta \qquad y^{23} = Q_2 \cos\zeta'$$
$$y^{11} = -Q_1 \sin\zeta \qquad y^{21} = -Q_2 \sin\zeta' \tag{3.8}$$

where

$$\zeta' = \zeta - \theta \qquad \zeta = \zeta(Q_1, Q_2, \theta) \tag{3.9}$$

The three relations among the cartesian coordinates $y^{i\alpha}$ become

$$y^{12} = 0 \quad ; \quad y^{22} = 0 \quad ; \quad f(\zeta) = 0 \tag{3.10}$$

Frames for which $\zeta = \zeta(\theta)$ will be referred to as "Norm independent frames" . For example, $\zeta = 0$ is the CHA frame, $\zeta = \theta/2$ is the bisector frame, $\zeta = \frac{\theta}{2} - \frac{\pi}{4}$ is the norm independent E.S. frame. In the general case the parameter ζ depends upon the three BRI coordinates. For instance, the E.S. frame is defined by imposing the condition $y^{23} = y^{11}$ on the cartesian coordinates

$$\cos\zeta = \frac{Q_1 + Q_2 \sin\theta}{D_+^{1/2}} \qquad (D_+ = Q_1^2 + Q_2^2 + 2Q_1 Q_2 \sin\theta) \tag{3.11}$$

Remark:

One can define the parametric family of frames by setting $\zeta = k\theta$ in order to construct the axis of quantization "somewhere" between $\vec{q}(1)$ and $\vec{q}(2)$. This procedure can be useful for systems where the two GJV do not represent equivalent fictitious particles; varying k from –1 to 1, all the norm independent frames are generated.

Linear Momenta and Vortex Momentum.

The linear momenta $\pi_{i\alpha}$ are given by:

$$\pi_{i\alpha} = -i\{ \frac{\partial Q_i}{\partial y^{i\alpha}} \frac{\partial}{\partial Q_i} + \frac{\partial \theta}{\partial y^{i\alpha}} \frac{\partial}{\partial \theta} \} \qquad (3.12)$$

$$= -i\{ \frac{y^{i\alpha}}{Q_i} \frac{\partial}{\partial Q_i} + \frac{1}{Q_i \sin\theta} [\frac{y^{i\alpha} \cos\theta}{Q_i} - \frac{y^{j\alpha}}{Q_j}] \frac{\partial}{\partial \theta} \}$$

$$\pi_{11} = i\{ \sin\zeta \frac{\partial}{\partial Q_1} + \frac{\cos\zeta}{Q_1} \frac{\partial}{\partial \theta} \}$$

$$\pi_{13} = -i\{ \cos\zeta \frac{\partial}{\partial Q_1} - \frac{\sin\zeta}{Q_1} \frac{\partial}{\partial \theta} \}$$

$$\pi_{21} = -i\{ -\sin\zeta' \frac{\partial}{\partial Q_2} + \frac{\cos\zeta'}{Q_2} \frac{\partial}{\partial \theta} \} \qquad (3.13)$$

$$\pi_{23} = -i\{ \cos\zeta' \frac{\partial}{\partial Q_2} + \frac{\sin\zeta'}{Q_2} \frac{\partial}{\partial \theta} \}$$

The Vortex angular momentum P_2° is zero: this can be seen by substituting (3.8) and (3.13) into $P_2^\circ = \Sigma_i(y^{i3}\pi_{i1} - y^{i1}\pi_{i3})$ with i=1,2. This is not surprizing since P_2° is a label space angular momentum, hence generator of label rotations keeping invariant the mass quadrupole. Since the set of GJV is fixed in label space, P_2° has to be zero.

The transformation of the linear momenta from the inertial ($p_{i\alpha}$) to the noninertial frame ($\pi_{i\alpha}$) was evaluated in reference 1

$$p_{i\alpha} = \Sigma_\beta R_{\alpha\beta} \mathcal{A}_{i\beta} \qquad (3.14)$$

where $\mathcal{A}_{i\beta}$ is the operator:

$$\mathcal{A}_{i\beta} = \pi_{i\beta} + \Sigma_\gamma I^i_{\beta\gamma}(P'_\gamma + K^\circ_\gamma) \qquad (3.15)$$

with the notation of reference 1 and by taking advantage of $P^\circ_\gamma = 0$ for γ=1,2,3.

Matrices I^i.

The matrix elements of Ω^i are given (ref.1, eqn.3.9) by:

$$\Omega^i_{\alpha\lambda} = i\Sigma_j y^{j\mu} p_{i\alpha} B_{\nu j} + R_{\alpha\mu} B_{\nu i} \qquad (3.16)$$

When acting on an intrinsic function f, $K^\circ_\gamma f = 0$. If f depends only upon

the Jacobi vectors defining the frame, $P'_\gamma f = 0$. Therefore, the result of the action of the linear momenta $p_{i\alpha}$ on an intrinsic function reduces to:

$$p_{i\alpha} f = \Sigma_\beta R_{\alpha\beta} \pi_{i\beta} f \qquad (3.17)$$

In particular, the coefficients $B_{\nu j}$ appearing in equation (3.15) are intrinsic functions (since functions of the BRI of the frame). By substituting this result in (3.15) and by identifying with equation (3.23) of reference 1, an explicit expression for the matrix elements $I^i_{\beta\lambda}$ is obtained:

$$I^i_{\beta\lambda} = -i[\Sigma_j y^{j\mu} \pi_{i\beta} B_{\nu j} - iB_{\nu i} \delta_{\mu\beta}] \qquad (3.18)$$

For a (2GJV) frame defined by the parameter $\zeta(Q_1,Q_2,\theta)$, the matrices I^i are obtained by substitution of (3.8) and (3.13) into (3.18). The results are:

$$\begin{aligned}
I^1_{21} &= -\frac{\sin\zeta'}{Q_1 \sin\theta} \quad ; \quad I^2_{21} = \frac{\sin\zeta}{Q_2 \sin\theta} \\
I^1_{23} &= \frac{\cos\zeta'}{Q_1 \sin\theta} \quad ; \quad I^2_{23} = -\frac{\cos\zeta}{Q_2 \sin\theta} \\
I^1_{12} &= \sin\zeta \frac{\partial\zeta}{\partial Q_1} + \frac{\cos\zeta}{Q_1}\left(\frac{\partial\zeta}{\partial\theta} - 1\right) \\
I^1_{32} &= -\cos\zeta \frac{\partial\zeta}{\partial Q_1} + \frac{\sin\zeta}{Q_1}\left(\frac{\partial\zeta}{\partial\theta} - 1\right) \\
I^2_{12} &= \sin\zeta' \frac{\partial\zeta}{\partial Q_2} - \frac{\cos\zeta'}{Q_2}\frac{\partial\zeta}{\partial\theta} \\
I^2_{32} &= -\cos\zeta' \frac{\partial\zeta}{\partial Q_2} - \frac{\cos\zeta'}{Q_1}\frac{\partial\zeta}{\partial\theta}
\end{aligned} \qquad (3.19)$$

or in more concise form:

$$\begin{aligned}
I^1_{12} &= \pi_{11}\zeta' \quad ; \quad I^2_{12} = -\pi_{21}\zeta \\
I^1_{32} &= -\pi_{13}\zeta' \quad ; \quad I^2_{32} = \pi_{23}\zeta
\end{aligned} \qquad (3.20)$$

4. Kinetic Energy Operator.

The rovib hamiltonian of an N–body system in cartesian coordinates for an arbitrary non–inertial frame has been partitioned[1] as follows:

$$H_{rovib} = T^{o}_{int} + T'_{int} + T^{c}_{int} + V + T_{rot} + T_{coup} \qquad (4.1)$$

where

(I) T^{o}_{int} are the internal operators related to Jacobi vectors defining the frame:

Linear momenta. *Vortex angular momenta.*

$$\sum_{i_o,\alpha} [\pi^{2}_{i_o\alpha} + i\Delta_{i_o\alpha}\pi_{i_o\alpha}] \quad + \quad \sum_{\gamma} [M_{\gamma\gamma}(P^{o}_{\gamma})^2 + M_{\alpha\beta}\{P^{o}_{\alpha},P^{o}_{\beta}\} + C_{\gamma}P^{o}_{\gamma}]$$

Coupling terms between internal operators.

$$+ \sum_{i_o,\gamma,\lambda} I^{i_o}_{\lambda\gamma}\{\pi_{i_o\lambda},P^{o}_{\gamma}\}$$

(II) T'_{int} are the internal operators related to the remaining Jacobi vectors $\vec{q}'_{k}$:

Linear momenta. *Internal angular momenta.*

$$\sum_{i',\alpha} \pi^{2}_{i'\alpha} \quad + \quad \sum_{\gamma} [M_{\gamma\gamma}(P'_{\gamma})^2 + M_{\alpha\beta}\{P'_{\alpha},P'_{\beta}\} + C_{\gamma}P'_{\gamma}]$$

(III) T^{c}_{int} are the coupling terms between the internal operators

$$2\Sigma_{\gamma} M_{\gamma\gamma}P^{o}_{\gamma}P'_{\gamma} + 2\Sigma_{\gamma} M_{\alpha\beta}(P^{o}_{\alpha}P'_{\beta} + P^{o}_{\beta}P'_{\alpha}) + 2\Sigma_{\gamma} d_{\gamma}P'_{\gamma}$$

(IV) V is the potential energy operator:

$$V(y^{i\alpha};\ i=1,2,...,N-1,\alpha=1,2,3;F_{\lambda}(y^{i\alpha}) = 0;\lambda=1,2,3)$$

(V) T_{rot} are the external operators (angular momenta):

$$\sum_{\gamma} [M_{\gamma\gamma}(K^{o}_{\gamma})^2 + M_{\alpha\beta}\{K^{o}_{\alpha},K^{o}_{\beta}\} + C_{\gamma}K^{o}_{\gamma}]$$

(VI) T_{coup} are the coupling terms between internal and external

operators:

$$\sum_{\gamma} \mathscr{D}_{\gamma} K^{\circ}_{\gamma}$$

The various operators appearing in these expressions are defined as follows:

$\pi_{i\alpha}$ is the linear momentum conjugate to the cartesian component $y^{i\alpha}$ of the Jacobi vectors with respect to the noninertial frame.

The angular momentum components P_{γ} are partitioned in the following manner:

$$P_{\alpha} = \sum_{i_o} (y^{i_o\beta}\pi_{i_o\gamma} - y^{i_o\gamma}\pi_{i_o\beta}) + \sum_{i'} (y^{i'\beta}\pi_{i'\gamma} - y^{i'\gamma}\pi_{i'\beta}) \qquad (4.2)$$

$$= \qquad P^{\circ}_{\alpha} \qquad + \qquad P'_{\alpha} \qquad (4.3)$$

where the P°_{α} are the vortex angular momentum components (generators of label space rotations leaving the mass quadrupole invariant) and P'_{α} are the components of the internal angular momentum describing the internal rotations of the remaining Jacobi vectors with respect to the noninertial frame.

$K^{\circ}_{\alpha} = (\vec{L}^{\circ}, \vec{f}_{\alpha})$ are the components along $\vec{f}_{\alpha}$ of the angular momentum of the Jacobi vectors defining the frame; they are the generators of the rotations of the noninertial frame with respect to the LPF.

$$\mathscr{D}_{\gamma} = M_{\gamma\gamma}P_{\gamma} + M_{\alpha\beta}(P_{\alpha} + P_{\beta}) + d_{\gamma} \qquad (4.4)$$

$$d_{\gamma} = \sum_{i_o} (I^{i_o}_{\alpha\gamma}\pi_{i_o\alpha} + I^{i_o}_{\beta\gamma}\pi_{i_o\beta}) \qquad (4.5)$$

The coefficients $M_{\alpha\beta}$ and C_{γ} are defined as:

$$M = \Sigma_i (I^i)^t (I^i) \ . \qquad (i=1,2) \qquad (4.6)$$

It can be shown (using equations (2.10) and (2.18)) that M is

actually the inverse of the tensor of inertia $\mathcal{J}$ of the Jacobi vectors $\vec{q}^{\,o}_k$ with respect to the noninertial frame. The mass quadrupole $\mathcal{M}$ and $\mathcal{J}$ are related by the relation :

$$\mathcal{J} = \mathrm{Tr}\,\mathcal{M} I_3 - \mathcal{M} \tag{4.7}$$

The coefficients C_γ are given by:

$$C_\gamma = \sum_{i,\lambda} [\pi_{i\lambda} I^i_{\lambda\gamma} + I^i_{\lambda\gamma} P_\gamma I^i_{\lambda\gamma} + i\Delta_{i\lambda} I^i_{\lambda\gamma}] + I^i_{\alpha\beta} P_\beta I^i_{\alpha\gamma} + I^i_{\beta\alpha} P_\alpha I^i_{\beta\gamma} \tag{4.8}$$

For a frame defined by two GJV, this general expression simplifies since:

(a) $P^o_\alpha = 0$ for any α=1,2,3 (since the frame is constructed with a fixed set of Jacobi vectors)

(b) The matrix elements $M_{12} = M_{21}$ and $M_{23} = M_{32}$ are zero.

(c) $C_1 = C_3 = 0$

$$C_2 = \sum_{i,\lambda} [\pi_{i\lambda} I^i_{\lambda 2} + i\Delta_{i\lambda} I^i_{\lambda 2}] \tag{4.9}$$

(d) $d_1 = d_3 = 0$

$$d_2 = \sum_{i,\lambda} I^i_{\lambda 2} \pi_{i\lambda} \tag{4.10}$$

After integrating over all the rotations, the KE operator is expressed in terms of the cartesian coordinates and the rotational quantum numbers:

$$KE = T^o_{int} + V_c + T'_{int} + T'_{ir} + T'_{ic} + T_{rot} + T^o_c + T'_c \tag{4.11}$$

where

T^o_{int} = (a) + (b):

(a) $\pi_{11}^2 + \pi_{13}^2 + \pi_{21}^2 + \pi_{23}^2$

(b) $i[\Delta_{11}\pi_{11} + \Delta_{13}\pi_{13} + \Delta_{21}\pi_{21} + \Delta_{23}\pi_{23}]$

are the terms related to the linear momenta of the Jacobi vectors defining

the frame.

By employing (3.8) and (3.13):

$$(a) = -\frac{\partial^2}{\partial Q_1^{\,2}} - \frac{1}{Q_1}\,\zeta_\theta\,\frac{\partial}{\partial Q_1}$$
$$-\frac{\partial^2}{\partial Q_2^{\,2}} - \frac{1}{Q_2}\,[1-\zeta_\theta]\,\frac{\partial}{\partial Q_2}$$
$$-\left[\frac{1}{Q_1^{\,2}} + \frac{1}{Q_2^{\,2}}\right]\frac{\partial^2}{\partial\theta^2} + \left\{\frac{1}{Q_1}\,\zeta_1 - \frac{1}{Q_2}\,\zeta_2\right\}\frac{\partial}{\partial\theta}$$

where $\zeta_\theta = \left[\frac{\partial\zeta}{\partial\theta}\right]$, and $\zeta_i = \left[\frac{\partial\zeta}{\partial Q_i}\right]$

$$(b) = \frac{1}{Q_1}\,\zeta_\theta\,\frac{\partial}{\partial Q_1} - \frac{1}{Q_2}\,\zeta_\theta\,\frac{\partial}{\partial Q_2} - \frac{2}{Q_1}\,\frac{\partial}{\partial Q_1} - \frac{1}{Q_2}\,\frac{\partial}{\partial Q_2}$$
$$+\left[\frac{1}{Q_2}\,\zeta_2 - \frac{1}{Q_1}\,\zeta_1\right]\frac{\partial}{\partial\theta} - \left[\frac{1}{Q_1^{\,2}} + \frac{1}{Q_2^{\,2}}\right]\cot\theta\,\frac{\partial}{\partial\theta}$$

Finally

$$T^{o}_{int} = -\frac{\partial^2}{\partial Q_1^{\,2}} - \frac{2}{Q_1}\,\frac{\partial}{\partial Q_1}$$
$$-\frac{\partial^2}{\partial Q_2^{\,2}} - \frac{2}{Q_2}\,\frac{\partial}{\partial Q_2}$$
$$-\left[\frac{1}{Q_1^{\,2}} + \frac{1}{Q_2^{\,2}}\right]\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta}\right] \qquad (4.12)$$

hence, T^{o}_{int} is independent of the choice of the frame.

V_c is the *Centrifugal potential* term obtained from T_{rot} after integration over the rotations:

$$V_c = \tfrac{1}{2}(M_{11} + M_{22})[L(L+1) - S^2] + M_{33}S^2 \qquad (4.13)$$

Of course V_c is zero for the rotational ground state (S=0;L=0)

T'_{int} are the terms related to the linear momenta of the remaining Jacobi vectors:

$$T'_{int} = \sum_{i',\alpha}(\pi_{i'\alpha})^2 \qquad (4.14)$$

where the summation is over $i' = 3,\ldots,n$ and $\alpha = 1,2,3$.

Internal rotation terms:

$$T_{ir} = \Sigma_\gamma M_{\gamma\gamma}(P'_\gamma)^2 + M_{13}\{P'_1,P'_3\} + C_2P'_2 + 2S(M_{33}P'_3+M_{13}P'_1) \tag{4.15}$$

Internal couplings:

$$T_{ic} = 2d_2P'_2 \tag{4.16}$$

The pure rotation terms T_{rot} are expressed in terms of step–up/step–down operators $\sigma_\pm$ and the rotational quantum numbers:

$$T_{rot} = \frac{\ell_+^2}{4}[M_{11} - M_{22}]\sigma_+^2 + \frac{\ell_-^2}{4}[M_{11} - M_{22}]\sigma_-^2 + \ell_+[SM_{13} + \frac{i}{2}C_2]\sigma_+ + \ell_-[SM_{13} - \frac{i}{2}C_2]\sigma_- \tag{4.17}$$

The internal–external coupling terms T_{coup} are:

$$T^o_c = i\ell_+d_2\sigma_+ - i\ell_-d_2\sigma_- \tag{4.18}$$

that is the coupling terms between the operators $\sigma_\pm$ and the operators associated with the internal coordinates relative to the Jacobi vectors defining the frame.

$$T'_c = \ell_+[M_{11}P'_1+M_{13}P'_3+ iM_{22}P'_2]\sigma_+ + \ell_-[M_{11}P'_1+M_{13}P'_3- iM_{22}P'_2]\sigma_- \tag{4.19}$$

represents the coupling terms between the $\sigma_\pm$ and the internal angular momenta P'_α.

The coefficients $M_{\alpha\beta}$ and C_2 are easily calculated in terms of the parameter ζ and the BRI coordinates:

$$M_{\gamma\gamma} = \Sigma_i[(I^i_{\alpha\gamma})^2 + (I^i_{\beta\gamma})^2] \tag{4.20}$$

that is

$$M_{11} = \frac{1}{\sin^2\theta}\left[\frac{\sin^2\zeta'}{Q_1^2} + \frac{\sin^2\zeta}{Q_2^2}\right]$$

$$M_{22} = \zeta_1^2 + \zeta_2^2 + \left[\frac{1}{Q_1^2} + \frac{1}{Q_2^2}\right]\zeta_\theta^2 - \frac{1}{Q_1^2}\left[1 - 2\zeta_\theta\right]$$

$$M_{33} = \frac{1}{\sin^2\theta}\left[\frac{\cos^2\zeta'}{Q_1^2} + \frac{\cos^2\zeta}{Q_2^2}\right]$$

The coefficient M_{13} is given by:

$$M_{13} = \Sigma_i I^i_{21} I^i_{23} \qquad (4.21)$$
$$= -\frac{1}{\sin^2\theta}\left[\frac{\sin\zeta'\cos\zeta'}{Q_1^2} + \frac{\sin\zeta\cos\zeta}{Q_2^2}\right]$$

Since $P^\circ_2 = 0$, the coefficient C_2 is evaluated by using (3.20):

$$C_2 = \pi_{11} I^1_{12} + \pi_{13} I^1_{32} + \pi_{21} I^2_{12} + \pi_{23} I^2_{32}$$
$$+ \mathcal{L}[I^1_{23} I^1_{12} - I^1_{21} I^1_{32} + I^2_{23} I^2_{12} - I^2_{21} I^2_{32}]$$

that is

$$C_2 = -\mathcal{L}\left\{T^\circ_{int}\zeta + \frac{\cot\theta}{Q_1^2}\right\} \qquad (4.22)$$

The operator d_2 is given by:

$$d_2 = I^1_{12}\pi_{11} + I^1_{32}\pi_{13} + I^2_{12}\pi_{21} + I^2_{32}\pi_{23}$$

that is

$$d_2 = \mathcal{L}\left\{\zeta_1\frac{\partial}{\partial Q_1} + \zeta_2\frac{\partial}{\partial Q_2} + \left[\frac{1}{Q_1^2} + \frac{1}{Q_2^2}\right]\zeta_{\theta\partial\theta} - \frac{1}{Q_1^2}\frac{\partial}{\partial\theta}\right\} \qquad (4.23)$$

The state (S=0;L=0) corresponds to the terms $T^\circ_{int} + T'_{int} + T_{ir} + T_{ic}$ where T°_{int} is invariant under change of the noninertial frame (i.e., rotations (parameterized) by the angle $\omega(Q_1,Q_2,\theta)$ about $\vec{i}_2$). The behaviour of the remaining terms under a change of frame will be carried out in the next sections by means of examples.

All that is needed in order to obtain an explicit expression for the

KE operator in any 2GJV frame are the coefficients $M_{\alpha\beta}$ and C_2 and the operator d_2.

3–Body Fragment Hamiltonian.

For 3–body systems, the KE operator reduces to the sum:

$$(KE)_3 = T^{\circ}_{int} + V_c + T_{rot} + T^{\circ}_c \qquad (4.24)$$

where T°_{int} is the KE operator for the state (S=0;L=0). V_c will not in general be separable into terms depending upon the BRI coordinates as is the case for the CHA frame[8]. Actually, the separability depends upon the choice of the non–inertial frame as well as the choice of curvilinear coordinates derived from the BRI (see examples below). In any case, V_c can be added to the source potential V and the separability of the effective potential $V_{eff} = V + V_c$ can be treated "globally":

$$V_{eff} = V_1 + V_2 + V_\theta + V_{ns} \qquad (4.25)$$

The 3–body hamiltonian becomes:

$$\begin{aligned} &-\frac{\partial^2}{\partial Q_1^{\,2}} - \frac{2}{Q_1}\frac{\partial}{\partial Q_1} + V_1 \\ &-\frac{\partial^2}{\partial Q_2^{\,2}} - \frac{2}{Q_2}\frac{\partial}{\partial Q_2} + V_2 \\ &-\left[\frac{1}{Q_1^{\,2}} + \frac{1}{Q_2^{\,2}}\right]\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + V'_\theta\right] \end{aligned} \qquad (4.26)$$

where

$$V'_\theta = \left[\frac{1}{Q_1^{\,2}} + \frac{1}{Q_2^{\,2}}\right]^{-1} V_\theta \qquad (4.27)$$

N–Body systems described by a (2GJV) frame.

To apply a (2GJV) frame to N–body systems, terms T'_{int}, T_{ir}, T_{ic} and T'_{c} are evaluated by employing the transformation of cartesian components into BRI of the remaining Jacobi vectors:

$$y^{k'\alpha} = Q_{k'}\cos\zeta_{k'\alpha} \qquad (k' = 3,...,n) \tag{4.28}$$

where $\zeta_{k'\alpha}$ is the angle between $\vec{q}_{k'}$ and $\vec{f}_{\alpha}$. The angles $\zeta_{k'\alpha}$ are not independent since they obey the usual direction cosines relations:

$$\begin{aligned} &\Sigma_{\alpha}\cos\zeta_{k'\alpha}\cos\zeta_{i'\alpha} = \cos\theta_{k'i'} \qquad (k',i' = 3,...,n) \\ &\Sigma_{\alpha}\cos\zeta_{k'\alpha}\cos\zeta_{i\alpha} = \cos\theta_{k'i} \qquad (k' = 3,...,n;\ i = 1,2) \end{aligned} \tag{4.29}$$

The linear momenta $\pi_{k'\alpha}$ conjugate to $y^{k'\alpha}$ are given by:

$$\pi_{k'\alpha} = -i\left\{ \cos\zeta_{k'\alpha}\frac{\partial}{\partial Q_{k'}} + \frac{1}{Q_{k'}}\left[\Sigma_{\ell}\,\Gamma^{\alpha}_{k'\ell}\frac{\partial}{\partial\theta_{k'\ell}}\right]\right\} \tag{4.30}$$

where the summation is over all the indices $\ell \neq k'$ and

$$\Gamma^{\alpha}_{k'\ell} = \frac{\cos\theta_{k'\ell}\cos\zeta_{k'\alpha} - \cos\zeta_{\ell\alpha}}{\sin\theta_{k'\ell}} \tag{4.31}$$

The internal angular momentum components P'_{α} are obtained by substitution of (4.28) and (4.30) into (4.3).

The problem reduces to that of finding an appropriate set of independent angles which are functions of the $\theta_{k'\ell}$ and adapted to the specific problem in hand. For example, a 4–body molecule can be described by choosing the azimuthal and polar angles of the vector $\vec{q}_3$ with respect to the noninertial frame together with Q_3 (see Figure I). The cartesian components are expressed in terms of these coordinates by:

$$\begin{aligned} y^{31} &= Q_3\sin\phi\,\cos\theta' \\ y^{33} &= Q_3\sin\phi\,\sin\theta' \\ y^{32} &= Q_3\cos\phi \end{aligned} \tag{4.32}$$

The linear momenta are:

$$\pi_{31} = -i[\sin\phi\cos\theta' \frac{\partial}{\partial Q_3} - \frac{\sin\theta'}{Q_3\sin\phi}\frac{\partial}{\partial\theta'} + \frac{\cos\phi\cos\theta'}{Q_3}\frac{\partial}{\partial\phi}]$$
$$\pi_{33} = -i[\sin\phi\sin\theta' \frac{\partial}{\partial Q_3} + \frac{\cos\theta'}{Q_3\sin\phi}\frac{\partial}{\partial\theta'} + \frac{\cos\phi\sin\theta'}{Q_3}\frac{\partial}{\partial\phi}] \qquad (4.33)$$
$$\pi_{32} = -i[\cos\phi \frac{\partial}{\partial Q_3} - \frac{\sin\phi}{Q_3}\frac{\partial}{\partial\phi}]$$

The angular momenta P'_α are given by the usual expressions:

$$P'_1 = i[\cos\theta'\cot\phi \frac{\partial}{\partial\theta'} + \sin\theta' \frac{\partial}{\partial\phi}]$$
$$P'_3 = i[\sin\theta'\cot\phi \frac{\partial}{\partial\theta'} - \cos\theta' \frac{\partial}{\partial\phi}] \qquad (4.34)$$
$$P'_2 = -i \frac{\partial}{\partial\theta'}$$

The angle ϕ is identified in this case with the angle ζ_{32} and is independent of the choice of the frame. θ' is the angle between the axis $\vec{f}_3$ and the projection of the Jacobi vector $\vec{q}_3$ on the plane of the fragment; θ' obviously depends upon the choice of the noninertial frame. To avoid this, it is preferable to choose $\xi = \theta' - \zeta$ where $\zeta = \zeta_{13}$ has been defined in section 3.

With this parameterization, the part of the KE operator that has to be added to $(KE)_3$ is:

$$(KE)_r = T'_{int} + T_{ir} + T_{is} \qquad (4.35)$$

This expression is evaluated by substitution of (4.34) and (4.35) into (4.14–16) and by using the coefficients (4.21–23) characteristic of the frame. The equations are derived for several frames and different parameterizations in section 7 for a molecule of the type $(AB_2)X$.

5. Examples of Norm Independent Frames.

As first examples, we consider in this section frames constructed independently of the lengths Q_i of the two Jacobi vectors, norm–independent frames. This requires restriction of the dependence of the parameter ζ to the angle θ between the vectors. The simplest norm–independent frame, hereafter denoted by CHA[8], is obtained by a Gram–Schmidt orthonormalization of the vectors $\vec{q}_i$. Two possible frames result, depending upon which vector is taken first.

1.Bisector Frame.

The bisector of the two Jacobi vectors is the axis of quantization $\vec{f}_3$. The frame adjusts to the instantaneous configuration of the two Jacobi vectors in a fashion independent of their lengths. In a sense, this frame can be viewed as a principal axes frame of two unit vectors. By applying the results of appendix I, the cartesian coordinates of the Jacobi vectors with respect to this frame obey the following relationship:

$$y^{13}y^{21} + y^{23}y^{11} = 0 \tag{5.1}$$

and the parameter $\zeta = \theta/2$.

In terms of the BRI the $y^{i\alpha}$ are expressed by:

$$\begin{aligned} y^{13} &= Q_1\cos\tfrac{\theta}{2} & y^{11} &= -Q_1\sin\tfrac{\theta}{2} \\ y^{23} &= Q_2\cos\tfrac{\theta}{2} & y^{21} &= Q_2\sin\tfrac{\theta}{2} \end{aligned} \tag{5.2}$$

The part of the internal KE operator related to the 3–body fragment becomes:

$$T^{\circ}_{int} + V_c =$$

$$-\frac{\partial^2}{\partial Q_1^{\,2}} - \frac{2}{Q_1}\frac{\partial}{\partial Q_1} + \frac{1}{8Q_1^{\,2}}[L(L+1) - S^2]$$

$$-\frac{\partial^2}{\partial Q_2^{\,2}} - \frac{2}{Q_2}\frac{\partial}{\partial Q_2} + \frac{1}{8Q_2^{\,2}}[L(L+1) - S^2] \qquad (5.3)$$

$$-\left[\frac{1}{Q_1^{\,2}} + \frac{1}{Q_2^{\,2}}\right]\left\{\frac{\partial^2}{\partial\theta^2} + \cot\theta\,\frac{\partial}{\partial\theta} - S^2\,\frac{\csc^2\theta}{2}\right.$$

$$\left. - \frac{\csc^2\theta}{4}\sin^2(\theta/2)[L(L+1) - 3S^2]\right\}$$

In this case, the centrifugal potential V_c is completely separable as in the CHA frame but here V_c is distributed in a symmetric fashion between the two radial oscillators Q_1 and Q_2. The system of three differential equations can be solved numerically for a given source potential V by the usual methods[9].

By defining:

$$\tilde{Q} = Q_1^{-2} + Q_2^{-2} \text{ and } \overline{Q} = Q_1^{-2} - Q_2^{-2} \qquad (5.4)$$

the rotational KE operator T_{rot} reads as:

$$T_{rot} = \frac{\lambda_+^2}{8}\tilde{Q}\tan^2(\theta/2)\,\sigma_+^2 + \frac{\lambda_-^2}{8}\tilde{Q}\tan^2(\theta/2)\,\sigma_-^2 \qquad (5.5)$$

$$+ \frac{\lambda_+}{2\sin\theta}\overline{Q}\left\{S\frac{\tilde{Q}}{\overline{Q}} + \frac{\cos\theta}{2}\right\}\sigma_+ + \frac{\lambda_-}{2\sin\theta}\overline{Q}\left\{S\frac{\tilde{Q}}{\overline{Q}} - \frac{\cos\theta}{2}\right\}\sigma_-$$

The internal–external coupling terms are:

$$T^{\circ}_c = \frac{\lambda_+}{2}\overline{Q}\frac{\partial}{\partial\theta}\sigma_+ - \frac{\lambda_-}{2}\overline{Q}\frac{\partial}{\partial\theta}\sigma_- \qquad (5.6)$$

As an illustration, consider the transformation into polar coordinates, with $Q_1 = \rho\cos\alpha$ and $Q_2 = \rho\sin\alpha$, $T^{\circ}_{int} + V_c$ becomes:

$$T^{\circ}_{int} + V_c =$$

$$-\frac{\partial^2}{\partial\rho^2} - \frac{5}{\rho}\frac{\partial}{\partial\rho}$$

$$-\frac{1}{\rho^2}\left[\frac{\partial^2}{\partial\alpha^2} - 4\cot(2\alpha)\frac{\partial}{\partial\alpha} + \frac{L(L+1)-S^2}{2}\csc^2(2\alpha)\right]$$

$$-\left[\frac{4\csc^2(2\alpha)}{\rho^2}\right]\left\{\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} - S^2\frac{\csc^2\theta}{2}\right.$$

$$\left. -\frac{\csc^2\theta}{4}\sin^2(\theta/2)[L(L+1) - 3S^2]\right\} \qquad (5.7)$$

Description of a N–body system (N>3) with the bisector frame.

The part of the KE operator corresponding to the remaining Jacobi vectors $\vec{q}'_k$ (k=3,...,n) is partitioned in the following way.

The coefficients appearing in equation (4.21–23) are given by:

$$M_{11} = \frac{\tilde{Q}}{4\cos^2(\theta/2)} \;;\; M_{22} = \frac{\tilde{Q}}{4} \;;\; M_{33} = \frac{\tilde{Q}}{4\sin^2(\theta/2)}$$

$$M_{12} = 0 \;;\; M_{13} = \frac{\tilde{Q}}{2\sin\theta} \;;\; M_{23} = 0$$

$$C_1 = 0 \;;\; C_2 = -i\overline{Q}\frac{\cot\theta}{2} \;;\; C_3 = 0$$

$$d_1 = 0 \;;\; d_2 = -i\frac{\overline{Q}}{2}\frac{\partial}{\partial\theta} \;;\; d_3 = 0 \qquad (5.8)$$

After substitution in the general expression (4.15), we obtain:

$$T_{ir} =$$

$$\frac{1}{4}\tilde{Q}\left\{\frac{(P'_1)^2}{\cos^2(\theta/2)} + (P'_2)^2 + \frac{(P'_3)^2}{\sin^2(\theta/2)} + 4\frac{P'_1P'_3}{\sin\theta}\right\}$$

$$-\frac{(i)}{2\sin\theta}\left\{\overline{Q}\cos\theta - \tilde{Q}\right\}P'_2 + S\tilde{Q}\left\{\frac{P'_3}{2\sin^2(\theta/2)} + \frac{P'_1}{\sin\theta}\right\} \qquad (5.9)$$

where the P'_α are the cartesian components of angular momentum of the remaining Jacobi vectors with respect to the noninertial bisector frame.

The expression of the P'_α in appropriate internal coordinates (lengths Q_k and a set of independent angles) of the vectors $\vec{q}'_k$ is carried out in section 7 together with the evaluation of T'_{int}.

As expected from the definition of norm independent frames, the coupling term between the internal operators of the fragment and the remaining vectors $\vec{q}'_k$ reduces to:

$$T_{in} = -i\tilde{Q}\frac{\partial}{\partial\theta}P'_2 \qquad (5.10)$$

that is to couplings between the angular coordinate θ and the components of the internal angular momentum.

Finally, the couplings between external rotations and the internal angular momentum are given by:

$$T_{ie} = \frac{\lambda_+}{4}\tilde{Q}\left\{\frac{P'_1}{\cos^2(\theta/2)} + \frac{2}{\sin\theta}P'_3 + iP'_2\right\}\sigma_+ + \frac{\lambda_-}{4}\tilde{Q}\left\{\frac{P'_1}{\cos^2(\theta/2)} + \frac{2}{\sin\theta}P'_3 - iP'_2\right\}\sigma_- \qquad (5.11)$$

Once again, in order to obtain some physical meaning, the operators P'_α have to be expressed in an appropriate set of internal coordinates.

2. Norm Independent E.S. Frame.

This frame is obtained by rotating the bisector frame about $\vec{f}_2$ by $\pi/4$. This corresponds (see appendix I) to the E.S. norm independent frame.

Let $\vec{c}_1$ and $\vec{c}_2$ be the two normalized Jacobi vectors:

$$\vec{c}_i = Q_i^{-1}\vec{q}_i \qquad (5.12)$$

The Gram matrix of the unit vectors $\vec{c}_i$ is:

$$G_{ij} = (\vec{c}_i, \vec{c}_j) = \cos\theta_{ij} \tag{5.13}$$

The E.S. frame $\{\vec{f}_3, \vec{f}_1\}$ of the two vectors $\vec{c}_i$ is given (see appendix 1) by:

$$\begin{aligned} \vec{f}_3 &= [\sqrt{G^{-1}}]_{11}\vec{c}_1 + [\sqrt{G^{-1}}]_{12}\vec{c}_2 \\ \vec{f}_1 &= [\sqrt{G^{-1}}]_{12}\vec{c}_1 + [\sqrt{G^{-1}}]_{22}\vec{c}_2 \end{aligned} \tag{5.14}$$

where $\sqrt{G^{-1}}$ is the unique positive square root of G^{-1}. In terms of the Jacobi vectors,

$$\begin{aligned} \vec{f}_3 &= B_{11}\vec{q}_1 + B_{12}\vec{q}_2 \\ \vec{f}_1 &= B_{12}\vec{q}_1 + B_{22}\vec{q}_2 \end{aligned} \tag{5.15}$$

The cartesian coordinates $y^{i\alpha}$ with respect to this frame obey:

$$y^{11}y^{21} - y^{13}y^{23} = 0 \tag{5.16}$$

and the parameter $\zeta = \theta/2 - \pi/4$

In terms of the BRI, the cartesian components are expressed by:

$$\begin{aligned} y^{13} &= Q_1 a_+ \quad ; \quad y^{11} = Q_1 a_- \\ y^{23} &= Q_2 a_- \quad ; \quad y^{21} = Q_2 a_+ \end{aligned} \tag{5.17}$$

where

$$a_\pm = \frac{\sqrt{2}}{2}\sqrt{(1 \pm \sin\theta)} \tag{5.18}$$

The part of internal KE operator related to the three body fragment becomes:

$$\begin{aligned} T^{o}_{int} + V_c = & \\ & -\frac{\partial^2}{\partial Q_1^{\,2}} - \frac{2}{Q_1}\frac{\partial}{\partial Q_1} + \frac{1}{8Q_1^{\,2}}[L(L+1) - S^2] \\ & -\frac{\partial^2}{\partial Q_2^{\,2}} - \frac{2}{Q_2}\frac{\partial}{\partial Q_2} + \frac{1}{8Q_2^{\,2}}[L(L+1) - S^2] \\ & -\tilde{Q}\left\{\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} - \frac{\csc^2\theta}{4}[L(L+1) + S^2]\right\} \\ & +\frac{\overline{Q}}{4\sin\theta}[L(L+1) - 3S^2] \end{aligned} \tag{5.19}$$

$$y^{11} = y^{23} \tag{6.1}$$

With this condition, the matrix B and its inverse Y are both symmetric hence Y is the positive square root of the Gram matrix G. The analytic evaluation of $G^{1/2}$ is carried out in appendix I; the result is:

$$y^{13} = \frac{Q_1(Q_1+Q_2\sin\theta)}{\Delta_+^{1/2}} \qquad y^{11} = \frac{Q_1Q_2\cos\theta}{\Delta_+^{1/2}}$$
$$y^{21} = \frac{Q_2(Q_2+Q_1\sin\theta)}{\Delta_+^{1/2}} \qquad y^{23} = \frac{Q_1Q_2\cos\theta}{\Delta_+^{1/2}} \tag{6.2}$$

where $\Delta_+ = Q_1^2 + Q_2^2 + 2Q_1Q_2\sin\theta$. The angle ζ is given by:

$$\cos\zeta = \frac{(Q_1+Q_2\sin\theta)}{\Delta_+^{1/2}} \qquad \sin\zeta = -\frac{Q_2\cos\theta}{\Delta_+^{1/2}} \tag{6.3}$$

$$\frac{\partial\zeta}{\partial Q_1} = \frac{Q_2\cos\theta}{\Delta_+}\,;\ \frac{\partial\zeta}{\partial Q_2} = -\frac{Q_1\cos\theta}{\Delta_+}\,;\ \frac{\partial\zeta}{\partial\theta} = \frac{Q_2(Q_2+Q_1\sin\theta)}{\Delta_+} \tag{6.4}$$

The coefficients $M_{\alpha\beta}$, C_2 and the operator d_2 are:

$$M_{11} = \frac{1}{Q_1^2\sin^2\theta} \qquad M_{22} = \frac{2Q_2^2}{Q_1^2\Delta_+} \qquad M_{33} = \frac{1}{Q_2^2\sin^2\theta}$$
$$M_{13} = \frac{\cos\theta\Delta_+}{Q_1Q_2\sin^2\theta}$$
$$d_2 = i\frac{1}{\Delta_+}\left\{\cos\theta(Q_2\frac{\partial}{\partial Q_1} - Q_1\frac{\partial}{\partial Q_2}) + \sin\theta(\frac{Q_1}{Q_2} - \frac{Q_2}{Q_1})\frac{\partial}{\partial\theta}\right\}$$
$$C_2 = 4i\frac{\cos\theta}{\Delta_+}\left[\frac{Q_1^2 - Q_2^2}{Q_1Q_2}\right] \tag{6.5}$$

The centrifugal potential V_c is nonseparable:

$$V_c(Q_1,Q_2,\theta) = \frac{1}{Q_1^2\sin^2\theta}\left[\frac{L(L+1)-S^2}{2}\right] + \frac{S^2}{Q_2^2\sin^2\theta} + \frac{Q_2^2}{Q_1^2\Delta_+}[L(L+1)-S^2] \tag{6.6}$$

It is interesting to compare with the centrifugal potential for the

norm–independent E.S.frame:

$$V_c(Q_1,Q_2,\theta) = V_c(Q_1) + V_c(Q_2) + V_c(\theta) + V_c^{ns} \tag{6.7}$$

where:

$$V_c(Q_i) = \frac{1}{Q_i{}^2}[L(L+1)-S^2]$$

$$V_c(\theta) = \tilde{Q}\,\frac{\csc^2\theta}{4}\,[L(L+1)+S^2]$$

$$V_c^{ns} = \frac{\overline{Q}}{4\sin\theta}\,[L(L+1)-3S^2] \tag{6.8}$$

Partial separability is possible in this case because the frame is constructed independently of the lengths of the Q_i.

To the limited extent that we are concerned with separability of V_c, BRI coordinates are not ideal. Polar coordinates ρ and α defined by $Q_1 = \rho\cos\alpha$; $Q_2 = \rho\sin\alpha$ fail to achieve complete separability but do permit the hyperadius to be factorized:

$$V_c(\rho,\alpha,\theta) = \frac{1}{\rho^2}\left\{4\,\frac{[L(L+1)-2S^2]\sin^2\alpha+S^2}{\sin^2 2\alpha\sin\theta} + \frac{\cot^2\alpha[L(L+1)-S^2]}{1+\sin 2\alpha\sin\theta}\right\} \tag{6.9}$$

To achieve greater separability, new coordinates obtained by "mixing" the three BRI coordinates would have to be constructed.

2.I.P.A.I Frame.

The condition imposed on the cartesian components is:

$$\mathscr{M}_{13} = y^{13}y^{11} + y^{23}y^{21} = 0 \tag{6.10}$$

that is, the mass quadrupole is diagonal.

The traditional parameterization[6] of the internal coordinates $y^{i\alpha}$ (together with the constraint (6.10)) is λ_1, λ_3, ϕ where λ_α are the two common eigenvalues of $\mathscr{M}$ and G (see appendix II) whereas ϕ is the

parameter of the (label) orthogonal transformation $\mathscr{R}$ diagonalizing G (the Gram matrix represents an operator acting in label space). Otherwise stated, $\mathscr{R}$ rotates the label basis representing the Jacobi vectors into a new basis representing a new set of Jacobi vectors and we are no longer dealing with a fixed representation of the system. Of course, the vortex momentum P_2° is not zero in this case. Alternatively, the choice of the BRI coordinates of a fixed set of Jacobi vectors leads to a zero vortex momentum. In order to obtain an expression for the KE operator in terms of the BRI, the KE operator may be first expressed in terms of the "label internal coordinates" λ_α and ϕ and subsequently re–expressed in terms of the BRI. This procedure is cumbersome and does not take advantage of the invariance of T_{int}° with respect to a change of frame. All that is needed to do so is to evaluate the coefficients $M_{\alpha\beta}$, C_2 and d_2 in BRI coordinates.

The cartesian coordinates $y^{i\alpha}$ are given in terms of the "label internal coordinates" by:

$$\begin{aligned} y^{13} &= \mu_3 \cos\phi \;\; ; \;\; y^{11} = -\mu_1 \sin\phi \\ y^{23} &= \mu_3 \sin\phi \;\; ; \;\; y^{21} = \mu_1 \cos\phi \end{aligned} \tag{6.11}$$

where $\mu_\alpha = \sqrt{\lambda_\alpha}$.

In this frame, the vortex momentum operators are given by:

$$P_1^\circ = 0 \;\; ; \;\; P_2^\circ = 2i\left[\frac{\mu_1^2 + \mu_3^2}{\mu_1 \mu_3}\right] \frac{\partial}{\partial\phi} \;\; ; \;\; P_3^\circ = 0 \tag{6.12}$$

and the coefficients are:

$$M_{11} = \frac{1}{\lambda_3} \;\; ; \;\; M_{22} = \frac{\lambda_1 + \lambda_3}{(\lambda_3 - \lambda_1)^2} \;\; ; \;\; M_{33} = \frac{1}{\lambda_1}$$

$$M_{12} = M_{13} = M_{23} = 0$$

$$C_1 = C_2 = C_3 = 0$$

$$d_1 = 0 \;\; ; \;\; d_2 = 2i\frac{1}{\mu_1\mu_3}\frac{\partial}{\partial\phi} \;\; ; \; d_3 = 0 \qquad (6.13)$$

The transformation of the label internal coordinates into BRI is carried out in appendix II. The results are as follows:

$$\lambda_3 = \tfrac{1}{2}[\rho^2 + (\rho^4 - \sigma^2)^{1/2}] \; ; \;\; \lambda_1 = \tfrac{1}{2}[\rho^2 - (\rho^4 - \sigma^2)^{1/2}]$$

$$\cos\phi = \left[\frac{Q_1^2 - \lambda_3}{\lambda_1 - \lambda_3}\right]^{1/2} \quad ; \quad \sin\phi = \left[\frac{Q_2^2 - \lambda_3}{\lambda_1 - \lambda_3}\right]^{1/2} \qquad (6.14)$$

where $\rho^2 = Q_1^2 + Q_2^2$ and $\sigma = 2Q_1Q_2\sin\theta$. The inverse transformation is:

$$Q_1 = (\lambda_1 - \lambda_3)\sin^2\phi + \lambda_3 \;\; ; Q_2 = (\lambda_3 - \lambda_1)\sin^2\phi + \lambda_1$$

$$\cos\theta = \frac{\lambda_3 - \lambda_1}{2Q_1Q_2}\sin(2\phi) \qquad (6.15)$$

The coefficients become:

$$M_{11} = \frac{2}{\rho^2 + \sqrt{(\rho^4 - \sigma^2)}}; \;\; M_{22} = \frac{\rho^2}{\rho^4 - \sigma^2} \; ; \;\; M_{33} = \frac{2}{\rho^2 - \sqrt{(\rho^4 - \sigma^2)}}$$

$$M_{12} = M_{13} = M_{23} = 0$$

$$C_1 = C_2 = C_3 = 0$$

$$d_1 = d_3 = 0$$

$$d_2 = -2i[\cot\theta(\frac{\partial}{\partial Q_1} - \frac{\partial}{\partial Q_2}) - \frac{\sqrt{(Q_1^4 + Q_2^4)}}{Q_1Q_2}\frac{\partial}{\partial\theta}] \qquad (6.16)$$

Expression of the KE operator in label internal coordinates.

$$T^{\circ}_{int} = -\frac{\partial^2}{\partial{\mu_1}^2} - \frac{1}{\mu_1}\left[\frac{3\lambda_1 - \lambda_3}{\lambda_1 - \lambda_3}\right]\frac{\partial}{\partial\mu_1}$$

$$-\frac{\partial^2}{\partial{\mu_3}^2} - \frac{1}{\mu_3}\left[\frac{3\lambda_3 - \lambda_1}{\lambda_3 - \lambda_1}\right]\frac{\partial}{\partial\mu_3}$$

$$-4\frac{(\lambda_1 + \lambda_3)^3}{\lambda_1\lambda_3(\lambda_1 - \lambda_3)^2}\frac{\partial^2}{\partial\phi^2} \qquad (6.17)$$

$$V_c = \frac{1}{2}\left[\frac{1}{\lambda_3} + \frac{\lambda_1+\lambda_3}{(\lambda_3-\lambda_1)^2}\right][L(L+1) - S^2] + \frac{1}{\lambda_1} S^2 \tag{6.18}$$

$$T_{rot} = \frac{\ell_+^2}{4}\left[\frac{1}{\lambda_3} - \frac{\lambda_1+\lambda_3}{(\lambda_3-\lambda_1)^2}\right]\sigma_+^2 + \frac{\ell_-^2}{4}\left[\frac{1}{\lambda_3} - \frac{\lambda_1+\lambda_3}{(\lambda_3-\lambda_1)^2}\right]\sigma_-^2 \tag{6.19}$$

$$T_c^{\circ} = -4\ell_+ \frac{\lambda_1+\lambda_3}{(\lambda_3-\lambda_1)^2}\frac{\partial}{\partial\phi}\sigma_+ + 4\ell_- \frac{\lambda_1+\lambda_3}{(\lambda_3-\lambda_1)^2}\frac{\partial}{\partial\phi}\sigma_- \tag{6.20}$$

$$T'_{int} + T_{ir} = \sum_{i',\alpha} (\pi_{i'\alpha})^2 + \Sigma_\gamma M_{\gamma\gamma}(P'_\gamma)^2 + \frac{2S}{\lambda_1} P'_3 \tag{6.21}$$

$$T_{ic} = \frac{8\ell}{\mu_1\mu_3}\frac{\lambda_1^2 - \lambda_3^2}{(\lambda_1-\lambda_3)^2}\frac{\partial}{\partial\phi} P'_2 \tag{6.22}$$

$$T'_c = \ell_+(M_{11}P'_1 + iM_{22}P'_2)\sigma_+ + \ell_-(M_{11}P'_1 - iM_{22}P'_2)\sigma_- \tag{6.23}$$

KE operator in standard hyperspherical coordinates

The coordinate transformation into standard hyperspherical coordinates is achieved by setting:

$$\mu_1 = \rho\cos\varphi;\ \mu_3 = \rho\sin\varphi \tag{6.24}$$

$$T_{int}^{\circ} =$$

$$-\frac{\partial^2}{\partial\rho^2} - \frac{5}{\rho}\frac{\partial}{\partial\rho}$$

$$-\frac{1}{\rho^2}\left[\frac{\partial^2}{\partial\varphi^2} + 4\cot(4\varphi)\frac{\partial}{\partial\varphi}\right]$$

$$- \frac{64}{\rho^2} \cot^2(4\varphi) \frac{\partial^2}{\partial \phi^2} \tag{6.25}$$

$$V_c = \frac{1}{2\rho^2} \left[\frac{L(L+1)}{\sin^2\varphi} + \frac{1}{\cos^2(2\varphi)} [L(L+1) - S^2] - 4S^2 \cot(2\varphi) \right] \tag{6.26}$$

$$T_{rot} = \frac{\ell_+^2}{4\rho^2} \left[\frac{\cos^2(2\varphi) - \sin^2\varphi}{\sin^2\varphi \cos^2(2\varphi)} \right] \sigma_+^2 + \frac{\ell_-^2}{4\rho^2} \left[\frac{\cos^2(2\varphi) - \sin^2\varphi}{\sin^2\varphi \cos^2(2\varphi)} \right] \sigma_-^2 \tag{6.27}$$

$$T_c^\circ = - \frac{4\ell_+}{\rho^2 \cos^2(2\varphi)} \frac{\partial}{\partial \phi} \sigma_+ + \frac{4\ell_-}{\rho^2 \cos^2(2\varphi)} \frac{\partial}{\partial \phi} \sigma_- \tag{6.28}$$

$$T'_{int} + T_{ir} = \sum_{i',\alpha} (\pi_{i'\alpha})^2 + \frac{1}{\rho^2} \left[\frac{(P'_1)^2}{\sin^2\varphi} + \frac{(P'_2)^2}{\cos^2(2\varphi)} + \frac{(P'_3)^2}{\cos^2\varphi} + \frac{2SP'_3}{\cos^2\varphi} \right] \tag{6.29}$$

$$T_{ic} = \frac{32\ell \csc(4\varphi)}{\rho^2} \frac{\partial}{\partial \phi} P'_2 \tag{6.30}$$

$$T'_c = \frac{\ell_+}{\rho^2} \left[\frac{P'_1}{\sin^2\varphi} + i \frac{P'_2}{\cos^2(2\varphi)} \right] \sigma_+ + \frac{\ell_-}{\rho^2} \left[\frac{P'_1}{\sin^2\varphi} - i \frac{P'_2}{\cos^2(2\varphi)} \right] \sigma_- \tag{6.31}$$

KE operator in BRI.

The KE operator in BRI coordinates is obtained once more from equations (4.12–19) by substituting the expressions for the coefficients $M_{\alpha\beta}$, C_2 and d_2 given by (6.16), the momenta P'_α being treated as above.

Up to this point, there is no significant advantage (apart from the symmetry in the coupling terms) in choosing one or another frame on a simple mathematical basis. The rotational ground state (S=0;L=0) of three bodies is described by the same KE operator irrespective of the choice of the noninertial 2GJV frame. This is not the case for N–body systems as illustrated in the next section. Selection of one or another frame appears to require additional physical input.

7. Application to Molecules of the Type $(AB_2)X$.

The purpose of this section is to illustrate the previous theory by means of the example of molecules of the type $(AB_2)X$. The contribution of the "additional" vector $\vec{q}_3$ to the total KE operator (S=0,L=0) is represented by the terms T_{int}, T_{ir} and T_{ic}. Some explicit realizations by means of curvilinear internal coordinates are presented below. Two kinds of frames are considered reflecting the nature of the constituent particles. For $m_X \leq m_{AB_2}$ (NO_2Cl), it is appropriate to choose the axis of quantization ($\vec{f}_3$) in the plane AB_2: the non–inertial frame is of the type (2GJV) and the Jacobi vector associated with the bond AX rotates internally about the axis of quantization. For molecules where $m_X > m_{AB_2}$ ($H_2C{=}O$), the situation is better represented by an axis of quantization along the Jacobi vector describing the bond AX; the axis $\vec{f}_1$ can be constructed for example by Gram–Schmidt with $\vec{F} = \alpha\vec{q}_1 + \beta\vec{q}_2$ (α and $\beta \neq 0$, the frame is global, otherwise, the frame is local). The final expression is more or less complicated depending on the choice of the frame and the curvilinear internal coordinates describing $\vec{q}_3$. Whereas

T'_{int} is independent of the choice of the frame, T_{ir} depends on the choice of the frame since, in the expressions of the components of the internal angular momentum, the parameter ζ defining the frame appears explicitly. This result has been demonstrated rigorously in reference 1, appendix II: whereas the P'_α are invariant under a rotation about the axis of quantization, this invariance is not maintained for a general rotation and in particular for a rotation in the plane of the Jacobi vectors constituting the frame (change of frame). As a result, the overall (S=0,L=0) KE operator depends on the choice of the non–inertial frame.

BRI Coordinates for $\vec{q}_3$.

Let the system be described as in Figure I. θ_{13} and θ_{23} are the angles between $\vec{q}_3$ and $\vec{q}_1$, $\vec{q}_2$ respectively. ζ_α are the angles between $\vec{q}_3$ and the axes of the frame $\{\vec{f}_\alpha\}$; they obey the direction cosine relationships:

$$\begin{aligned} \Sigma_\alpha \cos^2\zeta_\alpha &= 1 \\ \Sigma_\alpha \cos\zeta_\alpha \cos\zeta_{i\alpha} &= \cos\theta_{i3} \quad (i=1,2) \end{aligned} \tag{7.1}$$

With the conventions of equation (3.8), the last relations become:

$$\begin{aligned} \cos\zeta_1 \sin\zeta + \cos\zeta_3 \cos\zeta &= \cos\theta_{13} \\ \cos\zeta_1 \sin\zeta' + \cos\zeta_3 \cos\zeta' &= \cos\theta_{23} \end{aligned} \tag{7.2}$$

This system is easily solved and the parameters ζ_α are expressed in terms of θ_{i3} and θ:

$$\begin{aligned} \cos\zeta_1 &= \frac{\cos\theta_{13}\cos\zeta' - \cos\theta_{23}\cos\zeta}{\sin\theta} \\ \cos\zeta_3 &= \frac{\cos\theta_{23}\sin\zeta - \cos\theta_{13}\sin\zeta'}{\sin\theta} \end{aligned} \tag{7.3}$$

$$\cos\zeta_2 = \pm \frac{V}{\sin\theta}$$

where V is the volume of the paralelipiped constructed with the three unit vectors along the three Jacobi vectors:

$$V = [1 - \cos^2\theta - \cos^2\theta_{13} - \cos^2\theta_{23} + 2\cos\theta\cos\theta_{13}\cos\theta_{23}]^{1/2} \quad (7.4)$$

The cartesian components are:

$$y^{3\alpha} = Q_3\cos\zeta_\alpha \quad (7.5)$$

From (4.29), the linear momenta are:

$$\pi_{3\alpha} = -i \left[\cos\zeta_\alpha \frac{\partial}{\partial Q_3} - \frac{\Gamma^\alpha_{13}}{Q_3}\frac{\partial}{\partial\theta_{13}} - \frac{\Gamma^\alpha_{23}}{Q_3}\frac{\partial}{\partial\theta_{23}} \right] \quad (7.6)$$

where

$$\Gamma^\alpha_{i3} = \frac{\cos\zeta_{i\alpha} - \cos\zeta_\alpha\cos\theta_{i3}}{\sin\theta_{i3}} \quad (i=1,2) \quad (7.7)$$

By squaring (6.5), adding over α and making use of the relations (6.1), the expression for T'_{int} reads as:

$$T'_{int} =$$
$$-\left\{ \frac{\partial^2}{\partial Q_3^2} + \frac{2}{Q_3}\frac{\partial}{\partial Q_3} \right.$$
$$+ \frac{1}{Q_3^2}\left[\frac{\partial^2}{\partial\theta_{13}^2} + \cot\theta_{13}\frac{\partial}{\partial\theta_{13}} + \frac{\partial^2}{\partial\theta_{23}^2} + \cot\theta_{23}\frac{\partial}{\partial\theta_{23}} \right]$$
$$\left. + \frac{2}{Q_3^2}\cos A_3 \frac{\partial^2}{\partial\theta_{13}\partial\theta_{23}} \right\} \quad (7.8)$$

where A_3 is the spherical angle corresponding to $\vec{q}_3$[10]:

$$\cos A_3 = \frac{\cos\theta - \cos\theta_{13}\cos\theta_{23}}{\sin\theta_{13}\sin\theta_{23}} \quad (7.9)$$

The internal angular momentum components P'_α are evaluated from the expression (4.2):

$$P'_\alpha = -i[\, y^{3\beta}\pi_{3\gamma} - y^{3\gamma}\pi_{3\beta}\,] \quad (7.10)$$

where α,β,γ are cyclic permutations of 1,2,3 as usual. By substitution of (6.5) and (6.6) into (7.10), we obtain the cartesian components of the internal angular momentum expressed in terms of the momenta conjugate to the coordinates θ_{13} and θ_{23} (they obviously are independent of the radial linear momentum $\frac{\partial}{\partial Q_3}$). The result is given in a general form by:

$$P'_\alpha = -i \left[\frac{X_\alpha}{\sin\theta_{13}} \frac{\partial}{\partial\theta_{13}} + \frac{X'_\alpha}{\sin\theta_{23}} \frac{\partial}{\partial\theta_{23}} \right] \qquad (7.11)$$

where the coefficients X_α and X'_α (dependent on the choice of the non inertial frame) are given by:

$$\begin{aligned} X_\alpha &= (\cos\zeta_\gamma \cos\zeta_{1\beta} - \cos\zeta_\beta \cos\zeta_{1\gamma}) \\ X'_\alpha &= (\cos\zeta_\gamma \cos\zeta_{2\beta} - \cos\zeta_\beta \cos\zeta_{2\gamma}) \end{aligned} \qquad (7.12)$$

With the conventions of equations (3.8), these coefficients are expressed explicitly in terms of the parameter ζ defining the frame:

$$\begin{aligned} X_1 &= -\cos\zeta_{32}\cos\zeta \;\; ; \;\; X'_1 = -\cos\zeta_{32}\cos\zeta' \\ X_3 &= -\cos\zeta_{32}\sin\zeta \;\; ; \;\; X'_3 = -\cos\zeta_{32}\sin\zeta' \\ X_2 &= \cos\zeta_{33}\sin\zeta + \cos\zeta_{31}\cos\zeta \\ X'_2 &= \cos\zeta_{33}\sin\zeta' + \cos\zeta_{31}\cos\zeta' \end{aligned} \qquad (7.13)$$

The components of the internal angular momentum can now be introduced into equations (4.14,15) to provide an explicit expression of T_{ir} (S=0) and T_{ic}.

The general expression for T_{ir} is

$$T_{ir} = -\left[A_{11} \frac{\partial^2}{\partial\theta_{13}^2} + A_{22} \frac{\partial^2}{\partial\theta_{23}^2} + A_{12} \frac{\partial^2}{\partial\theta_{13}\partial\theta_{23}} + B_1 \frac{\partial}{\partial\theta_{13}} + B_2 \frac{\partial}{\partial\theta_{23}} \right] \qquad (7.14)$$

where the coefficients (Appendix III) are functions of θ_{13}, θ_{23} and ζ hence implicitly functions of Q_1, Q_2 and θ through ζ.

T_{ic} is obtained in a similar manner:

$$T_{ic} = 2d_2 P'_2 \tag{7.15}$$

where P'_2 is given by (7.11) with $\alpha = 2$ and d_2 has been defined in equation (4.22).

For most of the frames of interest, the coordinates θ_{i3} and θ are coupled ($A_{12} \neq 0$ in 7.14) whereas there are no coupling terms between the radial coordinates Q_i. The configuration metric tensor is partitioned into two diagonal blocks: G_r and G_a representing respectively the radial and the angular subtensors.

$$G = \begin{bmatrix} G_r & 0 \\ 0 & G_a \end{bmatrix} \tag{7.16}$$

G_a has the form[7]:

$$G_a = \begin{bmatrix} g_\theta & c_1 & c_2 \\ c_1 & g_{13} & 0 \\ c_2 & 0 & g_{23} \end{bmatrix} \tag{7.17}$$

This expresses the orthogonality of the coordinates θ_{13} and θ_{23} and the non orthogonality of θ with θ_{i3}. In the dual space (i.e., appropriate to the momenta), the metric tensor is G_a^{-1} in which the orthogonality is broken. One can show[7] that, in keeping θ as an internal coordinate, whatever the orthogonal curvilinear transformation of the angles θ_{i3} is, there are no zero terms in G_a^{-1}. In other words, any set of angular coordinates for $\vec{q}_3$ leads to couplings between them and couplings with the coordinate θ in the KE operator.

This is illustrated below with the spherical coordinates of $\vec{q}_3$: the

azimuthal and polar angles, as pointed out in section 4, are orthogonal but θ' and ϕ are not orthogonal to the angle θ between the vectors constituting the frame.

Spherical Coordinates for $\vec{q}_3$.

The azimuthal and polar angles ϕ and θ' represent another parameterization of the angles ζ_α. If the internal rotation is about $\vec{f}_2$, the angle ϕ is independent of the choice of the frame. If the internal rotation is about the axis of quantization, ϕ does depend on the frame. In either case, θ' is frame dependent.

Consider $\vec{q}_3$ rotating about $\vec{f}_2$ and θ' the polar angle in the plane of the frame. By squaring the linear momenta given in equation (4.32) and adding over α, the operator T'_{int} becomes:

$$T'_{int} = - \frac{\partial^2}{\partial Q_3^2} - \frac{2}{Q_3}\frac{\partial}{\partial Q_3} - \frac{1}{Q_3^{\,2}}\left[\frac{\partial^2}{\partial \phi^2} + \cot\phi \frac{\partial}{\partial \phi}\right] - \frac{1}{Q_3^2 \sin^2\phi}\frac{\partial^2}{\partial \theta'^2} \qquad (7.18)$$

Similarly, the expression for T_{ir} (S=0) is obtained from the angular momenta given in equation (4.33). The result is:

$$T_{ir} = -\left[A_{11}\frac{\partial^2}{\partial \theta'^2} + A_{22}\frac{\partial^2}{\partial \phi^2} + A_{12}\frac{\partial^2}{\partial \phi \partial \theta'} + B_1\frac{\partial}{\partial \theta'} + B_2\frac{\partial}{\partial \phi}\right] \qquad (7.19)$$

where

$$A_{11} = M_{22} + \cot^2\phi\ [\ M_{11}\cos^2\theta' + M_{33}\sin^2\theta' + 2M_{13}\sin2\theta']$$
$$A_{22} = M_{11}\sin^2\theta' + M_{33}\cos^2\theta' - 2M_{13}\sin2\theta'$$
$$A_{12} = 2\cot\phi[\sin2\theta'(M_{11} - M_{33}) - 2M_{13}\cos2\theta'] \qquad (7.20)$$
$$B_1 = \frac{\cos^2\phi+1}{2\sin^2\phi}\ [4M_{13}\cos2\theta' - \sin2\theta'(M_{11} - M_{33})] - iC_2$$
$$B_2 = \cot\phi[M_{11}\cos^2\theta' + M_{33}\sin^2\theta' + 2M_{13}\sin2\theta']$$

The coupling terms between the internal coordinates $\{Q_1,Q_2,\theta\}$ and the internal coordinates for $\vec{q}_3$ are given by $T_{ic} = -2d_2P_2'$. For norm independent frames, there is a single coupling $(\theta\text{–}\theta')$ whereas θ' is coupled to Q_1, Q_2 and θ for norm dependent frames. The existence of the extra terms in $(Q_1,Q_2\text{–}\theta')$ can be understood by considering the total configuration metric tensor:

$$\mathbf{G} = \begin{bmatrix} G_r & 0 & X \\ 0 & G_a & Y \\ X^t & Y^t & G_e \end{bmatrix} \qquad (7.21)$$

where G_e is the metric for the external rotations. For norm independent frames, $X \equiv 0$ but there exist non zero terms for norm dependent frames.

8. Summary and Conclusion.

A kinetic energy operator for N–body systems has been derived using a rotating frame (non–inertial frame) tied to the configuration of three non–collinear particles represented by two Jacobi vectors $\vec{q}_1$ and $\vec{q}_2$. This model is particularly suited for the discussion of three body and

$(AB_2)X$ systems where X may represent a single particle or a group of particles treated as a whole. In such a situation, the system is partitioned into two fragments:

(1) the defining fragment (D–fragment) comprised of the Jacobi vectors $\vec{q}_1$ and $\vec{q}_2$ and whose rotations with respect to the inertial frame are generated by the "external angular momentum" $\vec{L}$

(2) the internal fragment (I–fragment) comprised of the remaining vectors $\vec{q}_k$ (k=3,...,N–1) and whose rotations with respect to the non–inertial frame are generated by the "internal angular momentum" $\vec{P}'$.

The internal coordinates are the Basic Rotational Invariant coordinates of the Jacobi vectors that is:

(1) the three curvilinear coordinates Q_1, Q_2 and θ parameterizing the cartesian coordinates of the D–fragment with respect to the rotating frame and accounting for the three relationships defining the frame

(2) the N–3 lengths of the Jacobi vectors of the I–fragment and 2N–6 independent angles parameterizing the angles θ_{ij} other than θ.

The rotational motion is integrated out leading to an operator T_{rot} (equation 4.17) expressed in terms of the rotational quantum numbers, the step–up/down operators $\sigma_{\pm}$ mixing the vibrational states of the D–fragment alone and rotational invariant coefficients specifying the frame. As well, the coupling terms T_c° and T_c' between the (integrated) external and the vibrational motions are expressed in terms of the operators $\sigma_{\pm}$ and the linear momenta related to the two fragments (equations 4.18 and 4.19 respectively). In the former case, the internal operator d_2 (equation 4.23) is coupled with $\sigma_{\pm}$. For frames defined independently of the lengths Q_1 and Q_2, the term d_2 reduces to a single

term in the angular coordinate θ. In the general case, couplings occur between the external rotations and the radial parts as well. The same operator d_2 is coupled with the internal angular momentum P_2' (equation 4.16) describing the fashion in which the motion of the two fragments is determined by definition of the frame. The pure internal energy corresponding to the I–fragment is expressed by relations (4.14–15). These terms are explicitly expressed once a proper parameterization of the angles has been defined. In no case is there coupling between angular and the radial parts of the I–fragment. Nevertheless one should notice that for norm dependent frames, the angular motion of the I–fragment is coupled with the radial part of the D–fragment. The pure internal operator T°_{int} of the D–fragment is independent of the choice of frame (equation 4.12). Finally, the redistribution of the rotational energy (centrifugal potential V_c) among the internal oscillators related to Q_1, Q_2 and θ (given by equation 4.13) is not separable in general (except for the bisector frame) and must be appended to the non–separable part of the source potential.

It is not the purpose of this work to discuss the respective merits of one frame with respect to another for a given problem. Such a discussion requires more physical input. It is nevertheless worth mentioning the recovery of symmetry by using the frames descibed above comparatively to the CHA frame although introducing extra coupling terms. In particular, the use of norm dependent 2GJV frames (for example I.P.A.I) for the description of N–body systems generates couplings between the angular variables of the I–fragment and the radial variables of the D–fragment. The bisector frame appears as a valuable alternative to the I.P.A.I. (as such couplings do not exist) and to the CHA frame (as the

symmetry is recovered).

APPENDIX I.

ORTHONORMALIZATIONS IN E_3

Let $(\vec{F}_1,\vec{F}_2,\vec{F}_3)$ be a set of three vectors in E_3. With respect to an orthonormal frame $\{\vec{\ell}_\alpha\}$, their components are $F^{i\alpha} = (\vec{F}_i,\vec{\ell}_\alpha)$. The Gram matrix elements $G(F)_{ij}$ are given by:

$$G(F)_{ij} = (\vec{F}_i,\vec{F}_j) = \Sigma_\alpha F^{i\alpha}F^{j\alpha} = F_iF_j\cos\Psi_{ij} \qquad (AI.1)$$

We seek linear transformations O in E_3 such that:

$$OG(F)O^t = I_3 \qquad (AI.2)$$

(1) Eigenvectors of G(F)

Since G(F) is a real, symmetric, positive definite matrix, it can be diagonalized by a real, proper, orthogonal matrix R:

$$R_eG(F)R_e^t = \Lambda = \mathrm{diag}(\lambda_1,\lambda_2,\lambda_3) \qquad (AI.3)$$

One orthonormalizing procedure is obtained by pre– and postmultiplying (AI.3) by $\Lambda^{-1/2}$:

$$O_e = \Lambda^{-1/2}R_e \qquad (AI.4)$$

The set of three vectors:

$$\vec{e}_\alpha = \Sigma_\sigma[O_e]_{\alpha\sigma}\vec{F}_\sigma = \lambda_\alpha^{-1/2}[\Sigma_\sigma(R_e)_{\alpha\sigma}\vec{F}_\sigma] \ ; \ (\alpha=1,2,3) \qquad (AI.5)$$

is orthonormal and is referred as the "G(F)–eigenvectors frame".

R_e is the orthogonal matrix transforming the inertial frame $\{\vec{\ell}_\alpha\}$ into the new frame $\{\vec{e}_\alpha\}$: $(R_e)_{\alpha\beta} = (\vec{\ell}_a,\vec{e}_\beta)$.

The components $Y_e^{\sigma\alpha}$ of $\vec{F}_\sigma$ with respect to the frame $\{\vec{e}_\alpha\}$ are (dot

$\vec{F}_\sigma$ with $\vec{e}_\alpha$):

$$Y_e^{\sigma\alpha} = \lambda_\alpha^{1/2}(R_e)_{\alpha\sigma} \qquad \text{(AI.6)}$$

In matrix notation (invert equation 5):

$$Y_e = O_e^{-1} = R_e^t \Lambda^{1/2} \qquad \text{(AI.7)}$$

(2) Equivalent Symmetric Orthonormalization.

The E.S. orthonormalization O_s ($O_s = O_s^t$) is the positive square root of $G(F)^{-1}$:

$$O_s = \sqrt{G(F)^{-1}} = R_e^t \Lambda^{-1/2} R_e = R_e^t O_e \qquad \text{(AI.8)}$$

This defines an orthonormal frame $\{\vec{s}_\alpha\}$:

$$\vec{s}_\alpha = \Sigma_\sigma (O_s)_{\alpha\sigma} \vec{F}_\sigma \qquad \text{(AI.9)}$$

The components of $\vec{F}_\sigma$ with respect to this frame are given by:

$$Y_s^{\sigma\alpha} = (\vec{F}_\sigma, \vec{s}_\alpha) = [G(F)^{1/2}]_{\sigma\alpha} \qquad \text{(AI.10)}$$

or in matrix notation:

$$Y_s = G(F)^{1/2} = R_e^t \Lambda^{1/2} R_e = Y_e R_e \qquad \text{(AI.11)}$$

It is interesting to note that the same frame can be obtained by different procedures:

let A and A′ be two different linear combination matrices; there exists a transformation $\mathscr{A}$ such that :

$$A' = \mathscr{A} A$$

The corresponding Gram matrices are

$$G(F) = AG(q)A^t$$

$$G(F') = A'G(q)A'^t$$

$$\rightarrow \quad G(F) = \mathscr{A}^{-1} A' G(q) A'^t (\mathscr{A}^{-1})^t = \mathscr{A}^{-1} G(F') (\mathscr{A}^{-1})^t$$

Let O and O′ be the orthonormalization matrices generating the

same frame {f} from the different sets {F} and {F′}:

$$\rightarrow \quad OG(F)O^t = O'G(F')O'^t = O\mathscr{A}^{-1}G(F')(\mathscr{A}^{-1})^tO^t = I_3$$

$$\rightarrow \quad O' = O\mathscr{A}^{-1} \qquad \text{(a)}$$

Note: two orthonormalization matrices O and O′ of the same set of vectors {F} are related by $O' = \mathscr{R}O$ where $\mathscr{R}$ is orthogonal since $O'G(F)O'^t = \mathscr{R}OG(F)O^t\mathscr{R}^t = \mathscr{R}I_3\mathscr{R}^t = I_3$. O and O′ in equation (a) do not obey this rule since they are not orthonormalizations of the same set of vectors.

APPENDIX II

Gram Matrix and Mass Quadrupole.

With the notation of section 2, let $G = QQ^t$ and $\mathscr{M} = Q^tQ$ be respectively the Gram matrix and the mass quadrupole of a system of n linearly independent vectors $\vec{q}_i$ of the physical space. G is an n×n matrix representing an operator acting in label space and $\mathscr{M}$ acts in physical space. Both matrices are real, symmetric and positive–definite. They both are diagonalizable by real, proper orthogonal matrices respectively in label (ρ) and physical (R) spaces:

$$\rho G\rho^t = \Gamma \qquad R\mathscr{M}R^t = \Lambda \qquad \text{(AII.1)}$$

where $\Gamma = \text{diag}(\gamma_1,...,\gamma_n)$ and $\Lambda = \text{diag}(\lambda_1,\lambda_2,\lambda_3)$. All γ_i and λ_α are non–negative by the properties of the matrices G and $\mathscr{M}$.

The two matrices G and $\mathscr{M}$ have same trace:

$$\text{Tr}(G) = \text{Tr}(QQ^t) = \text{Tr}(Q^tQ) = \text{Tr}(\mathscr{M}) \qquad \text{(AII.2)}$$

Incidently, one has also $\text{Tr}(G^k) = \text{Tr}(\mathscr{M}^k)$ for k integer:

$$Tr(G^k) = Tr(QQ^tQQ^t...QQ^t) = Tr(Q\mathcal{M}^{k-1}Q^t) = Tr(\mathcal{M}^k) \tag{AII.3}$$

Theorem:

The eigenvalues γ_i of G are as follows:

$$\gamma_\alpha = \lambda_\alpha \qquad \text{for } \alpha=1,2,3$$
$$\gamma_\alpha = 0 \qquad \text{for } \alpha>3 \tag{AII.4}$$

⊥ The eigenvalue equation for $\mathcal{M}$ is:

$\mathcal{M}\vec{p}_\alpha = \lambda_\alpha \vec{p}_\alpha$

where $\vec{p}_\alpha$ is the (physical) eigenvector corresponding to λ_α. By premultiplying this relation by Q, we conclude that λ_α is also eigenvalue of G with corresponding eigenvector $Q\vec{p}_\alpha$:

$Q\mathcal{M}\vec{p}_\alpha = \lambda_\alpha Q\vec{p}_\alpha = (QQ^t)Q\vec{p}_\alpha = \lambda_\alpha(Q\vec{p}_\alpha) = G(Q\vec{p}_\alpha)$

By using the trace identity (A.2) and the non–negative property of the eigenvalues γ_i and λ_α, the theorem is proved. ⊥

With respect to the LPF, $\vec{p}_\alpha$ has components $(R_{1\alpha},R_{2\alpha},R_{3\alpha})$. The components of $Q\vec{p}_\alpha$ are then the cartesian components of the vectors $\vec{q}_i$ with respect to the axis $\vec{f}_\alpha$ of the non–inertial frame (Principal axes frame):

$$Q\vec{p}_\alpha = col(y_i^{1\alpha},...,y_i^{n\alpha}) \tag{AII.5}$$

where the subscript i refers to the PAI frame. After normalization and recalling the definition of the eigenvalues λ_α:

$$\lambda_\alpha = \Sigma_k(y_i^{k\alpha})^2 \tag{AII.6}$$

the eigenvalue equation for G is:

$$G\vec{g}_\alpha = \lambda_\alpha \vec{g}_\alpha \tag{AII.7}$$

where the eigenvectors $\vec{g}_\alpha$ are given by:

$$\vec{g}_\alpha = \lambda_\alpha^{-1/2} \Sigma_k y_i^{k\alpha} \vec{c}_k \qquad \text{(AII.8)}$$

with $\vec{c}_k$ being the unit basis vector in label space corresponding to the physical vector $\vec{q}_k$.

Of course the eigenvectors $\vec{g}_\kappa$ (κ>3) corresponding to the zero eigenvalues of G are degenerate and they span an (n–3) dimensional subspace of the label space orthogonal to the 3 dimensional subspace spanned by the $\vec{g}_\alpha$. The eigenvectors $\vec{g}_\kappa$ can be chosen in many different ways to be orthogonal among themselves.

For n =2 or 3, the problem is particularly simple since there are as many $\vec{g}_\alpha$ as $\vec{c}_i$ so that the components of $\vec{g}_\alpha$ with respect to $\vec{c}_i$ are the elements of the rotation matrix ρ:

$$\rho_{i\alpha} = g^{i\alpha} = (\vec{g}_\alpha, \vec{c}_i) \qquad \text{(AII.9)}$$

and ρ can be parameterized by one or three Euler angles Φ_i.

The expression for the principal axes of inertia $\vec{p}_\alpha$ in function of the vectors $\vec{q}_k$ is finally given by:

$$\vec{p}_\alpha = \lambda_\alpha^{-1/2} \Sigma_k g^{k\alpha}(\Phi_i) \vec{q}_k \qquad \text{(AII.10)}$$

or in matrix notation:

$$\mathbf{p} = \Lambda^{-1/2} . \rho . \mathbf{q} \qquad \text{(AII.11)}$$

where $\mathbf{p}$ and $\mathbf{q}$ are column matrices of the vectors $\vec{p}_\alpha$ and $\vec{q}_k$.

For n = 2, the eigenvalues λ_α can be written down analytically by solving the secular determinant $|G - \Lambda| = 0$. With the usual conventions of labeling the moments of inertia, the result is:

$$\begin{aligned} \lambda_3 &= \tfrac{1}{2}[r^2 + (r^4 - \sigma^2)^{1/2}] \\ \lambda_1 &= \tfrac{1}{2}[r^2 - (r^4 - \sigma^2)^{1/2}] \end{aligned} \qquad \text{(AII.12)}$$

where $r^2 = Q_1^2 + Q_2^2$ is the hyperadius and $\sigma = 2Q_1 Q_2 \sin\theta$ is the surface

of the triangle defined by the vectors $\vec{q}_1$ and $\vec{q}_2$. Observe that:

$$\lambda_1 + \lambda_3 = r^2 \text{ and } \lambda_3 - \lambda_1 = (r^4 - \sigma^2)^{1/2} \qquad \text{(AII.13)}$$

Let ρ be parameterized by the label angle Φ. From (AII.1), we have:

$$\sin\Phi = \left[\frac{Q_1^2 - \lambda_3}{\lambda_1 - \lambda_3}\right]^{1/2} \qquad \cos\Phi = \left[\frac{Q_2^2 - \lambda_3}{\lambda_1 - \lambda_3}\right]^{1/2} \qquad \text{(AII.14)}$$

The inversion of (A.13,14) gives expressions of the BRI coordinates Q_1, Q_2 and θ in terms of the "label coordinates" λ_1, λ_3 and Φ:

$$\begin{aligned} Q_1 &= (\lambda_1 - \lambda_3)\sin^2\Phi + \lambda_3 \\ Q_2 &= (\lambda_3 - \lambda_1)\sin^2\Phi + \lambda_1 \\ \cos\theta &= \frac{\lambda_3 - \lambda_1}{2Q_1Q_2}\sin(2\Phi) \end{aligned} \qquad \text{(AII.15)}$$

APPENDIX III

EVALUATION OF T_{IR} FOR A (2GJV) FRAME.

Let

$$P'_\alpha = -i\left[\, a_\alpha \frac{\partial}{\partial\theta_{13}} + b_\alpha \frac{\partial}{\partial\theta_{23}} \,\right]$$

where $a_\alpha = \dfrac{X_\alpha}{\sin\theta_{13}}$ and $b_\alpha = \dfrac{X'_\alpha}{\sin\theta_{23}}$

By squaring and adding over α, one obtains the expression:

$$T_{ir} = -\left[A_{11}\frac{\partial^2}{\partial\theta_{13}^2} + A_{22}\frac{\partial^2}{\partial\theta_{23}^2} + A_{12}\frac{\partial^2}{\partial\theta_{13}\partial\theta_{23}} + B_1\frac{\partial}{\partial\theta_{13}} + B_2\frac{\partial}{\partial\theta_{23}}\right]$$

where

$$A_{11} = \Sigma_\alpha M_{\alpha\alpha} a_\alpha^2 + 2M_{13} a_1 a_3$$

$$A_{22} = \Sigma_\alpha M_{\alpha\alpha} b_\alpha^2 + 2M_{13} b_1 b_3$$

$$A_{12} = 2[\Sigma_\alpha M_{\alpha\alpha} a_\alpha b_\alpha + M_{13}(a_1 b_3 + a_3 b_1)]$$

$$B_1 = a_1 \tau_{13} a_1 + b_1 \tau_{23} a_1 + a_2 \tau_{13} a_2 + b_2 \tau_{23} a_2 + a_3 \tau_{13} a_3 + b_3 \tau_{23} a_3 + a_1 \tau_{13} a_3 + a_3 \tau_{13} a_1 + b_1 \tau_{23} a_3 + b_3 \tau_{23} a_1 + iC_2 a_2$$

$$B_2 = a_1 \tau_{13} b_1 + b_1 \tau_{23} b_1 + a_2 \tau_{13} b_2 + b_2 \tau_{23} b_2 + a_3 \tau_{13} b_3 + b_3 \tau_{23} b_3 + a_1 \tau_{13} b_3 + a_3 \tau_{13} b_1 + b_1 \tau_{23} b_3 + b_3 \tau_{23} b_1 + iC_2 b_2$$

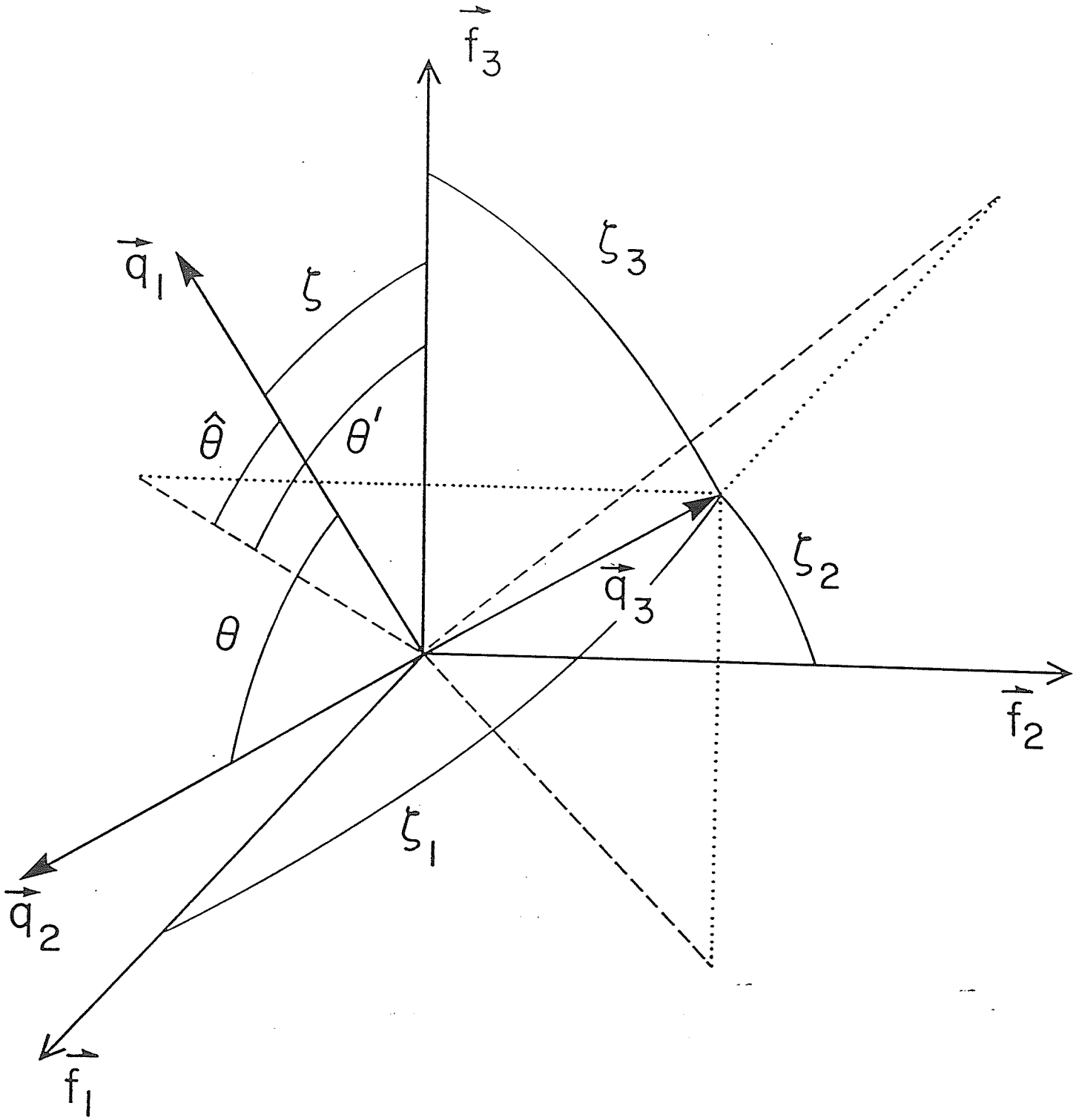
where $\tau_{i3} = \frac{\partial}{\partial \theta_{i3}}$, $M_{\alpha\beta}$ and C_2 are given by equations (4.20,21) as functions of the parameter ζ defining the non–inertial (2GJV) frame.

References.

1. J.P. Leroy, R.Wallace, to be published in Chemical Physics
2. J.P. Leroy, R.Wallace, Chemical Physics, 111 (1987) 11
3. R.Wallace, J.P. Leroy, submitted to Chemical Physics
4. "The Classical Groups", H. Weyl, Princeton University Press, Princeton, 1946
5. H.M. Pickett, J. Chem. Phys., 56 (1972) 1715
6. B. Buck, L.C. Biedenharn and R.Y. Cusson, Nucl. Phys., A317 (1979) 205
7. J.P. Leroy, Ph.D. thesis, to be published, University of Manitoba, Winnipeg R3T 2N2, Canada.
8. R. Wallace, Chemical Physics, 88 (1984) 247
9. J.P. Leroy, R. Wallace, J. Phys. Chem., 89 (1985) 1928, J.P. Leroy, R. Wallace, J. Comp. Phys., 67 (1986) 239
10. Trigonométrie Sphérique, R. de Marchin, Wesmael–Charlier,

Figure I : Angular variables for branched four–body systems.

The Jacobi vectors $\vec{q}_1$ and $\vec{q}_2$ (D–fragment) are in the plane defined by $\vec{f}_3$ and $\vec{f}_1$. ζ_α are the angles between $\vec{q}_3$ and the axes $\vec{f}_\alpha$. θ' is the angle between the axis of quantization $\vec{f}_3$ and the projection of $\vec{q}_3$ on the plane of the D–fragment (depends on the frame). $\hat{\theta}$ is the angle between the projection of $\vec{q}_3$ on the plane of the D–fragment and the vector $\vec{q}_1$ (independent of the definition of the frame).


$\vec{f}_3$
$\vec{q}_1$
ζ
ζ_3
$\hat{\theta}$
θ'
θ
$\vec{q}_3$
ζ_2
$\vec{f}_2$
ζ_1
$\vec{q}_2$
$\vec{f}_1$

The quantum kinetic energy operator for a group of particles in terms of scalar basic rotational invariant coordinates derived from a generalized Jacobi vectors (GJV) description. II. Frames derived from three GJV.

Abstract: Previous work[1] defining the quantum kinetic energy operator for relative motion of a group of particles in terms of cartesian components of generalized Jacobi vectors (GJV) is logically extended. The first such extension examines definitions of the noninertial reference frame which follow from its definition by three GJV, the second invokes the simplest scalar internal coordinates which are the basic rotational invariants of the GJV. KE operators are explicitly evaluated and assessed in terms of separability.

1. Introduction.

The present authors have recently[1] derived an expression for the kinetic energy operator of an N–body system which is valid for a general non–inertial reference frame provided that some prescription of the manner in which the moving frame is "attached" to the instantaneous internal configuration is given. The resulting kinetic energy operator was expressed in terms of the 3N–3 cartesian coordinates of a set of N–1 generalized Jacobi vectors[2] (GJV) which are orthogonal counterparts to the traditional (non–orthogonal) interparticle vectors. Lack of a systematic discussion of non–inertial frames provided some of the impetus for our previous work (hereinafter I) although this topic has in the past been[3] and continues to be of substantial interest[4,5].

The non–inertial frames commonly employed in molecular dynamics fall into two categories:

(1) global frames expressing some property of the entire system (for example, the instantaneous axes of inertia frame, Eckart molecular frame,...)

(2) local frames for which the rotational motion is tied to the instantaneous configuration of some fragment of the system.

The former are well suited to the description of systems possessing a semi–rigid structure which can rotate as a whole.

The latter are more convenient for molecules containing a semi–rigid fragment defined by a set of Jacobi vectors $\vec{q}^{\,0}_k$. These vectors define a non–inertial frame $\{\vec{f}_\alpha(\vec{q}^{\,0}_k);\ \alpha=1,2,3\}$ whose rotation with respect to the inertial frame is generated by the component angular momenta of the vectors

$\vec{q}_k^0$.

Frames identified by a three body fragment (two GJV) have already been investigated in a recent paper[6] (hereinafter II). The kinetic energy operators in basic rotational invariant (BRI) coordinates were derived for a variety of frames defined by 2GJV. That model applies to three–body systems in any kind of non–inertial frame in a particularly simple manner. In addition, it is applicable to N–body systems in which a three body fragment serves as a useful identifier. In that context, the KE operator for an $(AB_2)X$ ($m_X < m_{AB_2}$) molecule (such as formaldehyde) was derived.

The present paper is concerned with the hamiltonian for N–body systems described by BRI coordinates resulting from rotating frames characterized by three GJV. The model is particularly well suited to branched four–body systems (for example, of the type AB_3 as well as $(AB_2)X$ whose rotating frame is considered global). As in II, the model can be used for N–body systems $(AB_3)X$, especially where $m_X < M(AB_3)$.

In Section 2, the general kinetic energy operator (formulated in I) in cartesian coordinates is simplified for three GJV frames. The transformation into BRI coordinates is achieved in Section 3. As a result, the invariance under a change of frame of the operator T°_{int} (S=0;L=0 state of the frame–defining fragment) is demonstrated. This result is a generalization of the invariance of the internal hamiltonian described by global frames[7]. In Section 4, the instantaneous principal axes of inertia (IPAI) frame serves as an example. Finally, in Section 5, the complete hamiltonian for a four–body symmetric top is symmetrically separated into six one–dimensional eigenvalue equations and the angular internal coupling terms are evaluated by perturbation techniques.

2.Kinetic Energy Operator in Cartesian Coordinates.

Let an N–body system be described by a set of n=N–1 Jacobi vectors[2] and let its rotational motion with repect to a center–of–mass inertial frame be described by a non–inertial frame $\{\vec{f}_\alpha;\alpha = 1,2,3\}$ tied to the configuration of the three Jacobi vectors $\vec{q}_1$, $\vec{q}_2$ and $\vec{q}_3$. With the usual conventions, $\vec{f}_3$ is taken as the axis of quantization. This frame is entirely characterized by a set of three matrices[1,6] I^i whose elements are rotational invariant functions of the cartesian components of the three Jacobi vectors $\vec{q}_i$. It is shown in reference 6 that the reciprocal tensor of inertia $\mathcal{I}$ of the set $\{\vec{q}_i;\ i=1,2,3\}$ is given by:

$$M \equiv \mathcal{I}^{-1} = \sum_{i=3}^{i=3} (I^i)^t (I^i) \qquad (2.1)$$

With respect to this frame, the remaining Jacobi vectors $\vec{q}_k$ (k=4,...,n) have components $y^{k\alpha}$ whose conjugate linear momenta are $\pi_{k\alpha}$. Similarly, the angular momentum components of the $\vec{q}_k$ in the rotating frame are:

$$P'_\alpha = \sum_{k=4}^{k=n} (y^{k\beta}\pi_{k\gamma} - y^{k\gamma}\pi_{k\beta}) \qquad (2.2)$$

Once expressed in the cartesian coordinates $y^{i\alpha}$ and their conjugate momenta $\pi_{i\alpha}$, the rovib kinetic energy operator has the form[1] :

$$T_{rovib} = T^{\circ}_{int} + T_{rot} + T'_{int} + T^{c}_{int} + T_{coup} \qquad (2.3)$$

The different parts have the following meaning.

T°_{int} contains all the linear momentum terms $\pi_{i\alpha}$ related to $\vec{q}_i$ (i=1,2,3) and describes the pure vibrational motion of the Jacobi vectors constituting the frame in the rotational ground state:

$$T^{\circ}_{int} = \sum_{i=1}^{i=3} \sum_{\alpha=1}^{\alpha=3} [\pi^2_{i\alpha} + i\,\Delta_{i\alpha}\pi_{i\alpha}] \qquad (2.4)$$

where

$$\Delta_{i\alpha} = I^{i}_{\beta\gamma} - I^{i}_{\gamma\beta} \qquad (2.5)$$

The pure rotational part is given by

$$T_{rot} = \sum_{\gamma=1}^{\gamma=3} [M_{\gamma\gamma}K^2_{\gamma} + M_{\alpha\gamma}\{K_{\alpha},K_{\beta}\} + C_{\gamma}K_{\gamma}] \qquad (2.6)$$

(α,β,γ are C.P. of 1,2,3)

where K_{α} is the projection of the angular momentum $\vec{L}$ of the three vectors $\vec{q}_i$ on the non–inertial frame and $\{.\}$ stands for the anticommutator. After integrating over all the external rotations[8], T_{rot} is re–expressed in terms of the rotational quantum numbers S and L and the step–up/step–down operators $\sigma_{\pm}$. As a result, T_{rot} decomposes into a term T_r expressing the mixing of the rotational states and a centrifugal potential V_c describing the contribution of the rotational motion to the internal oscillators:

$$\begin{aligned} T_r = {} & \frac{\ell_+^2}{4}[M_{11}-M_{22}+ i\,M_{12}]\sigma_+^2 + \frac{\ell_-^2}{4}[M_{11}-M_{22}- i\,M_{12}]\sigma_-^2 \\ & +\tfrac{1}{2}\ell_+[SM_{13}+C_1 + i\,(SM_{23}+C_2)]\sigma_+ \\ & +\tfrac{1}{2}\ell_-[SM_{13}+C_1 - i\,(SM_{23}+C_2)]\sigma_- \end{aligned} \qquad (2.7)$$

$$V_c = \tfrac{1}{2}(M_{11}+M_{22})[L(L+1) - S^2] + M_{33}S^2 + C_3S \qquad (2.8)$$

The coefficients C_{γ} are characteristic of the frame and are given by:

$$C_{\gamma} = \sum_{i=1}^{i=3} \sum_{\lambda=1}^{\lambda=3} [\pi_{i\lambda}I^{i}_{\lambda\gamma} + i\,\Delta_{i\lambda}I^{i}_{\lambda\gamma}] \qquad (2.9)$$

T'_{int} contains all the intrinsic operators related to the vectors $\vec{q}_k$ which are not entering into the construction of the frame:

$$T'_{int} = \sum_{k=4}^{k=n} \sum_{\alpha=1}^{\alpha=3} \pi^2_{k\alpha} + \sum_{\gamma=1}^{\gamma=3} [M_{\gamma\gamma} P'^2_{\gamma} + M_{\alpha\gamma}\{P'_{\alpha}, P'_{\beta}\} + C_{\gamma} P'_{\gamma}] \quad (2.10)$$

T^c_{int} are the internal couplings between the two fragments of the system:

$$T^c_{int} = 2 \sum_{\gamma=1}^{\gamma=3} d_{\gamma} P'_{\gamma} \quad (2.11)$$

(α,β,γ are cyclic permutations of 1,2,3)

where the operators d_{γ} are given by

$$d_{\gamma} = \sum_{i=1}^{i=3} [I^i_{\alpha\gamma} \pi_{i\alpha} + I^i_{\beta\gamma} \pi_{i\beta}] \quad (2.12)$$

Finally the coupling terms between internal motion and the external rotational motion are given by:

$$T_{coup} = \sum_{\gamma=1}^{\gamma=3} \mathscr{D}_{\gamma} \Gamma_{\gamma} \quad (2.13)$$

The operators $\mathscr{D}_{\gamma}$ are

$$\mathscr{D}_{\gamma} = \mathscr{D}'_{\gamma} + d_{\gamma} \quad (2.14)$$

where

$$\mathscr{D}'_{\gamma} = M_{\gamma\gamma} P'_{\gamma} + M_{\alpha\beta}\{P'_{\alpha}, P'_{\beta}\} \qquad (\alpha,\beta,\gamma \text{ are C.P.}) \quad (2.15)$$

and the operators Γ_{α} are

$$\begin{aligned} \Gamma_1 &= \tfrac{1}{2}[\ell_+(L,S)\sigma_+ + \ell_-(L,S,)\sigma_-] \\ \Gamma_2 &= \tfrac{i}{2}[\ell_+(L,S)\sigma_+ - \ell_-(L,S,)\sigma_-] \\ \Gamma_3 &= S \end{aligned} \quad (2.16)$$

3. Transformation into BRI Coordinates.

The definition of the non–inertial frame leads to a set of three constraints on the cartesian coordinates $y^{i\alpha}$ (i=1,2,3) hence to a parameterization of the nine non–independent coordinates $y^{i\alpha}$.

In the present context, the six independent basic rotational invariant (BRI) coordinates constitute an appropriate preliminary choice for such a parameterization since any internal coordinates are expressible as polynomials of the BRI coordinates[9].

Let Q_i be the lengths of the Jacobi vectors $\vec{q}_i$ and θ_{ij} be the angles between them:

$$Q_i = \left[\Sigma_\alpha (y^{i\alpha})^2 \right]^{1/2} \tag{3.1}$$

$$\cos\theta_{ij} = \frac{\Sigma_\alpha y^{i\alpha} y^{j\alpha}}{Q_i Q_j} \tag{3.2}$$

where θ_{ij} is taken positive in going from $\vec{q}_i$ to $\vec{q}_j$.

This corresponds to a curvilinear transformation in configuration space of the nine cartesian coordinates $y^{i\alpha}$ into three radial internal curvilinear coordinates Q_i, three angular internal coordinates θ_{ij} and the three Euler (external) angles ϕ_s, which are functions of the internal coordinates. The angles ϕ_s are parameterizing the rotation transforming the inertial frame into the non–inertial frame. By inspection[10], the metric tensor (contravariant) has the following form:

$$G = \begin{bmatrix} \boxed{G_r} & 0 & 0 \\ 0 & \boxed{G_a \quad G_{ae}} \\ 0 & \boxed{G_{ae}^t \quad G_e} \end{bmatrix} \tag{3.3}$$

$$= \begin{bmatrix} G_r & 0 \\ 0 & G_A \end{bmatrix}$$

where the radial sub–tensor G_r is diagonal, that is the radial coordinates Q_i are orthogonal to each other. The angular sub–tensor G_a has no zero terms; this expresses the non–orthogonality of the angular coordinates θ_{ij}. The radial coordinates are orthogonal to all angular coordinates and the internal angles θ_{ij} are not orthogonal to the Euler angles ($G_{ae} \neq 0$). The inverse tensor G^{-1} (covariant) describes the orthogonality properties in the space of the momenta; that is, a non zero off–diagonal element in G^{-1} means there is a coupling term between the corresponding coordinates. It is not the purpose of the present work to discuss in detail the curvilinear transformations of the BRI coordinates leading to the partial or total elimination of the coupling terms. Nevertheless, it is worth describing briefly the general procedure.

Any curvilinear transformation of the angular internal sub–space will leave unaffected the overall form of the tensors G and G^{-1}: only G_a and G_{ae} will transform. One seeks "curvilinear orthogonalization procedures" of the vectors of the locally defined basis corresponding to the variables θ_{ij}. Such "infinitesimal" orthogonalizations (infinitesimal equivalents of the usual orthogonalizations) can be carried out in principle but lead to complicated systems of second order differential equations in the general case, especially if the symmetry of the angular coordinates has to be maintained (infinitesimal E.S. orthogonalization). Alternatively, mixing of the radial and internal angular coordinates can be considered. The effect is to modify completely the structure of the metric tensors. This is the case for the example of the generalized

hyperspherical coordinates[5]: the hyperadius is orthogonal to all the angles; the internal hyperspherical angles φ_i are not orthogonal to the label hyperspherical angles ϕ_i.

The cartesian components $y^{i\alpha}$ can advantageously be expressed as:

$$y^{i\alpha} = Q_i \cos\zeta_{i\alpha} \tag{3.3}$$

where $\zeta_{i\alpha}$ is the angle between the axis $\vec{f}_\alpha$ of the non–inertial frame and the vector $\vec{q}_i$. The nine angles $\zeta_{i\alpha}$ are functions of the BRI coordinates Q_i and θ_{ij}. They obey the usual direction cosines relations:

$$\sum_{\alpha=1}^{\alpha=3} \cos^2\zeta_{i\alpha} = 1 \quad (i=1,2,3) \tag{3.4}$$

$$\sum_{\alpha=1}^{\alpha=3} \cos\zeta_{i\alpha}\cos\zeta_{j\alpha} = \cos\theta_{ij} \quad (i<j) \tag{3.5}$$

Furthermore the three relationships among the cartesian coordinates are translated into three relations among the $\zeta_{i\alpha}$. For example, the instantaneous principal axes frame is characterized by zero off–diagonal elements of the tensor of inertia (really the mass quadrupole $\mathcal{M}$):

$$\sum_{i=1}^{i=3} y^{i\alpha} y^{i\beta} = 0 \quad (\alpha \neq \beta) \tag{3.6}$$

In terms of the angles $\zeta_{i\alpha}$, this reads as

$$\sum_{i=1}^{i=3} Q_i^2 \cos\zeta_{i\alpha}\cos\zeta_{i\beta} = 0 \tag{3.7}$$

The parameters $\zeta_{i\alpha}$ appear here as useful intermediates in the calculcations.

With this notation, the linear momenta are expressed as

$$\pi_{i\alpha} = -i\left\{ \cos\zeta_{i\alpha}\frac{\partial}{\partial Q_i} + \frac{\Gamma^{\alpha}_{ij}}{Q_i}\frac{\partial}{\partial\theta_{ij}} + \frac{\Gamma^{\alpha}_{ik}}{Q_i}\frac{\partial}{\partial\theta_{ik}}\right\} \qquad (3.8)$$

$(i\neq j\neq k \text{ and } j,k>i)$

where the terms Γ^{α}_{ij} are defined by

$$\Gamma^{\alpha}_{ij} = \frac{\cos\theta_{ij}\cos\zeta_{i\alpha} - \cos\zeta_{j\alpha}}{\sin\theta_{ij}}. \qquad (3.9)$$

By introducing the spherical angle $S_{j\alpha}$ (see figure I) relative to the vector $\vec{q}_j$, Γ^{α}_{ij} is expressable as

$$\Gamma^{\alpha}_{ij} = -\cos S_{j\alpha}\sin\zeta_{i\alpha}. \qquad (3.10)$$

Expressions analogous to (3.3) and (3.8) are now sought for the cartesian components of the remaining vectors $\vec{q}_k$ (k=4,...,n) in terms of the BRI coordinates and the angles $\zeta_{k\alpha}$ and $S_{k\alpha}$.

The expression of the kinetic operator in BRI requires the evaluation of the matrix elements $I^{i}_{\alpha\beta}$ as functions of the parameters $\zeta_{i\alpha}$ defining the frame and the BRI. The calculations are carried out in appendix I; the results are:

$$I^{i}_{\alpha\beta} = -i\,\pi_{i\alpha}\zeta_{\beta\alpha} \qquad (3.11)$$

The coefficients $\Delta_{i\alpha}$ (equation 2.5) read as:

$$\Delta_{i\alpha} = \pi_{i\beta}\zeta_{\gamma\beta} - \pi_{i\gamma}\zeta_{\beta\gamma} \qquad (3.12)$$

This permits the evaluation of the term T^{o}_{int} given by (2.4):

$$T^{o}_{int} =$$
$$-\sum_{i=1}^{i=3}\left[\frac{\partial^2}{\partial Q_i^{\,2}} + \frac{2}{Q_i}\frac{\partial}{\partial Q_i}\right]$$
$$-\sum_{i<j}\left[\frac{1}{Q_i^{\,2}} + \frac{1}{Q_j^{\,2}}\right]\left[\frac{\partial^2}{\partial\theta_{ij}^{\,2}} + \cot\theta_{ij}\frac{\partial}{\partial\theta_{ij}}\right]$$
$$-2\sum_{i<j}\frac{\cos S_{ij}}{Q_k^2}\frac{\partial^2}{\partial\theta_{ik}\partial\theta_{jk}} \quad (i\neq j\neq k) \qquad (3.13)$$

As for 2GJV frames, this part of the KE operator is independent of the

choice of the frame. As pointed out above, there are no coupling terms between the radial and angular parts whereas the angles θ_{ij} are all coupled with each other.

Actually, the coupling coefficients are quite small (cosine divided by the square of the length of the Jacobi vector). This is especially true near the equilibrium configuration and the hamiltonian derived from (3.13) can be used for AB_3 systems in the rotational ground state with a perturbation treatment of the couplings.

In a description of this system with a 2GJV frame contructed from the vectors $\vec{q}_1$ and $\vec{q}_2$ (angle θ), the term T°_{int} has the form[4]:

$$
\begin{aligned}
T^{\circ}_{int} = & \\
& -\sum_{i=1}^{i=3} \left[\frac{\partial^2}{\partial Q_i{}^2} + \frac{2}{Q_i} \frac{\partial}{\partial Q_i} \right] \\
& - \left[\frac{1}{Q_1{}^2} + \frac{1}{Q_2{}^2} \right] \left[\frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} \right] \\
& - \frac{1}{Q_3{}^2} \left[\frac{\partial^2}{\partial \theta_{13}{}^2} + \cot\theta_{13} \frac{\partial}{\partial \theta_{13}} + \frac{\partial^2}{\partial \theta_{23}{}^2} + \cot\theta_{23} \frac{\partial}{\partial \theta_{23}} \right] \\
& - \left[A_{11} \frac{\partial^2}{\partial \theta_{13}{}^2} + B_1 \frac{\partial}{\partial \theta_{13}} + A_{22} \frac{\partial^2}{\partial \theta_{23}{}^2} + B_2 \frac{\partial}{\partial \theta_{23}} \right] \\
& - \left[\frac{2\cos S_{12}}{Q_3{}^2} + A_{12} \right] \frac{\partial^2}{\partial \theta_{13} \partial \theta_{23}}
\end{aligned}
\qquad (3.14)
$$

where the coefficients A_{ij} and B_i are functions of Q_1, Q_2 and θ whose form depends upon the 2GJV frame via the parameter ζ. There is a single angular coupling but the form of the angular differential equations is quite complicated. To the extent that we might be concerned with the radial part only, both descriptions are identical.

The other terms of the kinetic energy operator are evaluated in a similar way after expressing the coefficients $M_{\alpha\beta}$ and C_α and the operators d_α in BRI coordinates. The procedure was described in detail in reference 4 for 2GJV frames and there seems no reason to repeat it here.

4. Example: Instantaneous Principal Axes of Inertia.

The diagonalization of the mass quadrupole of the three vectors constituting the fragment AB_3 of an N–body system leads to the definition of the IPAI frame. As far as the four–body fragment is concerned, this frame is typically global hence T°_{int} is given by equation (3.13). All that is needed is the evaluation of the matrix elements $I^i_{\alpha\beta}$ to derive the coefficients $M_{\alpha\beta}$ and C_α and the operators d_α.

The matrices I^i have been evaluated in reference 1 for this frame:

$$I^i = \mathcal{Q}_i \begin{bmatrix} 0 & \frac{\cos\zeta_{i3}}{\lambda_3-\lambda_1} & \frac{\cos\zeta_{i2}}{\lambda_1-\lambda_2} \\ \frac{\cos\zeta_{i3}}{\lambda_2-\lambda_3} & 0 & \frac{\cos\zeta_{i1}}{\lambda_1-\lambda_2} \\ \frac{\cos\zeta_{i2}}{\lambda_2-\lambda_3} & \frac{\cos\zeta_{i1}}{\lambda_3-\lambda_1} & 0 \end{bmatrix} \qquad (4.1)$$

where λ_a are the eigenvalues of the Gram matrix G of the three Jacobi vectors (actually, the common eigenvalues of G and the mass quadrupole[6] $\mathcal{M}$).

For this frame, the off–diagonal elements of the matrix M are zero whereas the elements $M_{\alpha\alpha}$ are given by[1]:

$$M_{\alpha\alpha} = \frac{\lambda_\beta + \lambda_\gamma}{\lambda_\beta - \lambda_\gamma} \quad (\alpha,\beta,\gamma \text{ are c.p}) \tag{4.2}$$

The eigenvalues of this 3×3 symmetric matrix can be obtained analytically by using the Cardan's formulas (see appendix II). The result is quite messy and is given here for information.

The secular equation for G reads as:

$$\lambda^3 - \rho^2\lambda^2 - S^2\lambda - V^2 = 0 \tag{4.3}$$

where ρ is the hyperadius:

$$\rho^2 = \Sigma_i Q_i^2 \tag{4.4}$$

$$S^2 = \sum_{i<j} S_{ij}^2 = \sum_{i<j} Q_i^2 Q_j^2 \sin^2\theta_{ij} \tag{4.5}$$

where S_{ij} is twice the surface of the triangle defined by the vectors $\vec{q}_i$ and $\vec{q}_j$ and V is the volume of the paralelipiped formed from the three vectors:

$$V^2 = Q_1^2 Q_2^2 Q_3^2 (1 - \cos^2\theta_{12} - \cos^2\theta_{13} - \cos^2\theta_{23} + 2\cos\theta_{12}\cos\theta_{13}\cos\theta_{23}) \tag{4.6}$$

With the usual convention of labeling the eigenvalues we have

$$\begin{aligned} \lambda_3 &= +\frac{\rho^2}{3} + P + Q \\ \lambda_1 &= +\frac{\rho^2}{3} + \omega P + \omega^2 Q \\ \lambda_2 &= +\frac{\rho^2}{3} + \omega^2 P + \omega Q \end{aligned} \tag{4.7}$$

where P, Q and ω are as in appendix II.

By employing equations (2.7), (3.11) and (3.12), one deduces that all the coefficients C_α are zero. The operators d_α are obtained similarly.

Four–body systems.

The rovib hamiltonian for a four body system described in a non–inertial frame coinciding with the instantaneous principal axes and in terms of BRI coordinates has the following form:

$$H = T^{\circ}_{int} + V + V_c + T_r \qquad (4.8)$$

where T°_{int} is given by equation (3.13), that is T°_{int} + V describes the rotational ground state and V is the potential expressed as a function of the six BRI coordinates.

For S≠0, the rotational energy is distributed among the six vibrational oscillators. The centrifugal potential V_c takes the form

$$V_c = = \tfrac{1}{2}(M_{11}+M_{22})[L(L+1) - S^2] + M_{33}S^2 \qquad (4.9)$$

There is no explicit separation of the contributions of V_c to each of the individual oscillators. Nevertheless, the decomposition of the effective potential $V_{eff} = V + V_c$ into a summation of separable parts $\Sigma_\sigma V_\sigma$ can be investigated as usual[11].

Finally, the mixing of the rotational states is described here by the terms T_r

$$T_r = \frac{\ell_+^2}{4}[M_{11}-M_{22}]\sigma_+^2 + \frac{\ell_-^2}{4}[M_{11}-M_{22}]\sigma_-^2 \qquad (4.10)$$

The coefficients $M_{\alpha\alpha}$ are given by equation (4.2) and are easily evaluated numerically.

N–Body–Systems.

The same procedure followed in II can be carried out for N–body systems composed of a four–body (frame–defining) fragment and an internal fragment X. The internal angular momenta P'_α are re–expressed in terms of the linear

momenta conjugate to the BRI coordinates Q_k and θ_{ik} (i=1,2,3; k=4,...,N–1) and substituted into the operators T'_{int}, T^c_{int} and $\mathscr{D}'_\alpha$ given by equations (2.10, 2.11 and 2.15). Even in the simplest case (X is a single particle), the calculations are quite lengthy in the general case. Nevertheless some general conclusions can be drawn concerning the pure internal hamiltonian. Irrespective of the choice of the frame, the radial part is given by:

$$-\sum_{i=1}^{i=N-1} \left\{ \frac{\partial^2}{\partial Q_i{}^2} + \frac{2}{Q_i} \frac{\partial}{\partial Q_i} \right\} \tag{4.11}$$

The angular equations do depend upon the choice of the frame whatever the choice of parameterization of the basic rotational invariant angles might be. As well there are coupling terms between the angular variables which depend on the choice of the frame and the way the angles θ_{ik} have been parameterized. Finally, norm dependent frames introduce extra coupling terms between the radial part of the three–body fragment and the angles θ_{ik} as pointed out in II for 2GJV frames.

5. Hamiltonian for the rotational ground state (S=0;L=0) of a four body symmetric top system.

In this section the case of symmetric top four body systems AB_3 is considered. The bond vectors AB are transformed into equivalent symmetric Jacobi vectors $\vec{q}_i$ (i=1,2,3). If O_{es} denotes the ES label orthonormalization, the Gram matrix G(q) of the Jacobi vectors is obtained from the Gram matrix G(r) of the bond vectors by

$$O_{es}G(r)O_{es} = G(q) \tag{5.1}$$

where O_{es} is given by[12]

$$O_{es} = \begin{bmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \alpha \\ \beta & \beta & \alpha \end{bmatrix} \tag{5.2}$$

with $\alpha = \frac{M+m}{Mm}$ and $\beta = \frac{m}{M+m}$, M and m being the masses of the top atom A and the equivalent atoms B respectively.

Equations (5.1) and (5.2) provide the relations transforming the BRI of the bond vectors (bond distances, bond angles) into their ES counterparts. Under exchange of the identical particles B, the Gram matrix G(q) remains invariant.

This section is mainly oriented towards the rotational ground state hamiltonian, consideration of the S≠0 states being easily obtained by extension.

A completely separable kinetic energy operator can be obtained in principle by some appropriate curvilinear transformation of the angular BRI variables whilw retaining the symmetry properties characterizing the three angles θ_{ij}. At present, such a hamiltonian is not available. Nevertheless, the coupled form discussed in the previous section presents some interest on its own for symmetric top systems since the couplings are easily evaluated by standard perturbation techniques. Moreover, the coupling coefficients become very small for some regions of configuration space (large radial amplitude and near $\pi/2$ angular configuration). This suggests that a fairly good approximation for those regions can be made by neglecting the angular couplings.

For S=0 and L=0, the kinetic energy operator reduces to T°_{int} and is independent of the choice of the rotating frame. Let V be some appropriate source potential re–expressed in BRI coordinates. Following the usual procedure[11], V is expressed as a sum of separable parts V_{σ} in each of the internal coordinates and a non–separable part V_{ns}:

$$V = V_{sep} + V_{ns} = \sum_i V_i + \sum_{i<j} V_{ij} + V_{ns} \tag{5.3}$$

where V_i and V_{ij} are functions respectively of Q_i and θ_{ij} only. For the purpose of this illustration, it is assumed that $V_{ns} << V_{sep}$.

The S≠0 states are treated in a similar fashion:

$$\begin{aligned} V_c &= (V_c)_{sep} + (V_c)_{ns} \\ &= \sum_i (V_c)_i + \sum_{i<j} (V_c)_{ij} + (V_c)_{ns} \end{aligned} \tag{5.4}$$

and the effective potential V_{eff} is expressed in the form

$$\begin{aligned} V_{eff} &= V + V_c \\ &= \sum_i (V_{eff})_i + \sum_{i<j} (V_{eff})_{ij} + (V_{eff})_{ns} \end{aligned} \tag{5.5}$$

For non–inertial frames invariant under exchange of identical particles, it is again reasonable to assume that $(V_c)_{ns} << (V_c)_{sep}$.

With this notation, the zero–order hamiltonian H_o

$$H_o = \sum_i H_i + \sum_{i<j} H_{ij} \tag{5.6}$$

is the sum of three equivalent radial one–dimensional terms

$$H_i = -\frac{\hbar^2}{2}\left\{\frac{\partial^2}{\partial Q_i^{\,2}} + \frac{2}{Q_i}\frac{\partial}{\partial Q_i} - V_i\right\} \tag{5.7}$$

and three equivalent one–dimensional angular terms

$$H_{ij} = -\frac{\hbar^2}{2}\tilde{Q}_{ij}\left[\frac{\partial^2}{\partial \theta_{ij}^2} + \cot\theta_{ij}\frac{\partial}{\partial \theta_{ij}} - \tilde{Q}_{ij}^{-1} V_{ij}\right] \tag{5.8}$$

where $\tilde{Q}_{ij} = Q_i^{-2} + Q_j^{-2}$

The angular equations

$$[\frac{\partial^2}{\partial\theta_{ij}^2} + \cot\theta_{ij}\frac{\partial}{\partial\theta_{ij}} - \tilde{Q}_{ij}^{-1}\, V_{ij}\,]A_n^{(ij)} = -\Lambda_n^{(ij)}A_n^{(ij)} \tag{5.9}$$

can be solved numerically by the renormalized Numerov method[13] (RNM) yielding the eigenvalues $-\Lambda_n^{(ij)}$ and the corresponding eigenfunctions $A_n^{(ij)}$. After substitution into (5.4), the radial zero– order hamiltonian becomes:

$$H_o(Q_i) = \sum_i H_o^{(i)}(Q_i) \tag{5.10}$$

where

$H_o^{(i)}(Q_i) =$

$$-\frac{\hbar^2}{2}\left\{\frac{\partial^2}{\partial Q_i^{\,2}} + \frac{2}{Q_i}\frac{\partial}{\partial Q_i} - \frac{1}{Q_i^{\,2}}(\Lambda_n^{(ij)} + \Lambda_m^{(ik)})\right\} + V_i \tag{5.11}$$

which leads to three separate one–dimensional eigenvalue equations

$$H_o^{(i)}(Q_i)R_\alpha^{(ijk)} = \epsilon_\alpha^{(ijk)}R_\alpha^{(ijk)} \tag{5.12}$$

These equations may be solved numerically by RNM establishing a zero–order basis

$$\chi = R(Q_1)R(Q_2)R(Q_3)A(\theta_{12})A(\theta_{13})A(\theta_{23}) \tag{5.13}$$

where the various labels have been omitted for simplicity.

The non–separable hamiltonian is comprised of V_{ns} and the coupling terms between the angular BRI momenta

$$V_{ns} + 2\sum_{i<j}\frac{\cos S_{ij}}{Q_k^2}\frac{\partial^2}{\partial\theta_{ik}\partial\theta_{jk}} \tag{5.14}$$

The matrix elements of the coupling potential are evaluated numerically employing the zero–order basis (5.13). The coupling operator treatment necessitates the evaluation of matrix elements of the form (using short–hand notation)

$$<\chi_\alpha^{(ij)}|\frac{\partial}{\partial\theta_{ij}}|\chi_\beta^{(ij)}> \tag{5.15}$$

that is, after taking advantage of the orthogonality of the radial eigenfunctions,

$$<A_{\alpha}^{(ij)}|\frac{\partial}{\partial\theta_{ij}}|A_{\beta}^{(ij)}> \qquad (5.16)$$

The evaluation of (5.15) does not represent extra work since the angular eigenfunctions $A^{(ij)}$ as well as their derivatives are stored in numeric form in the RNM and all that is needed is a numerical integration at each step.

The entire problem is therefore soluble in a symmetric fashion by known numeric techniques.

6. Summary and conclusions.

The main purpose of this study has been to derive a kinetic energy operator tailored to N–body systems whose rotational motion may be described by a fragment constituted from four non–coplanar particles possessing a semi–rigid stucture. Four–body systems characterized by such a behaviour are the simplest cases for which the present model applies. The frame independence of the pure internal kinetic energy operator has been demonstrated. This property does not hold for 2GJV frames as pointed out in II. A completely symmetric hamiltonian for four body symmetric–tops represented by orthogonal symmetric Jacobi vectors has been derived. As a result, the hamiltonian has been separated into six one–dimensional eigenvalue equations which one may proceed to solve numerically. The perturbation treatment which approximates the coupling terms between the angular variables involves no extra step since the matrix elements of the perturbing operators are readily obtained.

In addition to symmetric tops,the model applies to four body molecules of type $(AB_2)X$ where the axis of quantization is along the bond AX (i.e., for $m_X >> m_{AB_2}$) and where the two Jacobi vectors associated with both bonds AB

are involved in the construction of the axes $\vec{f}_1$ and $\vec{f}_2$. In this case, the rotating frame is global and the pure internal kinetic energy operator is still given by equation (3.13).

APPENDIX 1

Evaluation of the matrices I^i for a (3GJV)–N.I.F.

The matrices Ω^i are defined[3] by:

$$\Omega^i_{\alpha\lambda} = (\vec{f}_\mu, \frac{\partial \vec{f}_\nu}{\partial q^{i\alpha}}) \tag{A.1}$$

where the frame vectors $\vec{f}_\nu$ are defined by:

$$\vec{f}_\nu = \Sigma_j B_{\nu j} \vec{q}(j) \tag{A.2}$$

and λ,μ,ν are cyclic permutations of 1,2,3 as usual.

Expressed in terms of the linear momentum operators $p_{i\alpha} = -\iota \frac{\partial}{\partial q^{i\alpha}}$, (A.1) becomes:

$$\Omega^i_{\alpha\lambda} = i\,(\vec{f}_\mu, p_{i\alpha} \vec{f}_\nu) \tag{A.3}$$

Substitution of (A.2) into (A.3) gives:

$$\Omega^i_{\alpha\lambda} = i\,\Sigma_j y^{j\mu} p_{i\alpha} B_{\nu j} + R_{\alpha\mu} B_{\nu i} \tag{A.4}$$

where

$$(\vec{f}_\mu, \vec{q}(j)) = y^{j\mu}$$

and

$$i\,(\vec{f}_\mu, p_{i\alpha} \vec{q}(j)) = (\vec{f}_\mu, \vec{\ell}_\alpha) = R_{\alpha\mu}$$

Recall the transformation of the linear momenta from the inertial to the non inertial frame[1]:

$$p_{i\alpha} = \Sigma_\beta R_{\alpha\beta} [\pi_{i\beta} + \Sigma_\gamma I^i_{\beta\gamma} (P^\circ_\gamma + P'_\gamma + K^\circ_\gamma)]$$

If acting on an intrinsic function f, $K^\circ_\gamma(f) = 0$. If f depends only upon the GJV defining the frame, $P'_\gamma(f) = 0$. Furthermore, $P^\circ_\gamma \equiv 0$ since the set of three

GJV is fixed in label space, hence:

$$p_{i\alpha}(f) = \Sigma_\beta R_{\alpha\beta}\pi_{i\beta}(f) \tag{A.5}$$

In particular, the coefficients $B_{\nu j}$ are intrinsic functions expressible in terms of the elements G_{ij} of the Gram matrix of the GJV defining the frame and satisfy the above criteria:

$$p_{i\alpha}(B_{\nu j}) = \Sigma_\beta R_{\alpha\beta}\pi_{i\beta}(B_{\nu j}) \tag{A.6}$$

Substitute this result into (A.4) to obtain:

$$\Omega^{i}_{\alpha\lambda} = i\,\Sigma_\beta R_{\alpha\beta}[\Sigma_j y^{j\mu}\pi_{i\beta}B_{\nu j} - i\,B_{\nu i}\delta_{\mu\beta}] \tag{A.7}$$

The matrices I^i are given by:

$$\Omega^{i}_{\alpha\lambda} = \Sigma_\beta R_{\alpha\beta}I^{i}_{\beta\lambda} \tag{A.8}$$

By comparing the two last equations, we obtain the explicit expression for the matrix elements $I^{i}_{\beta\lambda}$:

$$I^{i}_{\beta\lambda} = i\,[\Sigma_j y^{j\mu}\pi_{i\beta}B_{\nu j} - i\,B_{\nu i}\delta_{\mu\beta}] \tag{A.9}$$

Using $B = Y^{-1}$ where Y is the matrix of elements $y^{i\alpha}$, we can replace $B_{\nu j}$ by $c^{j\nu}/c$ where $c^{j\nu}$ and c are respectively the cofactor of $y^{j\nu}$ and the determinant of Y

$$c^{i\alpha} = (-1)^{(i+\alpha)}(y^{j\beta}y^{k\gamma} - y^{j\gamma}y^{k\beta}) \tag{A.10}$$

where i,j,k and α,β,γ are cyclic permutations of 1,2,3

$$c = \Sigma_\alpha c^{i\alpha}y^{i\alpha} \tag{A.11}$$

By using the properties of the cofactors, we obtain:

$$I^{i}_{\beta\lambda} = -\,i\,[\Sigma_j c^{j\nu}\pi_{i\beta}y^{j\mu} + i\,c^{i\nu}\delta_{\mu\beta}] \tag{A.12}$$

The matrix elements of I^i are obtained by substituting $y^{i\alpha}$ and the linear momenta $\pi_{i\alpha}$ respectively by (3.3) and (3.8). The result takes on the simple form:

$$I^{i}_{\beta\lambda} = -\,i\,\pi_{i\beta}\zeta_{\lambda\beta} \tag{A.13}$$

that is the matrix elements of I^i are the result of the action of the linear

momenta in the non–inertial frame on the angles $\zeta_{\lambda\beta}$. It is easily seen that the diagonal elements of the I^i are zero.

APPENDIX 2

Eigenvalues of the 3×3 Gram Matrix : Cardan's Formulas.

Let G be the Gram matrix of the three Jacobi vectors $\vec{q}_i$; its elements are:

$$G_{ij} = Q_i Q_j \cos\theta_{ij} \qquad \text{(A.II.1)}$$

The secular determinant is given by equation (3.16):

$$\lambda^3 - \rho^2\lambda^2 + S^2\lambda - V^2 = 0 \qquad \text{(A.II.2)}$$

The analytic solutions for the roots of this cubic equation are given by the Cardan's formulas[14]:

let

$$p = S^2 - \frac{\rho^4}{3}$$

$$q = -\frac{2\rho^6}{27} + \frac{\rho^2 S^2}{3} - V^2$$

and

$$P = \left[-\frac{q}{2} + \left[\frac{p^3}{27} + \frac{q^2}{4} \right]^{1/2} \right]^{1/3}$$

$$Q = \left[-\frac{q}{2} - \left[\frac{p^3}{27} + \frac{q^2}{4} \right]^{1/2} \right]^{1/3} \qquad \text{(A.II.3)}$$

The roots are

$$\lambda_3 = P + Q + \frac{\rho^2}{3}$$

$$\lambda_2 = \omega P + \omega^2 Q + \frac{\rho^2}{3} \qquad \text{(A.II.4)}$$

$$\lambda_1 = \omega^2 P + \omega Q + \frac{\rho^2}{3}$$

where ω is a cube root of 1 ($\omega \neq 1$) that is

$$\omega = \frac{-1 \pm i\sqrt{3}}{2} \qquad \text{(A.II.5)}$$

The positiveness of the three eigenvalues λ_α permits to decide between the sign $\pm$ for ω.

References.

1. J.P. Leroy, R.Wallace, Chemical Physics, 118 (1987) 379
2. J.P. Leroy, R.Wallace, Chemical Physics, 111 (1987) 11
3. "Rotation of a Rigid Body in Quantum Mechanics", H.B.G. Casimir (Walters, Groningen, Netherlands, 1931)
   C. Eckart, Phys. Rev. 46 (1934) 383; 47 (1935) 552
   J.O.Hirschfelder and E. Wigner, Proc. Nat. Acad. Sci. 21 (1935) 113
   J.H. Van Vleck, Phys. Rev. 47 (1935) 487
4. J.D. Louck and H.W. Galbraith, Rev. of Mod. Phys. 48 (1976) 69; J.K.G. Watson, Mol. Phys. 15 (1968) 479
5. B. Buck, L.C. Biedenharn and R.Y. Cusson, Nucl. Phys., A317 (1979) 205; L.C. Biedenharn and J.D. Louck, "Encyclopedia of Mathematics, Angular Momentum in Quantum Physics" (Addison–Wesley,1981)
6. J.P. Leroy and R. Wallace, submitted to Chemical Physics
7. H.M. Pickett, J. Chem. Phys., 56 (1972) 1715
8. C.F. Curtiss, J.O. Hirschfelder and F.T. Adler, J. Chem. Phys. 18 (1950) 1638
9. "The Classical Groups", H. Weyl, Princeton University Press, Princeton, 1946
10. J.P. Leroy, Ph.D. thesis, to be published, University of Manitoba, Winnipeg.

11. R. Wallace, Chemical Physics, 88 (1984) 247

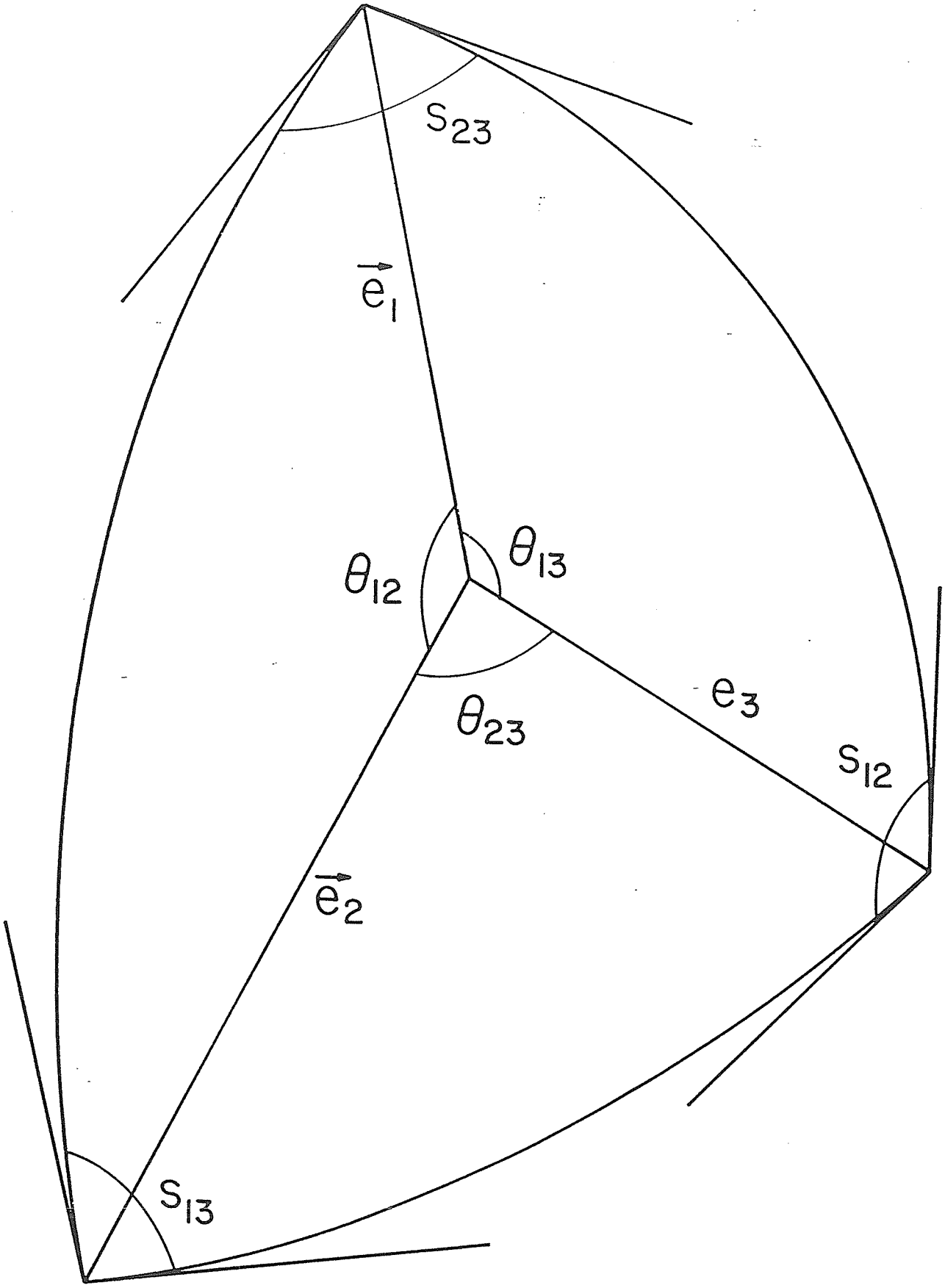
12. R.Wallace, J.P. Leroy, to be published in Chemical Physics

13. J.P. Leroy, R. Wallace, J. Comp. Phys., 67 (1986) 239

14. "Topics in Algebra", I.N. Herstein, John Wiley, New–York, 1975

Figure I.

Spherical angles S_{ij} for a four–body. $\vec{e}_i$ are the unit vectors along the Jacobi vectors $\vec{q}_i$. The spherical angles S_{ij} are the angles between the tangents on the unit sphere to the arcs of great circles.


s_{23}
$\vec{e}_1$
θ_{12}
θ_{13}
θ_{23}
e_3
s_{12}
$\vec{e}_2$
s_{13}

PART IV

APPENDICES

APPENDIX 1

1. EUCLIDEAN SPACES

1.Definitions

An n–dimensional vector space E_n is a *euclidean* space once a symmetric bilinear non–degenerate form has been defined. This means that, given the vectors $\vec{x}$, $\vec{y}$ and $\vec{z}$ of E_n and α (a scalar of the field F on which the vector space is defined), one has

$$(\vec{x},\vec{y}) = (\vec{y},\vec{x}) \tag{1}$$

$$(\alpha\vec{x},\vec{y}) = (\vec{x},\alpha\vec{y}) = \alpha(\vec{x},\vec{y}) \tag{2}$$

$$(\vec{x},\vec{y}+\vec{z}) = (\vec{x},\vec{y}) + (\vec{x},\vec{z}) \tag{3}$$

$$\text{for any } \vec{x}, \text{ if } (\vec{x},\vec{y}) = 0 \text{ then } \vec{y} = 0 \tag{4}$$

Once a basis $(\vec{e}_i)$ has been defined for E_n, any vector $\vec{x}$ and $\vec{y}$ is expressed as

$$\vec{x} = x^i\vec{e}_i \quad ; \quad \vec{y} = y^i\vec{e}_i \tag{5}$$

where the Einstein convention on the summation over repeated indices has been adopted (in any formula where the same index appears two times, once as superscript and once as subscript, the summation is implicitly assumed).

The bilinear form (*scalar product*) takes the form

$$(\vec{x},\vec{y}) = x^iy^j(\vec{e}_i,\vec{e}_j) = x^iy^jg_{ij} \tag{6}$$

where the scalar product of the base vectors has been represented by g_{ij}

$$g_{ij} = (\vec{e}_i,\vec{e}_j) \tag{7}$$

From axiom (1)

$$g_{ij} = g_{ji} \tag{8}$$

The non–degeneracy of the form means that the determinant $|g|$ of the (g_{ij}) is non zero. g is a second order tensor called the *metric tensor.*

Two vectors $\vec{x}$ and $\vec{y}$ are ***orthogonal*** if

$$(\vec{x},\vec{y}) = 0 \tag{9}$$

The ***norm*** $N\vec{x}$ of the vector $\vec{x}$ is given by

$$N\vec{x} = (\vec{x},\vec{x}) = g_{ij}x^i x^j \tag{10}$$

A normalized vector is a vector whose norm is 1.

An euclidean space is *properly euclidean* if the norm is strictly positive for any vector $\vec{x}$

The angle ϕ between the two vectors $\vec{x}$ and $\vec{y}$ is defined by

$$\cos\phi = \frac{(\vec{x},\vec{y})}{N\vec{x}.N\vec{y}}$$

$$= \frac{g_{ij}x^i y^j}{[(g_{ij}x^i x^j)(g_{ij}y^i y^j)]^{1/2}} \tag{11}$$

An orthonormal basis is a set of n vectors satisfying

$$(\vec{e}_i,\vec{e}_j) = \delta_{ij} \tag{12}$$

that is the metric tensor is the n dimensional unit tensor.

In such a basis, the components of the vector $\vec{x}$ are

$$x^i = (\vec{x},\vec{e}_i) \tag{13}$$

and the scalar product of the vectors $\vec{x}$ and $\vec{y}$ is simply

$$(\vec{x},\vec{y}) = x^i y^i \tag{14}$$

In particular, the norm of $\vec{x}$ is

$$N\vec{x} = \Sigma_i (x^i)^2 \tag{15}$$

Consequently it is always possible to transform (diagonalize) a given quadratic form $g_{ij}x^i y^j$ into the form $(x^i)^2$ by a suitable change of basis

$$\vec{e}'_j = A^i_j \vec{e}_i \tag{16}$$

or in terms of the components

$$x'^m = B^m_k x^k \tag{17}$$

Note:

The quantities A and B are not tensors. Although a tensor is related to a specific basis, these quantities are actually defined with respect to both bases. A and B are matrices representing a transformation of the system of axes.

2. Covariant and contravariant components

In an orthonormal basis the components of a vector are simply the scalar products of the vector with the base vectors. In a non–orthonormal basis $(\vec{e}_i)$ this does not hold anymore. In such a basis, the ***contravariant*** components of the vector $\vec{x}$ are the numbers x^i such that

$$\vec{x} = x^i \vec{e}_i \tag{18}$$

The ***covariant*** components of $\vec{x}$ are the numbers x_i defined by

$$x_i = (\vec{x}, \vec{e}_i) \tag{19}$$

In what follows, the covariance is expressed by *subscripts* and contravariance by *superscripts.*

It is easy to show that

$$x_i = g_{ij} x^j \tag{20}$$

This system of equations is a Cramer system. Let $|g|$ be the determinant of the tensor (g_{ij}) and α^{ji} be the coefficient of the development of the element g_{ij} in g. Then

$$x^j = g^{-1} \alpha^{ji} x_i \tag{21}$$

$$x^j = g^{ji}x_i \tag{22}$$

where

$$g^{ji} = g^{ij} = g^{-1}\alpha^{ji} = g^{-1}\alpha^{ij} \tag{23}$$

from what one deduces

$$\det(g^{ij}) = |g|^{-1} \tag{24}$$

The expression for the scalar product becomes

$$(\vec{x},\vec{y}) = g_{ij}x^iy^j = x^iy_i = x_iy^j \tag{25}$$

$$= g^{ij}x_iy_j \tag{26}$$

while the norm is expressed by

$$N\vec{x} = x^ix_i = g^{ij}x_ix_j \tag{27}$$

For a transformation of basis defined by

$$\vec{e}_i = B^j_i\vec{e}'_j \quad ; \quad \vec{e}'_j = A^i_j\vec{e}_i \tag{28}$$

the contravariant components transform according to the scheme

$$x^i = A^i_jx'^j \quad ; \quad x'^j = B^j_ix^i \tag{29}$$

while the covariant components transform according to the opposite scheme

$$x_i = B^j_ix'_j \quad ; \quad x'_j = A^i_jx_i \tag{30}$$

3. Dual Space and dual basis.

Let $\vec{x}$ be an arbitrary vector of E_n and $f(\vec{x})$ be a linear functional (i.e., a linear transformation of E_n into the reals $\mathbb{R}$ such that, to $\vec{x}$, there corresponds through f a real number):

$$f(\vec{x}+\vec{y}) = f(\vec{x}) + f(\vec{y}) \tag{31}$$

$$f(a\vec{x}) = af(\vec{x}) \tag{32}$$

In the basis $(\vec{e}_i)$, let x^i be the contravariant components of $\vec{x}$:

$$\vec{x} = x^i \vec{e}_i \tag{33}$$

$f(\vec{x})$ becomes

$$f(\vec{x}) = x^i f(\vec{e}_i) = x^i a_i \tag{34}$$

where

$$a_i = f(\vec{e}_i) \tag{35}$$

Let us call E_n^* the set of all the linear functionals f and let us write them as x*, y*,... Therefore

$$y^*(\vec{x}) = y_i^* x^i \tag{36}$$

Define the composition

$$(y^* + z^*)(\vec{x}) = y^*(\vec{x}) + z^*(\vec{x}) = (y_i^* + z_i^*)x^i \tag{37}$$

$$(ay^*)(\vec{x}) = ay^*(\vec{x}) = ay_i^* x^i \tag{38}$$

The set E_n^* with this operation constitutes a vector space called the *dual space* of E_n.

From equation (36), any linear functional can be expressed in a unique way as a linear combination of the n quantities x^i. The latter constitute a basis for E_n^* and is called the *dual basis* of $(\vec{e}_i)$. In the dual space, a linear functional y* is expressible in a unique way as a linear combination of the dual base vectors x^i as expressed in (36). The quantities y_i^* are the covariant components of y* in the basis (x^i).

Let E_n be euclidean. To any vector $\vec{y}$ of E_n, there corresponds a linear functional defined by the scalar product $(\vec{x},\vec{y})$ (actually this is a particular case of the Riesz theorem). Conversely, to any linear functional y*, there corresponds a unique vector $\vec{y}$ such that $y^*(\vec{x}) = (\vec{x},\vec{y})$. One may then identify the vector $\vec{x}$ of E_n with contravariant components x^i with respect to the basis $(\vec{e}_i)$ to the element of E_n^* of components x_i in the dual basis when those components are related by:

$$x_i = g_{ij} x^j \quad ; \quad x^j = g^{ij} x_i \tag{39}$$

There exists therefore in euclidean spaces an isomorphism between the spaces E_n and E^*_n.

Let us define another dual basis (e^{*i}) such that

$$e^{*i}(\vec{e}_j) = (\vec{e}_i, \vec{e}_j) = g_{ij} \tag{40}$$

We have successively

$$e^{*i}(\vec{x})\ e^{*i}(x^j \vec{e}_j) = (\vec{e}_i, \vec{x}) = x^j g_{ij} = x_i \tag{41}$$

2. AFFINE SPACES

1. Definition.

Let $\mathscr{E}$ be a set of points (A,B,...,) such that to any couple (A,B) one can associate in a 1:1 manner a vector $\vec{a}$ of a n–dimensional vector space E_n and such that

$$(A,B) = -(B,A) \tag{1}$$

$$(A,C) = (A,B) + (B,C) \tag{2}$$

Moreover if, given a point O of $\mathscr{E}$, to each vector $\vec{a}$ of E_n there corresponds one and only one point A such that

$$(O,A) = \vec{a} \tag{3}$$

then the set $\mathscr{E}$ is a (*point*) *affine space* $\mathscr{E}_n$ of dimension n.

2. Coordinate System.

One defines a repere for $\mathscr{E}_n$ in giving a point O and a basis $(\vec{e}_i)$ in E_n. If A is a point of $\mathscr{E}_n$, the *coordinates* of A with respect to the repere

$(O,\vec{e}_i)$ are the components x^i of the vector $\vec{a}$ with respect to the basis $(\vec{e}_i)$. There is a 1:1 mapping between the sets of n reals $(x^1,...,x^n)$ and the points A of $\mathscr{A}_n$ (see condition 3).

Two points A and B of the affine space are defined by their components (x^i) and (y^i) with respect to the repere $(O,\vec{e}_i)$. The components of the vector $(A,B) = (A,O) + (O,B) = (O,B) - (O,A)$ are the n quantities $(y^i - x^i)$

2. Change of repere.

Let $(O,\vec{e}_i)$ and $(O',\vec{e}'_i)$ be two reperes for $\mathscr{A}_n$. One has

$$(O,O') = a^i\vec{e}_i \quad ; \quad (O',O) = b^j\vec{e}'_j \tag{4}$$

respectively the vectors (O,O') and (O',O) in the two bases $(\vec{e}_i)$ and $(\vec{e}'_i)$

$$\vec{e}'_j = A^i_j\vec{e}_i \quad ; \quad \vec{e}_i = B^j_i\vec{e}'_j \tag{5}$$

Let M be a point of $\mathscr{A}_n$ with coordinates x^i with respect to $(\vec{e}_i)$ and x'^j with respect to $(\vec{e}'_j)$. Therefore

$$(O,M) = x^i\vec{e}_i \tag{6}$$

and

$$\begin{aligned}(O,M) &= (O,O') + (O',M)\\ &= a^i\vec{e}_i + x'^j\vec{e}'_j\\ &= (a^i + A^j_i x'^j)\vec{e}'_i\end{aligned} \tag{7}$$

By identification, one obtains

$$x^i = a^i + A^j_i x'^j \tag{8}$$

The inverse transformation gives the components x'^j in terms of the components x^i

$$x'^j = b^j + B^j_i x^i \tag{9}$$

In short hand notation, the vector $\vec{x} = (O,X)$ transforms into a new vector in the same basis according to

$$\vec{x}' = \vec{a} + B\vec{x} \qquad (10)$$

where B is a nonsingular nxn matrix and $\vec{a}$ is a vector of E_n. Such a transformation is an *affine transformation.* The set of all affine transformations constitute the affine group (n^2+n parameters).

3. Affine subspaces.

Any subset $\mathscr{V}$ of an affine space $\mathscr{S}_n$ such that, for any point O of $\mathscr{V}$, the vectors (O,M) which are associated with the points M of $\mathscr{V}$ constitute a vector subspace of E_n. In other words, the set of all vectors $\vec{m} = (O,M)$ constitute a vector space E_r, subspace of E_n and the dimension of $\mathscr{V}$ is r. For example, in the affine space of usual geometry, the planes are affine subspaces of $\mathscr{S}_3$.

4. Euclidean point space.

An euclidean point space is an affine space such that the associated vector space is euclidean. If E_n is properly euclidean, the affine space is also properly euclidean.

Let $(O,\vec{e}_i)$ be a repere for an euclidean point space $\mathscr{S}_n$. The distance between two points A and B can be defined: the square of the distance of the two points is the norm of the associated vector $(A,B)=\vec{x}$. Analytically, if (x^i) and (y^j) are the coordinates of A and B then the components of $\vec{x}$ are the n numbers (y^i-x^i) and the square of the distance

is given by

$$|\vec{x}|^2 = g_{ij}(y^i - x^i)(y^j - x^j) \qquad (11)$$

Consider now the infinitesimal distance between the points X and X+δX. With respect to the repere $(O,\vec{e}_i)$, their coordinates are respectivelly x^i and x^i+dx^i. The square of the infinitesimal distance between X and X+δX is

$$ds^2 = g_{ij}dx^i dy^j \qquad (12)$$

Obviously if the space is properly euclidean and the repere orthonormal, one has

$$ds^2 = (dx^i)(dx^i) = \Sigma_i (dx^i)^2 \qquad (13)$$

Note:

Let $\vec{a}$ be a "covariant" vector that is, a vector having covariant components a_i and $\vec{x}$ be a contravariant vector of components x^i. Construct the linear form

$$L(\vec{x}) = a_i x^i \qquad (14)$$

It is easy to demonstrate that the form $L(\vec{x})$ is invariant under any change of basis:

$$L(\vec{x}) = K \qquad (15)$$

Equation (14) defines a hyperplane in the reduced space of dimension n–1. The concept of covariant vector is therefore related to a system of parallel planes orthogonal to the covariant vector $\vec{a}$, the position of a particular plane is defined by specifying the value of the constant K. For example in a two dimensional space, the relation (14) defines a line. For a_1 and a_2 given, the slope of the line is determined and by specifying the

value of the constant K, the position of the line is uniquely determined:

$$a_1 x^1 + a_2 x^2 = K$$

The line intersects the axis x^1 in K/a_1 and the axis x^2 in K/a_2.

3. TENSOR PRODUCT OF EUCLIDEAN SPACES

Let E_n and F_p be two euclidean vector spaces over the same field and consider the bases $(\vec{e}_i)$ and $(\vec{f}_j)$. Suppose we are given a mapping f which assigns to every pair of vectors $(\vec{v},\vec{w})$, $\vec{v}\in E_n$ and $\vec{w}\in F_p$, a vector denoted by $\vec{v}\otimes\vec{w}$ which belongs to a third vector space L:

$$f:(\vec{v},\vec{w}) \rightarrow \vec{v}\otimes\vec{w}\in L \qquad (1)$$

We suppose further that the mapping f is linear in $\vec{v}$ and $\vec{w}$ separately

$$(\vec{v} + \vec{v}')\otimes\vec{w} = \vec{v}\otimes\vec{w} + \vec{v}'\otimes\vec{w} \qquad (2)$$

$$\vec{v}\otimes(\vec{w} + \vec{w}') = \vec{v}\otimes\vec{w} + \vec{v}\otimes\vec{w}' \qquad (3)$$

$$(a\vec{v})\otimes\vec{w} = \vec{v}\otimes(a\vec{w}) = a(\vec{v}\otimes\vec{w}) \qquad (4)$$

where a is a scalar of the field.

and that the set of np pairs $(\vec{e}_i\otimes\vec{f}_j)$ are mapped into the set $\vec{\sigma}_{ij} \equiv \vec{e}_i\otimes\vec{f}_j$ of linearly independent vectors of L. The vector space spanned by the vectors $\vec{\sigma}_{ij}$ is denoted by $E_n \otimes F_p$ and is called the tensor product space of E_n and F_p.

In the basis $(\vec{\sigma}_{ij})$, a tensor product vector is expressed analytically by

$$\vec{v}\otimes\vec{w} = v^i w^j \vec{\sigma}_{ij} \qquad (5)$$

On the other hand a vector $\vec{\chi}$ of L is expressible in one and only one way by

$$\vec{\chi} = \chi^{ij}\vec{\sigma}_{ij} \qquad (6)$$

The vector space $E_n \otimes F_p$ contains vectors that are not of the form $\vec{v}\otimes\vec{w}$ that is vectors that are not mappings (by f) of any pair $(\vec{v},\vec{w})$ (χ^{ij} can be expressed in many ways as a product of scalars v^i and w^j).

The euclidean metric in E_n and F_p defines an euclidean metric in L: let $\vec{\chi}$ and $\vec{\xi}$ be two vectors of L, then

$$(\vec{\chi},\vec{\xi}) = \chi^{ij}\xi^{kl}g^{e}_{ij}g^{f}_{kl} = \chi^{ij}\xi^{kl}\gamma_{ij,kl} \qquad (7)$$

4. CURVILINEAR COORDINATES IN EUCLIDEAN SPACES

1.Definition.

Let a coordinate system (CS) be arbitrarily defined for the affine vector space $\mathscr{E}_n$ and (x^i) be the set of coordinates of a point M. These coordinates are referred to as the rectilinear coordinates.

Let n continuously differentiable functions $f^i(y^1,...,y^n)$ of the n variables y^i be such that

$$x^i = f^i(y^1,...,y^n) \qquad (1)$$

Suppose the system (1) soluble, then

$$y^i = h^i(x^1,...,x^n) \qquad (2)$$

The functional determinants

$$\partial f^i/\partial y^j = \begin{vmatrix} \partial_1 f^1 & \partial_1 f^2 & \dots & \partial_1 f^n \\ \partial_2 f^1 & \partial_2 f^2 & \dots & \partial_2 f^n \\ & \dots & & \\ \partial_n f^1 & \partial_n f^2 & \dots & \partial_n f^n \end{vmatrix} \qquad (3)$$

and

$$\partial h^i/\partial x^j = \begin{vmatrix} \partial_1 h^1 & \partial_1 h^2 & \dots & \partial_1 h^n \\ \partial_2 h^1 & \partial_2 h^2 & \dots & \partial_2 h^n \\ & \dots & & \\ \partial_n h^1 & \partial_n h^2 & \dots & \partial_n h^n \end{vmatrix} \qquad (4)$$

are non zero.

If the functions f^i are not linear, the set (y^i) is no longer a system of rectilinear coordinates but a curvilinear coordinate system. Any point M is situated at the intersection of n curves which become straight lines for rectilinear coordinates.

At the point M the partial derivatives of a vector $\vec{x} = \overrightarrow{OM}$ may be defined relative to the n variables y^i

$$\vec{e}_i = \partial\vec{M}/\partial y^i \qquad (i=1,\dots,n) \qquad (5)$$

The system of n vectors $\vec{e}_i$ is linearly independent since the functional determinant is not zero. Geometrically, the n vectors $\vec{e}_i$ are collinear to the tangents in M.

The differential of M is expressed by

$$d\vec{M} = \Sigma_i dy^i\vec{e}_i = dy^i\vec{e}_i \qquad (6)$$

where the summation over repeated indices has been adopted.

The n quantities dy^i are the n contravariant components of the vector $d\vec{M}$ in the *local* coordinate system defined at M and having the set $(\vec{e}_i)$ as basis.

Note:

In linear transformations of coordinates, the coefficients A^i_j are constants (transformation of a rectilinear system of coordinates into another rectlinear system). The formulas (28–30) of section 1 are valid uniformly in the whole space and the quantities A and B have a matricial character. In curvilinear transformations the transformations are no longer valid in whole space but rather are taking different values at different points of the space although one should recover the linearity with infinitesimal displacements. This is discussed in the next section.

2.Change of Curvilinear Coordinates.

A change of curvilinear coordinates is performed when the coordinates (y^i) are substituted by a new set (z^i) related to (y^i) by

$$z^j = \alpha^j(y^1,,,,.,y^n) \; ; \; y^i = \beta^i(z^1,...,z^n) \qquad (7)$$

where the functions α^j and β^i are several times continuously differentiable. In doing so a new basis $(\vec{e}'_i)$ is locally defined at the point M so that

$$\vec{e}'_j = \partial\vec{M}/\partial z^j = \Sigma_i(\partial\vec{M}/\partial y^i)(\partial y^i/\partial z^j) \qquad (8)$$

the formulas permitting the transformation are

$$\vec{e}'_j = \Sigma_i(\partial y^i/\partial z^j)\vec{e}_i = \Sigma_i A^i_j \vec{e}_i \qquad (9)$$

$$\vec{e}_i = \Sigma_j(\partial z^j/\partial y^i)\vec{e}'_j = \Sigma_i B^j_i \vec{e}'_j \qquad (10)$$

where

$$A^i_j = \partial y^i/\partial z^j;\ B^j_i = \partial z^j/\partial y^i \qquad (11)$$

To any change of curvilinear coordinates there corresponds a change of the local basis at the point M given by the relations (9–10).

Let $\vec{x}$ be a vector whose contravariant components with respect to the CS $(M,\vec{e}_i)$ are the set (x^i). Under the change of CS $(M,\vec{e}_i) \rightarrow (M,\vec{e}'_i)$ defined by the relations (9–10 the components transform according to

$$x^k = \Sigma_m A^k_m x'^m \quad ; \quad x'^m = \Sigma_k B^m_k x^k \qquad (12)$$

The matrix elements A^k_m and B^m_j are related by the relation

$$B^m_k = (\text{minor of } A^k_m)/(\text{determinant of A}) \qquad (13)$$

so that

$$\Sigma_k A^k_m B^m_j = \delta^k_j \qquad (14)$$

Since the contravariant components of the infinitesimal vector $d\vec{M}$ are dy^i with respect to the local basis defined at M, the square of $d\vec{M}$ is given by

$$|d\vec{M}|^2 = (d\vec{M},d\vec{M}) = ds^2 = g_{ij}dy^i dy^j \qquad (15)$$

where

$$g_{ij} = (\vec{e}_i,\vec{e}_j) \qquad (16)$$

are the elements of the metric tensor of the CS $(M,\vec{e}_i)$.

When M varies the functions g_{ij} vary as some function of the coordinates y^i. ds^2 is the metric of the space. The length of an arc in $\mathscr{E}_n$ can be evaluated: let the curves defined by the coordinates y^i depends upon the parameter t and vary in the interval [A,B]. The length of the curve between the two space points A and B is given by

$$\text{arc(AB)} = \int_a^b g_{ij}(dy^i/dt)(dy^j/dt)dt \qquad (17)$$

Similarly the volume element is given by

$$dV = |g|^{\frac{1}{2}} dy^1 dy^2 ... dy^n \tag{18}$$

where $|g|$ is the determinant of the (g_{ij}).

Note 1: Geometric interpretation of the coefficients g_{ij}

Along the axis i (vector $\vec{e}_i$), to a displacement dy^i, there corresponds a real length

$$dl^i = |\vec{e}_i| dy^i \tag{N1.1}$$

From (15), if all the other components are zero, the square of the length is given by

$$ds^2 = g_{ii}(dy^i)^2 \tag{N1.2}$$

That is

$$g_{ii} = |\vec{e}_i|^2 \tag{N1.3}$$

Similarly, one obtains the value of g_{ij}

$$g_{ij} = (g_{ii} g_{jj})^{1/2} \cos\theta_{ij} \tag{N1.4}$$

This interpretation clarifies the concept of orthogonal curvilinear coordinates. To a diagonal tensor g, there corresponds a set of orthogonal curvilinear coordinates. Of course the concept of orthonormal curvilinear coordinates does not make any sense.

Note 2: Diagonalization of the tensor g

A space is euclidean when the coefficients g_{ij} are constant. In general (Riemann spaces), the coefficients are function of the coordinates.

In taking their value at a particular point, one can define an euclidean space (g_{ij} are constants): this space is called the *tangent euclidean space* to the Riemann space at this point. The reduction of the tensor g to a diagonal form can be carried out in a similar way as for the euclidean spaces by using infinitesimals. The same procedures are used. The example of the "*infinitesimal Gram–Schmidt*" orthonormalization is carried out hereafter.

Let us choose a new axis $\bar{x}^1$, to an infinitesimal displacement $d\bar{x}^1$, there corresponds ds^2:

$$\bar{e}_1 = A^k_1 e_k \quad ; \quad dx^i = A^i_1 d\bar{x}^1 \tag{N2.1}$$

$$ds^2_1 = g_{ik} A^i_1 A^k_1 (d\bar{x}^1)^2 = (d\bar{x}^1)^2 \tag{N2.2}$$

that is

$$\bar{g}_{11} = g_{ik} A^i_1 A^k_1 = 1 \tag{N2.3}$$

This particular direction being chosen, one proceeds to reduce the dimension of the space by one unit. A vector $\vec{\delta x}$ is decomposed into a component $\vec{\delta x}^1$ in the direction $\bar{e}_1$ and a component $\vec{\delta x}^*$ in a n–1 dimensional space but orthogonal to the new axis $\bar{x}^1$

$$\vec{\delta x} = \vec{\delta x}^1 + \vec{\delta x}^* \tag{N2.4}$$

with

$$(\vec{\delta x}, \bar{e})_1 = g_{ik} \delta x^{*1} A^k_1 = 0 \tag{N2.5}$$

This condition expresses the orthogonality of the vector $\vec{\delta x}^*$ of components δx^{*1} with the vector $\bar{e}_1$ of components A^k_1. The length of the vector $\vec{\delta x}$ is given by

$$\delta s^2 = g_{ik} [A^i_1 \delta\bar{x}^1 + \delta x^{*i}][A^k_1 \delta\bar{x}^1 + \delta x^{*k}] \tag{N2.6}$$

since every component δx^i is the sum of $\delta\bar{x}^1$ referred to the direction A^i_1 and of the remaining δx^{*1}, orthogonal to $\delta\bar{x}^1$. The development of (N2.6)

gives

$$\delta s^2 = \bar{g}_{11}(\delta\bar{x}^1)^2 + g_{ik}A^i_1\delta\bar{x}^1\delta x^{*k} + g_{ik}A^k_1\delta\bar{x}^1\delta x^{*i} + g_{ik}\delta x^{*i}\delta x^{*k}$$

The two first sums are zero (according to N2.5) so that

$$\delta s^2 = \bar{g}_{11}(\delta\bar{x}^1)^2 + \delta s^{*2} \qquad \text{(N2.7)}$$

$$\delta s^{*2} = g_{ik}\delta x^{*i}\delta x^{*k} \qquad \text{(N2.8)}$$

The term δs^{*2} corresponds to the n–1 dimensional space. In continuing the procedure, one finally obtains the new axes $\bar{x}^1$, $\bar{x}^2$, $\bar{x}^n$ which decompose the ds^2 into a sum of squares

$$ds^2 = \bar{g}_{kk}(d\bar{x}^k)^2 = (d\bar{x}^k)^2 \qquad \text{(N2.9)}$$

3. Tensor fields.

With any point of $\mathscr{E}_n$ we may associate some euclidean tensor defined with respect to the local basis $(\vec{e}_i)$ defined at M. The CS $(M,\vec{e}_i)$.defines bases in the euclidean space E_n for the tensor products of E_n. In doing so, one defines a *tensor field* in the CS (y^i). To any change of coordinates $(y^i) \rightarrow (z^j)$, there corresponds a change of the local basis $(\vec{e}_i) \rightarrow (\vec{e}'_j)$ and any tensor t will transform according to the formula

$$t^{ij}_k = B^i_j B^j_m A^n_k t'^{lm}_n \qquad (19)$$

where the summation convention is used. The A and B are defined by the relations (11). In the present context, the covariant metric tensor g_{ij} transforms according to the formula

$$\boxed{g_{ij} = A^k_i A^l_j g'_{kl}} \qquad (20)$$

In order to compare the metric tensor at two different points M and M', one must know how the local bases at points M and M' are related to

each other since the tensors are defined in terms of the two bases. In other words, the problem can be set up as follows:

The euclidean space E_n being defined in terms of curvilinear coordinates (y^i) for which the metric is given by $ds^2 = g_{ij}dy^i dy^j$, to determine the basis $(M+\vec{dM}, \vec{e}_i+\vec{de}_i)$ relative to the basis $(M,\vec{e}_i)$.

The local basis in $M+\vec{dM}$ will be determined once the contravariant components of the vectors $\vec{dM}$ and $\vec{de}_i$ will be expressed in terms of the CS $(M,\vec{e}_i)$.

The contravariant components of $\vec{dM}$ are given by

$$\vec{dM} = dy^i\vec{e}_i \tag{21}$$

The vector $\vec{de}_i$ is expressed in terms of the base vectors $\vec{e}_i$ by

$$\vec{de}_i = \Omega^j_i\vec{e}_j \tag{22}$$

The components Ω^j_i are expressible in terms of the differentials dy^k since

$$\vec{de}_i = \partial_k\vec{e}_j \quad (\partial_k\vec{e}_i \equiv \partial\vec{e}_i/\partial y^k) \tag{23}$$

and the vectors $\partial_k\vec{e}_i$ are vectors of $\mathscr{E}_n$ hence expressible in terms of the base vectors $\vec{e}_i$ by

$$\partial_k\vec{e}_i = \Gamma^i_{kl}\vec{e}_l \tag{24}$$

so that equation (23) becomes

$$\vec{de}_i = \Sigma_{lk}\Gamma^l_{ki}dy^k\vec{e}_l \tag{25}$$

Finally

$$\Omega^j_i = \Gamma^j_{ki}dy^k \tag{26}$$

where the Γ^j_{ki} are n^3 functions of the variables (y^k). and equation (22) becomes

$$\vec{de}_i = \Gamma^j_{ki}dy^k\vec{e}_j \tag{27}$$

and the problem reduces to determine the n^3 functions Γ^j_{ki} from the

$n(n+1)/2$ functions g_{ij}.

4.Determination of the coefficients Γ^j_{ki}.

At a point M of $\mathscr{E}_n$, the euclidean metric g_{ij} is defined by

$$g_{ij} = (\vec{e}_i, \vec{e}_j) \tag{28}$$

By differentiation we obtain

$$dg_{ij} = (\vec{e}_i, d\vec{e}_j) + (\vec{e}_j, d\vec{e}_i) \tag{30}$$

hence, by (22)

$$dg_{ij} = \Omega^h_j g_{ih} + \Omega^h_i g_{jh} \tag{31}$$

Recall that the covariant components of a vector $\vec{x}$ are defined by

$$x_i = (\vec{x}, \vec{e}_i) = (x^j \vec{e}_j, \vec{e}_i) = x^j g^{ij} \tag{32}$$

The covariant components of $d\vec{e}_i$ are then given by

$$\Omega_{ij} = (d\vec{e}_i, \vec{e}_j) = (\Omega^k_i \vec{e}_k, \vec{e}_j) = \Omega^k_i g_{jk} \tag{33}$$

This result can be expressed as well in the form

$$\Omega_{ij} = (\Gamma^h_{ki} dy^k \vec{e}_h, \vec{e}_j) = \Gamma^h_{ki} g_{jh} dy^k \tag{34}$$

$$= \Gamma_{kji} dy^k \tag{35}$$

where

$$\Gamma_{kji} = \Gamma^h_{ki} g_{jh} \tag{36}$$

The transformations are summarized in the following table

$$\boxed{\begin{aligned} \Omega_{ij} &= g_{jk} \Omega^k_i \\ \Gamma_{kji} &= g_{jh} \Gamma^h_{ki} \\ \Gamma^j_{ki} &= g^{jh} \Gamma_{khi} \end{aligned}}$$

We can then write dg_{ij} in the form

$$dg_{ij} = \Omega_{ji} + \Omega_{ij}$$

$$= (\Gamma_{kji} + \Gamma_{kij}) dy^k \tag{37}$$

Recalling that

$$dg_{ij} = \partial_k g_{ij} dy^k \tag{38}$$

and identifying the coefficients of dy^k in (37) and (38), we obtain

$$\partial_k g_{ij} = \Gamma_{kji} + \Gamma_{kij} = \Gamma^h_{ki}\, g_{jh} + \Gamma^h_{kj} g_{ih} \tag{39}$$

The system (39) is composed of $n^2(n+1)/2$ equations since there exist $n(n+1)/2$ distinct g_{ij} and the index k runs from 1 to n.

The equations (21) and (22) must be integrable, that is

$$\partial^2_{kj} M = \partial^2_{jk} M \tag{40}$$

and

$$\partial^2_{kj} \vec{e}_i = \partial^2_{jk} \vec{e}_i \tag{41}$$

From equation (5), the integrability condition (40) becomes

$$\overrightarrow{\partial^2_{kj} M} = \partial_k (\overrightarrow{\partial_j M}) = \partial_k \vec{e}_j \tag{42}$$

but from (22)

$$d\vec{e}_j = (\partial_k \vec{e}_j) dy^k = \Gamma^l_{kj} \vec{e}_l dy^k \tag{43}$$

so that

$$\partial_k \vec{e}_j = \Gamma^l_{kj} \vec{e}_l = \overrightarrow{\partial^2_{kj} M} \tag{44}$$

In a similar fashion, we obtain

$$\overrightarrow{\partial^2_{jk} M} = \Gamma^l_{jk} \vec{e}_l \tag{45}$$

By using the integrability condition, we obtain finally

$$\Gamma^l_{kj} = \Gamma^l_{jk} \tag{46}$$

$$\Gamma_{klj} = \Gamma_{jlk} \tag{47}$$

These two systems furnish $n(n-1)/2$ equations for each value of l and since l runs from 1 to n, the sets (46) or (47) furnishes $n^2(n-1)/2$ equations. The systems (39) and (46) provide then n^3 equations for the n^3

unknowns Γ_{kji}. All we have to do is to expressthese equations in terms of the g_{ij} and their derivatives.

5. Determination of the coefficients Γ_{klj}

By cyclic permutation of the indices in equation (39) and taking into account (47), we obtain

$$\Gamma_{jik} + \Gamma_{kji} = \partial_k g_{ij} \tag{48}$$

$$\Gamma_{kji} + \Gamma_{ikj} = \partial_i g_{jk} \tag{49}$$

$$\Gamma_{ikj} + \Gamma_{jik} = \partial_j g_{ki} \tag{50}$$

(48) + (49) − (50) gives

$$2\Gamma_{kji} = \partial_k g_{ij} + \partial_i g_{jk} - \partial_j g_{ki} \tag{51}$$

Let us define the algorithm [ki,j] such as

$$[ki,j] = \Gamma_{kji} = (\partial_k g_{ij} + \partial_i g_{jk} - \partial_j g_{ki})/2 \tag{52}$$

The values of Γ^i_{kj} are determined by

$$\Gamma^i_{kj} = g^{jh}\Gamma_{khi} = g^{jh}[ki,h] \tag{53}$$

Let us define a second algorithm

$$\left(\begin{matrix} j \\ k\ i \end{matrix}\right) = \Gamma^j_{ki} = g^{jh}[ki,h] \tag{54}$$

The two symbols (*Christoffel symbols of first and second kind*, respectively) provide the way to evaluate the values of Γ_{kji} and Γ^j_{ki} from the metric tensor g_{ij} and their derivatives. The problem formulated by equation (27) is then solved either by

$$d\vec{e}_i = \left(\begin{matrix} j \\ k\ i \end{matrix}\right) dy^k \vec{e}_j \tag{55}$$

or by

$$d\vec{e}_i = g^{jh}[ki,h]dy^k\vec{e}_j \tag{56}$$

6.Example: spherical coordinates.

Let

$$x = r\cos\theta\cos\phi$$

$$y = r\cos\theta\sin\phi$$

$$z = r\sin\theta$$

The inverse transformations are

$$r = [x^2 + y^2 + z^2]^{\frac{1}{2}}$$

$$\phi = \mathrm{atn}(y/x)$$

$$\theta = \mathrm{atn}[z/(x^2+y^2)]^{\frac{1}{2}}$$

The rectangular coordinates (cartesian) are

$$x^1 = x;\ x^2 = y;\ x^3 = z$$

while the curvilinear coordinates are

$$y^1 = r;\ y^2 = \phi;\ y^3 = \theta$$

The curves crossing at M are the radius $\overrightarrow{OM}$, the parallel of axis z passing by M and the meridian of center O passing by M. The base vectors are the unit vector along $\overrightarrow{OM}$, the tangent vector to the parallel (length = $r\cos\theta$) and the tangent vector to the meridian (length = r). Notice that the three vectors are always orthogonal whatever the point M. Such curvilinear coordinates are orthogonal curvilinear coordinates.

The metric is

$$ds^2 = dr^2 + r^2\cos^2\theta d\phi^2 + r^2 d\theta^2$$

The components of the metric tensor are then

$$g_{11} = 1$$

$$g_{22} = r^2\cos^2\theta$$

$$g_{33} = r^2$$

$$g_{ij} = 0 \ (i \neq j)$$

Since the metric tensor is diagonal, $g^{ij} = 0$ for $i \neq j$ and

$$[ki,j] = \begin{pmatrix} j \\ k\ i \end{pmatrix} = 0 \text{ for } i \neq j \neq k$$

$$[kk,j] = \frac{1}{2}\,\partial_j g_{kk} \ ; \ \begin{pmatrix} j \\ k\ k \end{pmatrix} = \frac{1}{2} g_{jj}\,\partial_j g_{kk} \text{ for } j \neq k$$

$$[ki,k] = [ik,k] = \frac{1}{2}\partial_i g_{kk}$$

$$\begin{pmatrix} i \\ k\ k \end{pmatrix} = \begin{pmatrix} k \\ i\ k \end{pmatrix} = \frac{1}{2} g_{kk}\,\partial_i g_{kk}$$

7.Change of Coordinates for the coefficients Γ

The coefficients Ω^j_i and Γ^i_{kj} are not the components of tensor quantities. Let the change of basis be defined by the following usual formulas

$$\vec{e}_i = B^{l}_{i\ l}\vec{e}' \ ; \ \vec{e}'_j = A^{k}_{j\ k}\vec{e} \tag{57}$$

where A and B are defined by equation (11). By differentiating (57), we obtain

$$d\vec{e}_i = B^{l}_{i\ l}\overrightarrow{de}' + dB^{l}_{i\ l}\vec{e}' \tag{58}$$

Since

$$d\vec{e}_i = \Omega^{j}_{i\ j}\vec{e} \text{ and } d\vec{e}'_l = \Omega'^{m}_{l\ m}\vec{e} \tag{59}$$

we have successively

$$\Omega^{j}_{i\ j}\vec{e} = B^{l}_{i\ l}\Omega'^{m}_{\ l\ m}\vec{e}' + dB^{l}_{i\ l}\Omega^{j}_{\ i\ l}\vec{e}' \tag{60}$$

$$= B^{l}_{i\ l}\Omega'^{m}_{\ l\ m}A^{j}_{\ m\ j}\vec{e} + dB^{l}_{i\ l}A^{j}_{\ l\ j}\vec{e} \tag{61}$$

Therefore

$$\Omega^{j}_{i} = B^{l}_{i\ l}\Omega'^{m}_{\ l\ m}A^{j}_{\ m} + dB^{l}_{i\ l}A^{j}_{\ l} \tag{62}$$

In terms of the partial differentials, we have

$$\Omega^{j}_{i} = \Gamma^{j}_{ki}dy^{k} \quad ; \quad \Omega'^{j}_{\ i} = \Gamma'^{j}_{ki}dy'^{k} \tag{63}$$

The components dy'^k transform as

$$dy'^k = B^k_m dy^m \tag{64}$$

and since

$$dB^l_i = \partial_k B^l_i dy^k \tag{65}$$

relation (62) becomes

$$\begin{aligned}\Gamma^j_{ki} dy^k &= B^l_i A^j_m \Gamma'^m_{nl} dy'^n + A^j_l \partial_k B^l_i dy^k \\ &= B^l_i B^n_k A^j_m \Gamma'^m_{nl} dy^k + A^j_l dy^k \partial_k B^l_i\end{aligned}$$

hence,

$$\Gamma^j_{ki} = B^l_j A^j_m B^n_k \Gamma'^m_{nl} + A^j_l \partial_k B^l_i \tag{66}$$

8.Absolute differential of a vector

a. Contravariant components

Let $\vec{v}$ be a vector in the space $\mathscr{E}_n$. We want to determine an expression for $d\vec{v}$ corresponding to a change $M \to M + d\vec{M}$. We know that the components v^i of $\vec{v}$ change during the transformation $M \to M + d\vec{M}$, but we must also take into account the change of the local basis $(M,\vec{e}_i) \to (M+d\vec{M},\vec{e}_i+d\vec{e}_i)$

At the point M, we have the expression for $\vec{v}$ in terms of its contravariant components

$$\vec{v} = v^i \vec{e}_i \tag{67}$$

By differentiating, we obtain

$$d\vec{v} = dv^i \vec{e}_i + v^i d\vec{e}_i \tag{68}$$

By using the definition of $d\vec{e}_i$ given by (22), equation (68) becomes

$$\begin{aligned} d\vec{v} &= dv^i\vec{e}_i + v^h\Omega_h{}^i\vec{e}_i \\ &= (dv^i + v^h\Omega_h{}^i)\vec{e}_i \\ &= \nabla v^i\vec{e}_i \end{aligned} \tag{69}$$

The components of the vector $d\vec{v}$ are expressed by

$$\nabla v^i = dv^i + v^h\Omega_h{}^i \tag{70}$$

The quantities ∇v^i transform as contravariant components of a vector whereas dv^i does not. They are called *absolute differentials* of v^i.

Using equation (24), we obtain an alternate definition employing the partial derivatives

$$\begin{aligned} d\vec{v} &= dv^i\vec{e}_i + v^h\Gamma^i_{kh}dy^k\vec{e}_i \\ &= \partial_k v^i dy^k\nabla\vec{e}_i + v^h\Gamma^i_{kh}dy^k\vec{e}_i \\ &= \nabla_k v^i\vec{e}_i dy^k \end{aligned} \tag{71}$$

where we have introduced

$$\nabla_k v^i = \partial_k v^i + v^h\Gamma^i_{kh} \tag{72}$$

We have therefore

$$\nabla v^i = \nabla_k v^i dy^k \tag{73}$$

The components (72) are the components of a tensor, covariant in the derivation index. this tensor is called the *covariant derivative* of the vector $\vec{v}$. the quantities $\partial_k v^i$ are not tensorial quantities.

b.Covariant components.

Let $\vec{v}$ be given by its covariant components v_i. We want to evaluate $d\vec{v}$ by its covariant components ∇v_i. Let $\vec{w}$ be a uniform vector field defined in $\mathscr{E}_n$ hence $d\vec{w} = 0$. The scalar product is

$$(\vec{w},\vec{v}) = w^i v_i \tag{74}$$

By differentiating we obtain (since $d\vec{w}=0$)

$$(\vec{w},d\vec{v}) = w^i dv_i + dw^i v_i \tag{75}$$

By using (73) and $d\vec{w}=0$ (hence, $\nabla w^i=0$), it follows

$$\nabla w^i = dw^i + \Omega^i_h w^h = 0 \tag{76}$$

that is

$$dw^i = -\Omega^i_h w^h \tag{77}$$

therefore

$$(\vec{w},d\vec{w}) = w^i dv_i - \Omega^i_{h\,i} v_i w^h \tag{78}$$

By using (70) and (74)

$$(\vec{w},d\vec{w}) = w^i \nabla v_i = w^i dv_i - v_i \Omega^i_h w^h \tag{79}$$

$$= w^i (dv_i - v_h \Omega^h_i) \tag{80}$$

We obtain finally the expression of the absolute differential of v_i

$$\nabla v_i = dv_i - v_h \Omega^h_i \tag{81}$$

By using the same procedure as in the previous section, we get also

$$\nabla_k v_i = \partial_k v_i - \Gamma^h_{ki} v_h \tag{82}$$

giving the *covariant components of the covariant derivative tensor of the vector* $\vec{v}$ so that

$$\nabla v_i = \nabla_k v_i dy^k \tag{83}$$

Summary.

Absolute differential	Covariant derivative
$\nabla v^i = dv^i + \Omega^i_h v^h$	$\nabla_k v^i = \partial_k v^i + \Gamma^i_{kh} v^h$
$\nabla v_i = dv_i - \Omega^h_i v_h$	$\nabla_k v_i = \partial_k v_i - \Gamma^h_{ki} v_h$

(84)

These results can be generalized to the concept of absolute differential and covariant derivative of a tensor. For example, let us consider the mixed tensor t^j_i

$$\nabla t^j_i = dt^j_i - \Omega^h_i t^h_i \tag{85}$$

The quantities ∇t^j_i are again linear differential forms of the dy^k

$$\nabla t^j_i = \nabla_k t^j_i dy^k \tag{86}$$

where

$$\nabla_k t^j_i = \partial_k t^j_i - \Gamma^h_{ki} t^j_h + \Gamma^j_{kh} t^h_i \tag{87}$$

which are the components of the covariant derivative tensor of the tensor T.

Application to the metric tensor g_{ij}

The absolute differential of g_{ij} is

$$\begin{aligned} \nabla g_{ij} &= dg_{ij} - \Omega^h_i g_{hj} - \Omega^h_j g_{ih} \\ &= 0 \quad \text{(by using equation 26)} \end{aligned} \tag{88}$$

This result is known as the *Ricci theorem*:

The absolute differential of the metric (fundamental) tensor g_{ij} is zero.

9. Differential Operators in Curvilinear Coordinates.

a) Gradient of a scalar field.

Let a field of scalars defined by means of a function ϕ of the curvilinear coordinates y^i. Since ϕ is independent of the basis, the absolute differential $\nabla\phi$ reduces to the ordinary differential $d\phi$ which is itself a scalar. Similarly, the covariant derivative tensor reduces to the vector of components $\nabla_k \phi = \partial_k \phi$. By changing the basis, the components

of this vector transform in a covariant way. This vector is the *gradient* of the scalar ϕ

$$\vec{u} = \overrightarrow{\text{grad}\phi} = \partial_i \phi \vec{e}_i \tag{89}$$

The components are usually written as follows

$$u_k = \text{grad}_k \vec{u}\phi = \nabla_k \phi = \partial_k \phi \tag{90}$$

We may define the contravariant components u^k

$$\text{grad}^k \phi = g^{ik} \partial_k \phi \tag{91}$$

The *norm* of the gradient (Beltrami differential parameter of first order) is given by

$$\Delta_1 \phi = g^{ij} \partial_i \phi \partial_j \phi \tag{92}$$

b) Curl of a vector field.

Let $\vec{v}$ be a vector of a vector field defined in $\mathscr{E}_n$ by the covariant components v_i. Recall the covariant derivative given in terms of the covariant components:

$$\nabla_j v_i = \partial_j v_i - \Gamma^k_{ji} v_k \tag{93}$$

By permuting the indices i and j in (93) and using the symmetry of Γ in their lower indices

$$\Gamma^k_{ji} = \Gamma^k_{ij} \tag{94}$$

we get

$$\nabla_i v_j = \partial_i v_j - \Gamma^k_{ji} v_k \tag{95}$$

(93)–(95) gives

$$\nabla_j v_i - \nabla_i v_j = \partial_j v_i - \partial_i v_j = r_{ij} \tag{96}$$

which are the covariant components of a twice covariant tensor R. It is obvious that R is an anti– symmetric tensor. This tensor is called the *curl*

tensor of the vector $\vec{v}$

$$\underset{ij}{\text{curl}}\,\vec{v} = \partial_j v_i - \partial_i v_j \tag{97}$$

If the vector $\vec{v}$ is itself a gradient of some scalar ϕ, then the curl of the gradient of ϕ is zero since $\partial^2_{ij}\phi = \partial^2_{ji}\phi$

$$\text{curl}\,\overrightarrow{\text{grad}\phi} = 0 \tag{98}$$

c) Divergence of a vector field.

Let $\vec{v}$ be a vector of a vector field defined in $\mathscr{E}_n$ by the contravariant components v^i. The divergence of $\vec{v}$ is the scalar defined by

$$\overrightarrow{\text{div}}\,\vec{v} = \nabla_i v^i \tag{99}$$

From the expression of the covariant derivative given by (72), we deduce

$$\overrightarrow{\text{div}}\,\vec{v} = \partial_i v^i + \Gamma^i_{ih} v^h \tag{100}$$

By using Ricci theorem, the quantities Γ^i_{ih} are given by

$$\Gamma^i_{ih} = \tfrac{1}{2} g^{ij} \partial_h g_{ij} \tag{101}$$

$$= \tfrac{1}{2} g^{-1} \partial_h g = \frac{\partial_h |g|^{1/2}}{|g|^{1/2}} \tag{102}$$

and the divergence can be written

$$\overrightarrow{\text{div}}\,\vec{v} = |g|^{-1/2} \partial_i [|g|^{1/2} v^i] \tag{103}$$

d) Laplacian of a scalar function ϕ

In $\mathscr{E}_n$, the *laplacian* (Beltrami differential parameter of second order) of a function ϕ is the operator

$$\Delta_2 \phi = \text{div}\,\overrightarrow{\text{grad}}\,\phi \tag{104}$$

By substituting the expressions of the gradient and the divergence one obtains

$$\Delta_2 \phi = g^{ij}[\partial_{ij} - \Gamma^k_{ij} \partial_k]\phi \qquad (105)$$

where ∂_{ij} stands for the second derivative with respect to y^i and y^j.

APPENDIX 2

ROTATIONS IN 3–D SPACE

1.–Definition

Recall that a rotation in 3d–euclidean space is a linear transformation leaving one point fixed (origin of the reference frame) such that all distances and angles are conserved as well as the handedness of the frame. This can be expressed by:

$$R: \vec{q} \to \vec{r} = R\vec{q} \quad (\vec{q} \text{ is transformed into } \vec{r} \text{ under R})$$

$$R: (\vec{q},\vec{r}) \to (R\vec{q},R\vec{r}) \equiv (\vec{q},\vec{r}) \quad \text{(scalar product conserved)}$$

$$R: \vec{q}\times\vec{s} \to R\vec{q}\times R\vec{s} \equiv R\vec{q}\times\vec{s} \quad \text{(vector product rotated)}$$

It is well known that a rotation leaves all points fixed along some line through the fixed point: the axis of rotation $\vec{u}$ is a unit vector along this fixed line. A rotation is then characterized by an axis and an angle ϕ of rotation ($0 \le \phi \le 2\pi$) and is denoted by $R(\phi,\vec{u})$. The rotated vector $R\vec{q}$ can be expressed as the linear combination:

$$R(\phi,\vec{u}): \vec{q} \to R\vec{q} = \cos\phi.\vec{q} + (1-\cos\phi)(\vec{u},\vec{q})\vec{u} + \sin\phi(\vec{u}\times\vec{q})$$

2.–The set of all rotations forms a group.

The product of two rotations, denoted by R_1R_2 is obtained rotating the system by R_2 followed by the rotation R_1. Clearly, the product is associative: $(R_1R_2)R_3 = R_1(R_2R_3) = R_1R_2R_3$. The inverse of

the rotation $R(\phi,\vec{u})$ is $R(-\phi,\vec{u})$ and is denoted by $R^{-1}(\phi,\vec{u})$. The identity is $R(0,\vec{u})$, $\vec{u}$ being arbitrary (i.e., no rotation).

In general, rotations do not commute: $R_1R_2 \neq R_2R_1$. However, rotations having a common axis $\vec{u}$ commute and form then an abelian subgroup:

$$R(\phi,\vec{u})R(\phi',\vec{u}) = R(\phi',\vec{u})R(\phi,\vec{u}) = R(\phi+\phi',\vec{u})$$

Finally, rotations having same angle ϕ form a normal subgroup and define an equivalence class C_ϕ: for an arbitrary rotation S, one has:

$$SR(\phi,\vec{u})S^{-1} = R(\phi,S\vec{u})$$

3.–The group of rotation can be represented by SO(3)

In order to obtain a matrix representation of the group of rotations, let us choose some fixed orthonormal basis $\{\vec{e}_\alpha\}$ having origin at the fixed point O. Any vector $\vec{q}$ of the physical space is represented by the column matrix $\bar{q} \equiv (q^1,q^2,q^3)^t$ with $q^\alpha = (\vec{q},\vec{e}_\alpha)$. Therefore, a rotation R has a well defined action on the base vectors (**passive meaning:** the frame is rotated whereas the vectors are unchanged but received new labels $\{q'^\alpha\}$; **active meaning:** each vector is transformed and the frame is invariant).

Consider the 3×3 matrix [R] whose elements are:

$$[R]_{\alpha\beta} = (\vec{e}_\alpha,R\vec{e}_\beta)$$

To each rotation R there corresponds one matrix [R] and the action of a rotation R on an arbitrary vector $\vec{q}$ is well defined:

$$R\vec{q} = \sum_\alpha(\Sigma_\beta[R]_{\alpha\beta}q^\beta)\vec{e}_\alpha$$

Writing the vectors $\vec{q}$ and $R\vec{q} = \vec{q}'$ as column matrices $\bar{q}$ and $\bar{q}'$, one obtains the matrix equation $\bar{q}' = [R]\bar{q}$.

One can now show that the matrices [R] form the group of real, proper orthogonal 3×3 matrices SO(3), i.e., real coefficients, detR = +1 and $R^t = R^{-1}$. That [R] belongs to SO(3) is shown in note (1) below. The homomorphism R → [R] ≡ SO(3) is a representation of the group of rotations defined relative to the fixed reference frame $\{\vec{e}_\alpha\}$. It can also be shown that a matrix [R]ϵSO(3) does not necessarily determine a unique rotation.

4.–Parameterizations of the Group of Rotations.

The representation of rotations by SO(3) can be implemented by various parameterizations. we shall concern ourselves with the two most common: (a) the $(\phi,\vec{u})$ and (b) the Euler angles $(\alpha_1,\alpha_2,\alpha_3)$.

Any matrix of SO(3) has 3×3=9 entries; from the orthogonality relation $RR^t = I_3$, there exists therefore 6 relationships between those 9 entries leaving three independent parameters which can be taken arbitrarily provided the orthogonality is respected.

The $(\phi,\vec{u})$ parameters.

Wrt the inertial frame $\{\vec{\ell}_\alpha\}$, let u^α be the component of the unit vector $\vec{u}$: $u^\alpha = (\vec{u},\vec{\ell}_\alpha)$. Construct the skew–symmetric matrix N such that:

$$N_{\alpha\beta} = -n^\gamma \qquad (\alpha,\beta,\gamma \text{ are cyclic permutations})$$

The rotation matrix $[R(\phi,\vec{u})]$ takes the form:

$$[R(\phi,\vec{u})] \equiv I_3 + \sin\phi N + (1-\cos\phi)N^2$$

Noting that $N^3 = -N$, one can use also the exponential form:

$$[R(\phi,\vec{u})] = e^{\phi N}$$

using the well known exponential function of matrices:

$$e^{A} = \sum_{p=0}^{\infty} \frac{A^{p}}{p!}$$

The domain of definition of the parameters, $0 \leq \phi \leq \pi$, $(\vec{u},\vec{u}) = 1$, covers exactly once the elements of the group SO(3), except that, for $\phi=\pi$, $\vec{u}$ and $-\vec{u}$ determine the same rotation.

The inverse relationship, expressing ϕ and $\vec{u}$ in terms of [R] is:

$$\cos\phi = (\mathrm{tr}(R) - 1)/2$$

$$u^{\alpha}\sin\phi = -([R]_{\beta\gamma} - [R]_{\gamma\beta}) \qquad (\alpha,\beta,\gamma \text{ are cyclic perm.})$$

The angle ϕ and the polar angles (θ,φ) of the unit vector $\vec{u}$ wrt the inertial frame $\{\vec{\ell}_{\alpha}\}$ constitutes another appropriate set of parameters for the rotation matrix [R]

One shows easily that:

$$u^{1} = \sin\theta\cos\varphi \quad ; \quad u^{2} = \sin\theta\sin\varphi \quad ; \quad u^{3} = \cos\theta$$

The Euler Angles.

If we consider the active transformation, then $R(\vec{\alpha})$ maps an arbitrary vector $\vec{q}$ to the new vector $\vec{q}' = R(\vec{\alpha})\vec{q}$. The components of $\vec{q}'$ are related to those of $\vec{q}$ (in the inertial frame) by:

$$\vec{q}' = [R(\vec{\alpha})]\vec{q}$$

where, (R_{λ} being a rotation of α_{λ} about $\vec{\ell}_{\lambda}$)

$$[R] = R_1 R_2 R_3$$

$$= \begin{bmatrix} \cos\alpha_1 & -\sin\alpha_1 & 0 \\ \sin\alpha_1 & \cos\alpha_1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \cos\alpha_2 & 0 & \sin\alpha_2 \\ 0 & 1 & 0 \\ -\sin\alpha_2 & 0 & \cos\alpha_2 \end{bmatrix} \begin{bmatrix} \cos\alpha_3 & -\sin\alpha_3 & 0 \\ \sin\alpha_3 & \cos\alpha_3 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} c_1c_2c_3 - s_1s_3 & -c_1c_2s_3 - s_1c_3 & c_1s_2 \\ s_1c_2c_3 + c_1s_3 & -s_1c_2s_3 + c_1c_3 & s_1s_2 \\ -s_2c_3 & s_2s_3 & c_2 \end{bmatrix}$$

The domain of definition is:

$$0 \leq \alpha_1 < 2\pi \quad ; \quad 0 \leq \alpha_2 \leq \pi \quad ; \quad 0 \leq \alpha_3 < 2\pi$$

Distinct sets of numbers $\{\vec{\alpha}\}$ lying in these intervals correspond to different rotations except for $\alpha_2 = 0$ or $\alpha_2 = \pi$. In the first case, the rotation is through an angle $\alpha_1 + \alpha_3$ about $\vec{\ell}_3$; in the second case, the rotation is through $\alpha_1 - \alpha_3$ about $\vec{\ell}_3$. In these cases, distinct values of α_1 and α_3 may determine the same rotation.

The inverse of $R(\vec{\alpha})$ is $R^{-1}(\vec{\alpha}) = R(2\pi-\alpha_3, \pi-\alpha_2, 2\pi-\alpha_1)$

The frame new $\{\vec{f}_\lambda\}$ is obtained from $\{\vec{\ell}_\lambda\}$ by application of the rotation $R = R_1R_2R_3$ in the passive interpretation; the matrix elements appear as the direction cosines between axes: $R_{\lambda\mu}(\vec{\alpha}) = (\vec{\ell}_\lambda, \vec{f}_\mu)$

5.–Infinitesimal Generators of SO(3)

We assign the null parameters to the identity element $R(\vec{0})$ Let us now investigate the properties of the group elements in the neighborhood of the identity element. For sufficiently small values of the parameters we

may represent an element $R(\vec{\alpha})$ lying close to the identity by a Taylor expansion:

$$R(\vec{\alpha}) = R(\vec{0}) + \sum_{\lambda=1}^{\lambda=3} \alpha_\lambda \left[\frac{\partial R}{\partial \alpha_\lambda}\right]_{\alpha_\lambda=0} + \frac{1}{2}\sum_{\lambda,\mu=1}^{\lambda,\mu=3} \alpha_\lambda \alpha_\mu \left[\frac{\partial R}{\partial \alpha_\lambda}\right]_{\alpha_\lambda=0}\left[\frac{\partial R}{\partial \alpha_\mu}\right]_{\alpha_\mu=0} + O(\alpha^3)$$

$$R(\vec{\alpha}) = R(\vec{0}) + \sum_{\lambda=1}^{\lambda=3} \alpha_\lambda X_\lambda + \frac{1}{2}\sum_{\lambda,\mu=1}^{\lambda,\mu=3} \alpha_\lambda \alpha_\mu X_\lambda X_\mu + O(\alpha^3)$$

where:

$$X_\lambda = \left[\frac{\partial R}{\partial \alpha_\lambda}\right]_{\alpha_\lambda=0}$$

The X_λ are referred to as the infinitesimal group generators of SO(3). If the inverse element $R(\vec{\alpha})^{-1}$ is also in the neighborhood of the identity, then writing:

$$R(\vec{\alpha}) = R(\vec{0}) - \sum_{\lambda=1}^{\lambda=3} \alpha_\lambda X_\lambda + \frac{1}{2}\sum_{\lambda,\mu=1}^{\lambda,\mu=3} \alpha_\lambda \alpha_\mu X_\lambda X_\mu + O(\alpha^3)$$

we have:

$$R(\vec{\alpha})^{-1} R(\vec{\alpha}) = R(\vec{0}) + O(\alpha^2)$$

Let us define the commutator of two group elements $R(\vec{\alpha})$ and $R(\vec{\alpha}')$ lying near the identity as

$$R(\vec{\alpha})^{-1} R(\vec{\alpha}')^{-1} R(\vec{\alpha}) R(\vec{\alpha}')$$

The commutator must itself define a group element $R(\vec{\alpha}'')$ lying close to the identity. Therefore, for sufficiently small values of the parameters, we find, to second order in α and α':

$$R(\vec{\alpha}'') = R(\vec{0}) + \Sigma \alpha_\lambda \alpha_\mu [X_\lambda, X_\mu]$$

where $[X_\lambda, X_\mu] = X_\lambda X_\mu - X_\mu X_\lambda$

is the commutator of the group generators.

With the above parameterization in terms of Euler angles, we obtain:

$$X_1 = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X_2 = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{bmatrix}$$

$$X_3 = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

APPENDIX 3

ROTATION MATRICES AND ANGULAR MOMENTUM

1. Definitions

Let $|\Psi>$ be the state of the system, i.e., a vector of the state space (separable infinite Hilbert space) and let $\{|\vec{q}(i)>\}$ be the usual orthonormal basis; $|\vec{q}(i)>$ is the shorthand notation for the tensor product

$$|\vec{q}(i)> = |q^{11}>\otimes|q^{12}>\otimes|q^{13}>\otimes....\otimes|q^{n-1,3}> \qquad (1)$$

$|\vec{q}(i)>$ represents a state in which particle (i) is perfectly localized at the point $\vec{q}(i)$. The corresponding *wave function* is

$$<\{\vec{q}(i)\}|\Psi> = \psi(q^{i\beta}) \qquad (2)$$

that is a function of the 3N–3 coordinates $q^{i\beta}$.

Under a rotation $\mathcal{R}$, the state $|\Psi>$ transforms into a new state $|\Psi'>$

$$|\Psi'> = \mathcal{R}[|\Psi>] = \mathcal{U}|\Psi> \qquad (3)$$

while conserving the physical properties of the system. It is easy to show that $\mathcal{U}$ is a unitary operator acting in the state space. This sets up a 1:1 correspondence between the rotations $\mathcal{R}$ of the 3–d euclidean space and the unitary operators of the state space. Actually, this is true for any transformation $\mathcal{T}$ of the configuration space). $\mathcal{U}$ is called the *rotation operator* (this is true only for infinitesimal rotations, for finite rotations, there correspond two rotation operators $\mathcal{U}'$ and $\mathcal{U}''$ related by

$$\mathcal{U}'' = D\mathcal{U}' \qquad (4)$$

where D=1 for J integral and −1 for J half integral)

With respect to the wave functions, the value of the components of $|\Psi'>$ at a given point $\vec{q}(i)$ of the configuration space is equal to the value of the $|\Psi>$ at the point $\vec{q}_o(i)$ which transforms into $\vec{q}(i)$ by the rotation $\mathcal{R}$

$$\psi'(\vec{q}(i)) = \psi(\mathcal{R}^{-1}\vec{q}(i)\ ) \tag{5}$$

therefore

$$<\vec{q}(i)|\,\mathcal{U}|\,\Psi> = <\mathcal{R}^{-1}\vec{q}(i)|\,\Psi> = <\vec{q}'(i)|\,\Psi> \tag{6}$$

or

$$<y^{i\beta}|\,\Psi> = <q^{i\beta}|\,\mathcal{U}|\,\Psi> \tag{7}$$

Under the rotation $\mathcal{R}$, the observables of the system undergo the same unitary transformation as the state vectors: if $\mathcal{Q}$ is an observable, $\mathcal{R}[\mathcal{Q}] = \mathcal{Q}'$ with $\mathcal{Q}' = \mathcal{U}\mathcal{Q}\mathcal{U}^{\dagger}$. In particular, any scalar observable $\mathcal{S}$ (i.e., invariant under the rotations) commutes with $\mathcal{U}$:

$$\mathcal{S}' = \mathcal{U}\mathcal{S}\mathcal{U}^{\dagger} = \mathcal{S} \Rightarrow [\mathcal{U},\mathcal{S}] = 0 \tag{8}$$

If $\vec{\mathcal{B}} = (\mathcal{B}_1,\mathcal{B}_2,\mathcal{B}_3)$ is a vector operator (see footnote) attached to the system where $\mathcal{B}_\beta = (\vec{\mathcal{B}},\vec{u}_\beta)$, then

$$\mathcal{U}\mathcal{B}_\beta\mathcal{U}^{-1} = \sum_\gamma \mathcal{R}^t_{\beta\gamma}\,\mathcal{B}_\beta \tag{9}$$

The fundamental commutation relation characterizing the *total angular momentum* J is

$$[(\vec{J},\vec{u}),(\vec{\mathcal{K}},\vec{a})] = i(\vec{u}\times\vec{a},\vec{\mathcal{K}}) \tag{10}$$

where $\vec{\mathcal{K}}$ is any vector operator.

Corresponding to a rotation along an axis $\vec{u}$ through an infinitesimal angle ϵ, the infinitesimal operator in state space is expressed in terms of the total angular momentum $\vec{J}$

$$\mathcal{R}(\epsilon,\vec{u}) = \mathcal{I} - i\epsilon(\vec{J},\vec{u}) \tag{11}$$

where $\mathcal{I}$ is the identity operator in state space and $(\vec{J},\vec{u})$ is the component of $\vec{J}$ along $\vec{u}$. For a finite rotation $\mathcal{R}(\theta_s)$ parameterized by the Euler angeles θ_s, the corresponding rotation operator (parameterized by the angles θ_s as well) is given by the relation

$$\mathcal{U}(\theta_s) = \exp(-i\theta_1 J_3)\exp(-i\theta_2 J_2)\exp(-i\theta_3 J_3) \qquad (12)$$

The usual representations of the rotation operator are obtained choosing the standard bases $|kJM\rangle$, common eigenkets of the hamiltonian operator $\mathcal{H}$, J^2 and J_3. The 2J+1 vectors $|kJM\rangle$ with k and J fixed, M variable, have same energy.

With respect to these bases, the components J_β of the total angular momentum operator are represented by the $(2J+1)\times(2J+1)$ matrices $J_\beta^{(J)}$ acting in the invariant subspaces $\mathcal{E}_J$ (irreducible with respect to the rotation operator). The angular momentum matrices $J_\beta^{(J)}$ are obtained from the characteristic equation

$$\prod_{M=-J}^{M=J} (J_\beta^{(J)} - MI^{(J)}) = 0 \qquad (13)$$

where $I^{(J)}$ is the unit matrix of dimension (2J+1).

The general matrix element of the angular momentum operator $\vec{J}$ is given by

$$\langle kJ'M'|J_\pm|kJM\rangle = [(J\mp M)(J\pm M+1)]^{1/2}\delta_{JJ'}\delta_{M'M\pm1} \qquad (14)$$

$$\langle J'M'|J_3|JM\rangle = M\delta_{JJ'}\delta_{MM'} \qquad (15)$$

where $J_\pm$ are the usual non–hermitian operators

$$J_{\pm} = J_1 \pm iJ_2 \tag{16}$$

The (abstract, hermitian) total angular momentum operator $\vec{J}$ is represented by its action on the eigenkets of any physical system in block form. In general, the block matrix $\vec{J}^{(J)}$ will occur with repetition n_{2J+1}, different for each angular momentum J.

The rotation operator $\mathcal{U}(\theta_s)$ is represented in the same irreducible (2J+1) dimensional spaces $\mathcal{E}_J$ by the *rotation matrices* $D^{(J)}(\theta_s)$

$$D^{(J)}(\theta_s) = \exp(-i\theta_1 J_3^{(J)}) \exp(-i\theta_2 J_2^{(J)}) \exp(-i\theta_3 J_3^{(J)}) \tag{17}$$

with matrix elements

$$D^{(J)}_{M'M} = \langle JM' | \mathcal{U}(\theta_s) | JM \rangle \tag{18}$$

From the group properties of the rotations $\mathcal{R}$, one deduces

$$\mathcal{R}(\theta_s)\mathcal{R}(\theta'_s) = \mathcal{R}(\theta''_s) \Rightarrow \mathcal{U}(\theta_s)\mathcal{U}(\theta'_s) = \mathcal{U}(\theta''_s) \tag{19}$$

$$\Rightarrow$$

$$D^{(J)}(\theta_s)D^{(J)}(\theta'_s) = D^{(J)}(\theta''_s) \tag{20}$$

The general properties of the rotation matrices can be found in reference . Equation (17) gives the complete expression for the elements of the rotation matrices. Using the fact that $J_3^{(J)}$ is diagonal, we find

$$D^{(J)}_{M'M}(\theta_s) = \exp(-iM'\theta_1) d^{(J)}_{M'M}(\theta_2) \exp(-iM\theta_3) \tag{21}$$

where $d^{(J)}_{M'M}(\theta_2)$ is defined by

$$d^{(J)}_{M'M}(\theta_2) = \langle JM' | \exp(-i\theta_2 J_2) | JM \rangle \tag{22}$$

that is

$$d^{(J)}(\theta_2) = \exp(-i\theta_2 J_2^{(J)}) \tag{23}$$

2. Wave Functions for Angular Momentum Systems

It is customary to use the viewpoint of wave functions instead of

that of eigenkets |kJM>. This shift of point of view is not trivial and will be discussed in detail here.

The wave functions for angular momentum systems is understood by considering the product law for rotation matrices

$$D^{(J)}_{MM'}(\theta''_s) = \sum_{M''} D^{(J)}_{MM''}(\theta_s) D^{(J)}_{M''M'}(\theta'_s) \qquad (24)$$

We seek to interpret this result as a transformation induced by the rotation $\mathcal{U}$ acting on the system described by the wave function $D^{(J)}_{M''M'}(\theta'_s)$. Consider this same action of $\mathcal{U}$ on the ket |kJM>

$$\mathcal{U}\colon |kJM> \rightarrow |kJM>' = \mathcal{U}|kJM> = \sum_{M'} D^{(J)}_{M'M}(\theta_s)|kJM'> \qquad (25)$$

since $\mathcal{U}$ transforms |kJM> into |kJM>' belonging to the invariant subspace $\mathcal{E}_J$.

Let us regard the function $D^{(J)}_{MM'}(\theta''_s)$ in equation (24) as the transformed system

$$[D^{(J)}_{MM'}(\theta'_s)]' = D^{(J)}_{MM'}(\theta''_s) \qquad (26)$$

The product law implies that

$$\mathcal{U}\colon D^{(J)}_{MM'}(\theta'_s) \rightarrow [D^{(J)}_{MM'}(\theta'_s)]' = \sum_{M''} D^{(J)}_{MM''}(\theta_s) D^{(J)}_{M''M'}(\theta'_s) \qquad (27)$$

The indices in this equation do not accord with the standard form (25). To remedy this defect, we use the fact that $D^{(J)}$ are unitary: replace $\mathcal{U}$ by $\mathcal{U}^{-1}$ and take the complex conjugate of the equation. We obtain

$$\mathcal{U}\colon D^{(J)}_{MM'}{}^*(\theta'_s) \rightarrow [D^{(J)}_{MM'}{}^*(\theta'_s)]' = \sum_{M''} D^{(J)}_{M''M}(\theta_s) D^{(J)}_{M''M'}{}^*(\theta'_s) \qquad (28)$$

This equation shows that it is the function $D^{(J)}_{MM'}{}^*(\theta_s)$ – as opposed to $D^{(J)}_{MM'}(\theta_s)$ – that transforms properly as *state vectors* carrying angular momentum labels (J,M). This result is true for each M' = J,...,–J.

Alternate proof

Let us write equation (7) in the standard basis

$$<y^{i\beta}|kJM> = <q^{i\beta}|\mathcal{U}|kJM> \qquad (29)$$

Using the transformation (25) for the kets under the rotation operator, we obtain

$$<y^{i\beta}|kJM> = <q^{i\beta}|\Sigma_{M'}D^{(J)}_{M'M}(\theta_s)|kJM'>$$
$$= \Sigma_{M'}D^{(J)}_{M'M}<q^{i\beta}|kJM'> \qquad (30)$$

By taking the complex conjugate, transposing and using $\mathcal{U}^{-1} = \mathcal{U}^{\dagger}$, one obtains

$$<q^{i\beta}|kJM'> = \Sigma_{M}D^{(J)}_{M'M}{}^{*}(\theta_s)<y^{i\beta}||kJM> \qquad (31)$$

By changing M' into M and M into K, one gets

$$<q^{i\beta}|kJM> = \Sigma_{K}D^{(J)}_{MK}{}^{*}(\theta_s)<y^{i\beta}||kJK> \qquad (32)$$

which expresses the relationships between the state vector in the $|q^{i\beta}>$ representation and in the rotated representation $|y^{i\beta}>$. This expresses formally the separation of variables: the wave function $<q^{i\beta}|kJM>$ depends on the $(q^{i\beta})$ while the wave function $<y^{i\beta}|kJM>$ depends upon the rotational invariant $(y^{i\beta})$.

3. Realization with Differential Operators

By differentiating $D^{(J)}(\theta_s)$ (given by equation 17) with respect to θ_s, the following results are obtained

$$\frac{\partial}{\partial\theta_1} D^{(J)}(\theta_s) = -iJ_3^{(J)}D^{(J)}(\theta_s)$$

$$\frac{\partial}{\partial\theta_2} D^{(J)}(\theta_s) = -i(-J_1^{(J)}\sin\theta_1 + J_2^{(J)}\cos\theta_1)D^{(J)}(\theta_s) \qquad (33)$$

$$\frac{\partial}{\partial\theta_3} D^{(J)}(\theta_s) = -i(-J_1^{(J)}\cos\theta_1\sin\theta_2 + J_2^{(J)}\sin\theta_1\sin\theta_2 + J_3^{(J)}\cos\theta_2)D^{(J)}(\theta_s)$$

One can invert those results to obtain the action (realization) of the matrix operators $J_\beta^{(J)}$ on the matrices $D^{(J)}$ as differential operators $\mathscr{J}_\beta$

$$J_\beta^{(J)}D^{(J)}(\theta_s) = -\mathscr{J}_\beta D^{(J)}(\theta_s) \qquad (34)$$

The differential operators are

$$\begin{aligned}
\mathscr{J}_1 &= i[\cos\theta_1\cot\theta_2\,\frac{\partial}{\partial\theta_1} + \sin\theta_1\frac{\partial}{\partial\theta_2} - \frac{\cos\theta_1}{\sin\theta_2}\,\frac{\partial}{\partial\theta_3}] \\
\mathscr{J}_2 &= i[\sin\theta_1\cot\theta_2\,\frac{\partial}{\partial\theta_1} - \cos\theta_1\frac{\partial}{\partial\theta_2} - \frac{\sin\theta_1}{\sin\theta_2}\,\frac{\partial}{\partial\theta_3}] \qquad (35) \\
\mathscr{J}_3 &= -i\,\frac{\partial}{\partial\theta_1}
\end{aligned}$$

The minus sign in equation (34) has been introduced in order to preserve the commutation relation $\vec{\mathscr{J}}\times\vec{\mathscr{J}} = i\vec{\mathscr{J}}$ (actually the sign has its origin in the use of $D^{(J)}_{MM'}{}^*$ as wave function). Expressed in terms of the complex extension $\vec{\mathscr{J}}_\pm$, the relations (35) become

$$\vec{\mathscr{J}}_\pm = \vec{\mathscr{J}}_1 \pm i\vec{\mathscr{J}}_2 = \exp(\pm i\theta_1)[i\cot\theta_2\,\frac{\partial}{\partial\theta_1} \pm \frac{\partial}{\partial\theta_2} - \frac{i}{\sin\theta_2}\,\frac{\partial}{\partial\theta_3}] \qquad (36)$$

We obtain therfore the standard action of the differential operators $\mathscr{J}_\beta$.

$$\mathcal{J}_{\pm} D^{(J)}_{M'M}{}^{*}(\theta_s) = [(J \mp M')(J \pm M' + 1)]^{1/2} D^{(J)}_{M' \pm 1, M}{}^{*}(\theta_s) \tag{37}$$

$$\mathcal{J}_3 D^{(J)}_{M'M}{}^{*}(\theta_s) = M' D^{(J)}_{M'M}{}^{*}(\theta_s) \tag{38}$$

$\vec{\mathcal{J}}$ is the physical total angular momentum operator of the system (differential operator acting in the space of the angular momentum wave functions $D^{(J)}_{M'M}{}^{*}(\theta_s)$. Indeed, take $M = 0$ in equation (21): this removes the angle θ_3 in the rotation matrices and equation (35) just become the expressions for the components of the angular momentum of a single particle where θ_1 and θ_2 are identified respectively to the azimuthal and polar angles of the position vector of the particle. Moreover, since it is consistent to delete $\frac{\partial}{\partial\theta_3}$ in equation (38), this implies that $\frac{\partial}{\partial\theta_3}$ must commute with the $\vec{\mathcal{J}}$ It follows that the hermitian operator $\mathcal{P}_3 = -i\frac{\partial}{\partial\theta_3}$ completes the set of operators defining the rotation wave functions. To the equation (38) we add

$$\mathcal{P}_3 D^{(J)}_{M'M}{}^{*}(\theta_s) = M D^{(J)}_{M'M}{}^{*}(\theta_s) \tag{39}$$

One can now solve equations (35) for $\mathcal{P}_3$

$$\mathcal{P}_3 = \Sigma_\beta R_{\beta 3}(\theta_s)\mathcal{J}_\beta \tag{40}$$

The commutation relations are easily derived

$$[\mathcal{P}_\beta, \mathcal{P}_\gamma] = -i\mathcal{P}_\sigma \quad (\beta,\gamma,\sigma \text{ are cyclic}) \tag{41}$$

$$[\mathcal{P}_\beta, \mathcal{J}_\gamma] = 0 \quad (\beta,\gamma = 1,2,3) \tag{42}$$

4. Physical interpretation of the Angular Momentum Operators

With respect to an inertial frame $\{\vec{\ell}_\alpha\}$, the total angular momentum $\vec{\mathcal{J}}$ is expressed by

$$\vec{\mathcal{J}} = \vec{\ell}_1 \mathcal{J}_1 + \vec{\ell}_2 \mathcal{J}_2 + \vec{\ell}_3 \mathcal{J}_3 \tag{43}$$

It is therefore correct that $\vec{\mathcal{P}}$ is defined by

$$\vec{\mathcal{P}} = \vec{f}_1 \mathcal{P}_1 + \vec{f}_2 \mathcal{P}_2 + \vec{f}_3 \mathcal{P}_3 \tag{44}$$

where $\{\vec{f}_\alpha\}$ is a new frame (noninertial) obtained from $\{\vec{\ell}_\alpha\}$ by the rotation $R(\theta_s)$. $\mathcal{P}_\alpha$ is the component of the total angular momentum referred to the moving frame $\{\vec{f}_\alpha\}$.

The commutation relations of the $\mathcal{J}_\gamma$ with the $R_{\alpha\beta}(\theta_s)$ are easily found

$$[\mathcal{J}_\alpha, R_{\beta\lambda}] = i\epsilon_{\alpha\beta\gamma} R_{\gamma\lambda} \tag{45}$$

where $\{\alpha,\beta,\gamma\}$ are cyclic and λ=1,2,3.

Let $\mathcal{R}(\omega,\vec{n})$ be a rotation of the frame $\{\vec{f}_\alpha\}$ along the axis $\vec{n}$ and about the angle ω. $\mathcal{R}$ transforms $\vec{f}_\alpha$ into $\vec{f}'_\alpha$ hence, $\mathcal{R}(\omega,-\vec{n})\vec{f}_\alpha = \vec{f}'_\alpha$. The component of $\vec{\mathcal{J}}$ along $\vec{n}$ is $(\vec{\mathcal{J}},\vec{n}) = \mathcal{J}_n = \Sigma_\alpha n_\alpha \mathcal{J}_\alpha$.

By using equation (45), one finds the commutator

$$[\mathcal{J}_n, \vec{f}_\alpha] = -i(\vec{n}\times\vec{f}_\alpha) \tag{46}$$

Under the rotation $\mathcal{R}(\omega,\vec{n})$, $\mathcal{J}_\alpha \vec{f}_\beta$ transforms into

$$(\mathcal{J}_\alpha \vec{f}_\beta)' = \mathcal{R}(\omega,\vec{n})\,\mathcal{J}_\alpha \mathcal{R}(\omega,-\vec{n})\vec{f}'_\beta \tag{47}$$

therefore, $\mathcal{J}_\alpha$ transforms into

$$\mathcal{R}(\omega,\vec{n})\,\mathcal{J}_\alpha \mathcal{R}^{-1}(\omega,\vec{n}) = \sum_{k=o}^{k=\infty} \frac{1}{k!} [-i\omega \mathcal{J}_n, \vec{\mathcal{J}}]_{(k)} \tag{48}$$

By using the commutation relation (46), we obtain

$$\vec{f}_\beta = \exp(-i\omega \mathcal{J}_n)\vec{f}_\beta \exp(i\omega \mathcal{J}_n) \tag{49}$$

which expresses the fundamental result:

The total angular momentum operator $\vec{\mathcal{J}}$ *is the generator of the rotations of the moving frame* $\{\vec{f}_\alpha\}$ *and is to be identified as the total angular momentum of a rigid body whose instantaneous orientation is specified by the frame* $\{\vec{f}_\alpha\}$ *which is itself fixed (no relative motion) in the system.*

Remarks

In equation (41), that is the set of operators $-\mathcal{P}_a$ that satisfy the usual commutation relations of angular momentum. This is a direct consequence of the fact that the $\mathcal{J}_a$ do not commute with the rotated axes $\vec{f}_\beta$. Observe also that the $\mathcal{P}_\alpha$ are invariant with respect to the rotations generated by $\vec{\mathcal{J}}$ and $\vec{f}_\alpha$ simultaneously, thereby leaving their scalar product invariant.

Notice also that $\hat{\mathcal{J}}^2 = \mathcal{P}^2$ that is

$$\mathcal{P}^2 D^{(J)}_{M'M}{}^*(\theta_s) = J(J+1) D^{(J)}_{M'M}{}^*(\theta_s) \tag{50}$$

In order to obtain the action of the $\mathcal{P}_\alpha$ on the rotation matrices, transpose equation (34) and use the symmetric and antisymmetric properties of the $J^{(J)}_\alpha$

$$\begin{aligned} J^{t(J)}_1 &= J^{(J)}_1 \\ J^{t(J)}_2 &= -J^{(J)}_1 \\ J^{t(J)}_3 &= J^{(J)}_3 \end{aligned} \tag{51}$$

and

$$D^{t(J)}(\theta_3,-\theta_2,\theta_1) = D^{(J)}(\theta_1,\theta_2,\theta_3) \tag{52}$$

The operators $\mathscr{P}_\alpha$ take now the explicit form

$$\mathscr{P}_- = \mathscr{P}_1 + i\mathscr{P}_2 = \exp(-i\theta_3)[-i\cot\theta_2 \frac{\partial}{\partial\theta_3} + \frac{\partial}{\partial\theta_2} + \frac{i}{\sin\theta_2}\frac{\partial}{\partial\theta_1}] \tag{53}$$

$$\mathscr{P}_+ = \mathscr{P}_1 - i\mathscr{P}_2 = \exp(i\theta_3)[-i\cot\theta_2 \frac{\partial}{\partial\theta_3} - \frac{\partial}{\partial\theta_2} + \frac{i}{\sin\theta_2}\frac{\partial}{\partial\theta_1}] \tag{54}$$

$$\mathscr{P}_3 = -i\frac{\partial}{\partial\theta_3} \tag{55}$$

The action of the body–referred angular momentum operators $\mathscr{P}_\beta$ are now obtained by complex conjugating equation (52) and by taking the matrix elements

$$\mathscr{P}_- D^{(J)}_{M'M}{}^*(\theta_s) = [(J-M)(J+M+1)]^{1/2} D^{(J)}_{M'M+1}{}^*(\theta_s) \tag{56}$$

$$\mathscr{P}_+ D^{(J)}_{M'M}{}^*(\theta_s) = [(J+M)(J-M+1)]^{1/2} D^{(J)}_{M'M-1}{}^*(\theta_s) \tag{57}$$

$$\mathscr{P}_3 D^{(J)}_{M'M}{}^*(\theta_s) = M D^{(J)}_{M'M}{}^*(\theta_s) \tag{58}$$

It is important to notice that is now $\mathscr{P}_-$ *and* $\mathscr{P}_+$ *that are acting as step–up and step–down operators respectively*

Physically, the wave functions $D^{(J)}_{M'M}{}^*(\theta_s)$ are the wave functions of a solid body with center of mass fixed in space: $\mathscr{J}_3$ is the z–component of the angular momentum referred to space–fixed axes while $\mathscr{P}_3$ is the component of the angular momentum referred to the body–fixed z–axis.

APPENDIX 4

DYADICS

The notation of **dyadics** constitutes an alternate way to describe systems of n particles.

A **dyad** is a pair of vectors written in a definite order $\vec{a}\vec{b}$; $\vec{a}$ is the antecedent, $\vec{b}$, the consequent.

We define the scalar products:

$$(\vec{a}\vec{b},\vec{c}) = \vec{a}(\vec{b},\vec{c})$$

$$(\vec{c},\vec{a}\vec{b}) = \vec{b}(\vec{a},\vec{c})$$

$$(\vec{a}\vec{b};\vec{c}\vec{d}) = (\vec{a},\vec{c})(\vec{b},\vec{d}) = (\vec{c},\vec{a}\vec{b},\vec{d})$$

A **dyadic** is a linear polynomial of dyads:

$$\tilde{d} = \Sigma_i \vec{a}_i \vec{b}_i$$

Let $\vec{a}_i$ and $\vec{b}_i$ be expressed in terms of the bases $\{\vec{c}_\alpha\}$ and $\{\vec{e}_\beta\}$ respectively:

$$\vec{a}_i = \Sigma_\alpha a^{i\alpha} \vec{c}_\alpha \qquad\qquad \vec{b}_i = \Sigma_\beta b^{i\beta} \vec{e}_\beta$$

and therefore:

$$\tilde{d} = \Sigma_{\alpha,\beta} A_{\alpha\beta} \vec{c}_\alpha \vec{e}_\beta \qquad \text{with } A_{\alpha\beta} = \Sigma_i a^{i\alpha} b^{i\beta}$$

Take now the scalar products with some vector $\vec{v}$:

$$(\vec{v},\tilde{d}) = (\vec{v},\Sigma_i \vec{a}_i \vec{b}_i) = \Sigma_i (\vec{v},\vec{a}_i \vec{b}_i) = \Sigma_i \vec{b}_i (\vec{a}_i,\vec{v})$$

$$(\tilde{d},\vec{v}) = (\Sigma_i \vec{a}_i \vec{b}_i,\vec{v}) = \Sigma_i \vec{a}_i (\vec{b}_i,\vec{v})$$

The dyadic $\tilde{d}$ may be regarded as an operator acting through the scalar products on a vector $\vec{v}$ from the right or the left to yield a superposition of vectors in a possibly different space

Assume that the bases $\{\vec{c}_\alpha\}$ and $\{\vec{e}_\beta\}$ are orthonormal:

$$(\vec{c}_{\alpha'},\vec{c}_{\alpha'}) = \delta_{\alpha\alpha'} \qquad (\vec{e}_{\beta'},\vec{e}_{\beta'}) = \delta_{\beta\beta'}$$

we obtain a representation of the dyadic $\tilde{d}$ by the m×n matrix by taking the scalar product with the the base vectors:

$$d_{\alpha\beta} = (\vec{c}_\alpha,\tilde{d},\vec{e}_\beta) = \Sigma_i(\vec{c}_\alpha,\vec{a}_i)(\vec{b}_i,\vec{e}_\beta) = \Sigma_i a^{i\alpha} b^{i\beta}$$

With this notation we can encode all the internal position variables of the n–particle system into a single dyadic, denoted by:

$$\tilde{D} = \Sigma_i \vec{e}_i \vec{q}(i) \qquad (i=1,...,n)$$

where the prefactors $\{\vec{e}_n\}$ form the orthonormal basis of the relative label space corresponding to the GJV $\vec{q}(i)$.

The transposed dyadic $\tilde{D}^t$ is defined by:

$$\tilde{D}^t = \Sigma_i \vec{q}(i)\vec{e}_i$$

The individual particle positions are easily recovered by the operations:

$$(\vec{e}_i,\tilde{D}) = (\tilde{D}^t,\vec{e}_i) = \vec{q}(i)$$

in using the orthonormality of the basis $\{\vec{e}_i\}$.

Consider now the two "square" dyadics defined in terms of the n×3 dyadic $\tilde{D}$:

(a) the 3×3 quadrupole dyadic:

$$\tilde{M} = (\tilde{D}^t,\tilde{D}) = \Sigma_{i,j}\vec{q}(i)(\vec{e}_i,\vec{e}_j)\vec{q}(j) = \Sigma_i \vec{q}(i)\vec{q}(j)$$

$\tilde{M}$ is an operator acting in the 3–d physical space. Resolved along three orthonormal axes $\{\vec{f}_\alpha\}$, $\tilde{M}$ is represented by the 3×3 matrix:

$$(\vec{f}_\alpha,\tilde{M},\vec{f}_\beta\} = (M)_{\alpha\beta} = \Sigma_i q^{i\alpha} q^{i\beta}$$

which is the **mass quadrupole matrix.**

(b) The n×n label dyadic:

$$\tilde{G} = (\tilde{D},\tilde{D}^t) = \Sigma_{i,j}\vec{e}_i\vec{e}_j(\vec{q}(i),\vec{q}(j))$$

$\tilde{G}$ is an operator acting in the n–d label space. Resolved along the $\vec{e}_i$ vectors, $\tilde{G}$ is represented by the n×n matrix:

$$(\vec{e}_i,\tilde{G},\vec{e}_j) = (G)_{ij} = (\vec{q}(i),\vec{q}(j)) = \Sigma_\alpha q^{i\alpha}q^{j\alpha}$$

which is the **Gram matrix** of the vectors $\{\vec{q}(i)\}$

The two matrices G and M have several properties in common: they are both real and symmetric and their elements are formed out of products of components of n three–dimensional GJV. Both matrices are positive semi–definite. It follows that they can be brought to diagonal form, with non–negative eigenvalues, by orthogonal transformations. Finally, both matrices have same trace:

$$Tr\tilde{M} = \Sigma_\alpha(\Sigma_i(q^{i\alpha})^2) = \Sigma_{i,\alpha}(q^{i\alpha})^2$$

$$Tr\tilde{G} = \Sigma_i\{\Sigma_\alpha(q^{i\alpha})^2\} = Tr\tilde{M}$$

APPENDIX 5

TENSOR PRODUCT OF STATE SPACES.

Let V and W be two vector spaces over the same field (real or complex) and consider the discrete bases $\{\vec{e}_i;i=1,...,n\}$ and $\{\vec{f}_k;k=1,...,m\}$ (generalization to continuous bases will be done below). Suppose we are given a mapping f which assigns to every pair of vectors $(\vec{v},\vec{w})$, $\vec{v}\epsilon V$, $\vec{w}\epsilon W$, a vector, denoted by $\vec{v}\otimes\vec{w}$ which belongs to a third vector space L:

$$f:(\vec{v},\vec{w}) \rightarrow \vec{v}\otimes\vec{w}\epsilon L$$

We suppose further that

(a) the mapping f is linear in $\vec{v}$ and $\vec{w}$ separately:

$(\vec{v}+\vec{v}')\otimes\vec{w} = \vec{v}\otimes\vec{w} + \vec{v}'\otimes\vec{w}$

$\vec{v}\otimes(\vec{w}+\vec{w}') = \vec{v}\otimes\vec{w} + \vec{v}\otimes\vec{w}'$

$(\alpha\vec{v})\otimes\vec{w} = \vec{v}\otimes(\alpha\vec{w}) = \alpha(\vec{v}\otimes\vec{w})$

and

(b) that it maps the set of nm pairs $(\vec{e}_i,\vec{f}_k)$ into a set $\vec{\sigma}_{ik} \equiv \vec{e}_i\otimes\vec{f}_k$ of linearly independent vectors of L.

The vector space spanned by the set of vectors $\vec{\sigma}_{ik}$ (subspace of L, which may be L itself) is denoted by V⊗W and is called the <u>tensor product space of V and W.</u>

Let $\vec{v} = \Sigma_i v^i\vec{e}_i$ and $\vec{w} = \Sigma_k w^k\vec{f}_k$. The generic tensor product vector $\vec{v}\otimes\vec{w}$ is expressed in the basis $\{\vec{\sigma}_{ik}\}$ by:

$$\vec{v}\otimes\vec{w} = \Sigma_{ik} v^i w^k\vec{\sigma}_{ik}$$

A generic vector $\vec{\chi}$ of the tensor product space is expressed as:

$$\vec{\chi} = \Sigma_{ik}\chi^{ik}\vec{\sigma}_{ik}$$

therefore, the vector space V⊗W contains vectors that are not of the form $\vec{v}\otimes\vec{w}$, that is vectors that are not mappings (by f) of any pair $(\vec{v},\vec{w})$ (this is an important result for the interpretation of pure and mixed states).

Let us note that if V and W are equipped with scalar products $(,)_V$ and $(,)_W$, respectively, then one can also define a scalar product $(,)_\otimes$ in V⊗W

For each pair $(\vec{\chi},\vec{\zeta})$ of V⊗W:

$$(\vec{\chi},\vec{\zeta})_\otimes = \sum_{ii'kk'} (\chi^{ik})^* (\zeta^{i'k'})(\vec{e}_i,\vec{e}_{i'})_V(\vec{f}_k,\vec{f}_{k'})_W$$

Let O_V and O_W be linear operators acting in V and W respectively. Their tensor product is the linear operator acting in V⊗W defined by the following relation:

$$[O_V\otimes O_W](\vec{v}\otimes\vec{w}) = [O_V\vec{v}]\otimes[O_W\vec{w}]$$

As a particular case, one consider the extension $\tilde{O}_V$ to V⊗W of an operator O_V acting in V as $O_V\otimes I_W$, where I_W is the identity operator in W and therefore the tensor product $O_V\otimes O_W$ coincides with the usual product of the extensions $\tilde{O}_V$ and $\tilde{O}_W$:

$$O_V\otimes O_W = \tilde{O}_V\tilde{O}_W$$

It is important to notice that the operators $\tilde{O}_V$ and $\tilde{O}_W$ always commute in V⊗W.

It is customary to simplify the notation in omitting the symbol ⊗:

$\vec{v}\vec{w}$ means $\vec{v}\otimes\vec{w}$

O_VO_W means $O_V\otimes O_W$

O_V means $O_V\otimes I_W = \tilde{O}_V$

In the first case, no confusion is possible, since $\vec{v}\vec{w}$ has never been defined. The two other cases are somewhat ambiguous; when the context is clear, we shall adopt the simplified version.

Consider now the eigenvalue equations of O_V (discrete spectrum $\{\nu_n\}$):

$$O_V\vec{a}_n^i = \nu_n\vec{a}_n^i \qquad (i=1,\ldots,g(n))$$

where g(n) is the degeneracy of ν_n.

We want to solve the eigenvalue equation of the extension $\tilde{O}_V$ in V⊗W:

$$\tilde{O}_V\vec{\chi} = \lambda\vec{\chi}$$

Every vector of the form $\vec{a}_n^i\otimes\vec{w}$ (with $\vec{w}$ arbitrary of W) is an eigenvector of $\tilde{O}_V$ with eigenvalue ν_n:

$$\tilde{O}_V\vec{a}_n^i\vec{\chi} = (\tilde{O}_V\vec{a}_n^i)\vec{\chi} = \nu_n\vec{a}_n^i\vec{\chi}$$

If O_V is an observable in V, the set $\{\vec{a}_n^i\}$ is a basis for V hence, the set $\{\vec{a}_n^i\vec{f}_k\} \equiv \{\vec{t}_n^{i,k}\}$ is a basis for V⊗W as well and we therefore have an orthonormal basis for V⊗W constituted of the eigenvectors of $\tilde{O}_V$; this solves the equation $\tilde{O}_V\vec{\chi} = \lambda\vec{\chi}$.

Therefore, if O_V is an observable in V, it is also an observable in V⊗W and the spectrum of O_V and $\tilde{O}_V$ are the same. However, an eigenvalue ν_n which is g(n)–fold degenerate in V, has a degree of degeneracy m×g(n) in V⊗W.

The results obtained above are now generalized to n infinite vector spaces

Finally, let us solve the eigenvalue equation of $C_{V\otimes W} = \tilde{O}_V + \tilde{O}_W$ when the eigenvalues and eigenvectors of O_V and O_W are known in V and W respectively (to simplify, assume that both spectra are discrete and non–degenerate in V and W):

$$O_V\vec{a}_n = \nu_n\vec{a}_n \qquad ; \qquad O_W\vec{b}_m = \zeta_m\vec{b}_m$$

O_V and O_W commute and the $\vec{a}_n\vec{b}_m$ which form a basis in V⊗W,

are eigenvectors common to O_V and O_W:

$$\tilde{O}_V \vec{a}_n \vec{b}_m = \nu_n \vec{a}_n \vec{b}_m \qquad \vec{O}_W \vec{a}_n \vec{b}_m = \zeta_m \vec{a}_n \vec{b}_m$$

They are also eigenvectors of C:

$$C\vec{a}_n \vec{b}_m = (\nu_n + \zeta_m)\vec{a}_n \vec{b}_m = \xi_{nm} \vec{a}_n \vec{b}_m$$

Therefore, the eigenvalues of C are the sums of an eigenvalue of O_V and an eigenvalue of O_W. one can find a basis of eigenvectors of C which are tensor products of an eigenvector of O_V and an eigenvector of O_W.

It is important to notice here that if two different pairs of values of n and m which give the same value foe ξ_{nm} do not exist, then ξ_{nm} is not degenerate (assuming that ν_n and ζ_m are not degenerate). The corresponding eigenvector of C is necessarily the tensor product $\vec{a}_n \vec{b}_m$. If, on the other hand, is for example 2–fold degenerate (there exists n' and m' such that $\xi_{n'm'} = c_{nm}$), all that can be asserted is that every eigenvector of C corresponding to this eigenvalue is written:

$$\lambda \vec{a}_n \vec{b}_m + \mu \vec{a}_n \vec{b}_m$$

where λ and μ are arbitrary complex numbers. In this case, there exist eigenvectors of C that are not tensor products.

The above results can now be extended to any number of vector spaces with infinite dimension.

Let E be the state space (i.e., an infinite separable Hilbert space) of a system constituted of N particles. With respect to a fixed origin O, let $\vec{x}(i)$ be the position vectors in the physical space E(3) and $\{\vec{\ell}_\alpha\}$ be a fixed orthonormal frame. Let $E_{i\alpha}$ be the state space associated with $x^{i\alpha}$. To $x^{i\alpha}$, there corresponds the observable $X_{i\alpha}$; in $E_{i\alpha}$, let $|x^{i\alpha}>$ be the infinite dimensional orthonormal basis and the eigenvector equation is:

$$X_{i\alpha}|x^{i\alpha}> = x^{i\alpha}|x^{i\alpha}>$$

In this representation, a vector $|\phi>$ of $E_{i\alpha}$ has components given by the scalar product $<x^{i\alpha}|\phi> = \phi(x^{i\alpha})$.

The entire state space of the system is the tensor product of the 3N state spaces $E_{i\alpha}$:

$$E = E_{11}\otimes E_{12}\otimes...\otimes E_{N3} = \otimes_{i\alpha} E_{i\alpha}$$

We obtain a basis in E from the tensor product of the 3N bases $\{|x^{i\alpha}>\}$; we shall denote it by $\{|x^{11},...,x^{N3}>\} = \{|\vec{x}(1),...\vec{x}(N)>\} = \{|\vec{x}(i),i=1,...N>\}$ with:

$$|x^{11},...,x^{N3}> \equiv |x^{11}>\otimes|x^{12}>\otimes...\otimes|x^{N3}>$$

Let now $|\Psi>$ be a vector of the state space E. In the basis $|\vec{x}(i)>$, the wave function (component of $|\Psi>$) is:

$$\Psi(\vec{x}(i)) = <\vec{x}(i)|\Psi>$$

The $x^{i\alpha}$ individual dependences cannot, in general, be factorized and each of the wave functions associated with the vectors $|\Psi>$ of E is a wave function of all or some of the 3N variables.

The most general state $|\Psi>$ is then:

$$|\Psi> = \int \Psi(\vec{x}(i))|x^{i\alpha}>dx^{11}...dx^{N3}$$

Therefore, an arbitrary vector of E can always be decomposed into an "infinite" (since the bases $\{|x^{i\alpha}>\}$ are continuous) linear combination of tensor product vectors.

APPENDIX 6

GJV DESCRIPTION OF AB_n MODELS

1. General Considerations

The object of this appendix is to give an alternate point of view in the matter of the construction of Jacobi vectors reflecting in "some way" the symmetry of the system.

Ultimately, we are seeking a set of (3N–3) generalized coordinates derived from Jacobi vectors and leaving the relative hamiltonian invariant under exchange of identical particles.

If H is the relative hamiltonian expressed in terms of 3n–3 internal coordinates Q^σ and three "external" coordinates (Euler angles) θ_s derived from a set of n Jacobi vectors $\vec{q}(i)$ and if $P(\gamma)$ is the permutation operator (in state space) corresponding to the element γ of the symmetric group $\mathscr{S}_n$ (in label space) then

$$[H,P(\gamma)] = 0 \quad \text{for any } \gamma \epsilon \mathscr{S}_n \tag{1}$$

A first step in this direction is to construct a set of Jacobi vectors reflecting themselves the symmetry of the system that is, equivalent symmetric Jacobi vectors which are the orthogonal analogues of the equivalent interparticle vectors (the static model has same symmetry once expressed in ES Jacobi vectors). This description can then be used to generate "derived" descriptions by some suitable label orthogonal transformation ρ and reflecting some other aspects of the symmetry of the

system.

The symmetry properties we are concerned with are then related to the n vectorial quantities defined by a contravariant basis in the relative label space as opposed to the scalar coordinates defining a basis in relative configuration space. Permutations of identical particles are represented by permutation matrices acting in the label space (actually, a subgroup of the orthogonal group O_n).

We consider systems comprised of a particle A of mass m and n identical particles B of mass m′: the total mass is $M = m + nm'$.

The contravariant label basis is

$$B \equiv \{x^0, x^1, \ldots, x^n\} \tag{2}$$

where 0 labels particle A and i=1,...,n are labels for the identical particles B.

The contravariant metric tensor is then

$$g(x) = \mathrm{diag}(m^{-1}, m'^{-1}, \ldots, m'^{-1}) \tag{3}$$

The interparticle label base vectors are defined as

$$r^k = x^k - x^0 \tag{4}$$

The transformation into CM/relative description is achieved by the matrix Z such that

$$[r] = Z[x] \tag{5}$$

where the matrix Z is given by

$$Z = \begin{bmatrix} -1 & 1 & 0 & \dots & 0 \\ -1 & 0 & 1 & \dots & 0 \\ & \dots & & & \\ -1 & 0 & 0 & \dots & 1 \\ \frac{m}{M} & \frac{m'}{M} & \frac{m'}{M} & \cdots & \frac{m'}{M} \end{bmatrix} \tag{6}$$

The corresponding metric tensor is given by

$$g(CM,r) = Zg(x)Z^t \tag{7}$$

$$g(CM,r) = \begin{bmatrix} g(r) & 0 \\ 0 & \frac{1}{M} \end{bmatrix} \tag{8}$$

g(r) is the relative metric tensor and is given by

$$g(r) = \begin{bmatrix} \mu & \frac{1}{m} & \frac{1}{m} & \dots & \frac{1}{m} \\ \frac{1}{m} & \mu & \frac{1}{m} & \dots & \frac{1}{m} \\ & \dots & & & \\ \frac{1}{m} & \frac{1}{m} & \frac{1}{m} & \dots & \frac{1}{m} \end{bmatrix} \tag{9}$$

where μ is the reduced mass

$$\mu = \frac{m+m'}{mm'} \tag{10}$$

As expected the relative label subspace is orthogonal to the 1–dimensional subspace spanned by the CM base vector.

Let us introduce the length α of r^i

$$\alpha = \mu^{1/2} \tag{11}$$

and the angle ϕ between any couple of vectors r^i and r^j

$$a = \cos\phi = \frac{m'}{m+m'} \tag{12}$$

With these conventions, the metric tensor g(r) becomes

$$g(r) = [r][r]^t = \begin{bmatrix} 1 & a & a & \dots & a \\ a & 1 & a & \dots & a \\ & \dots & & & \\ a & a & a & \dots & 1 \end{bmatrix} \tag{13}$$

where [r] denotes the column of the vectors r^i.

The relative basis $B_{rel} = \{r^1, r^2, \dots, r^n\}$ is not orthonormal and we are seeking orthonormalization matrices O such that

$$O[r] = [q] \tag{14}$$

2. Equivalent Symmetric Descriptions (ES_+ and ES_-)

Let γ be a permutation of the identical particles B. γ is represented in label space (carrier space) by an nxn permutation matrix $p(\gamma)$ of the base vectors such that

$$(r^1, \dots, r^n) \xrightarrow{\gamma} p(\gamma)(r^1, \dots, r^n) = (q^1, \dots, q^n) \tag{15}$$

The group of matrices $p(\gamma)$ is a representation of the symmetric group $\mathscr{S}_n$. The matrices $p(\gamma)$ are orthogonal. Details concerning the symmetric group can be found in appendix . g(r) is obviously invariant under the symmetric group that is, for any γ

$$[g(r),p(\gamma)] = 0 \tag{16}$$

Observe also that $g(r)^{-1}$ commutes with any $p(\gamma)$ since a polynomial in $g(r)$ and any polynomial in $g(r)^{-1}$ will commute with all the $p(\gamma)$ as well.

We are seeking the orthonormalizing matrices O that commute with all the $p(\gamma)$

$$[O,p(\gamma)] = 0 \tag{17}$$

By using the definition of the orthonormalizing matrices

$$Og(r)O^t = I_n \tag{18}$$

it follows (see publication I) that $O = O^t$ and $g(r) = O^{-2}$ or

$$O = g(r)^{-1/2} \tag{19}$$

The positive solution O_+ of $g(r)^{-1/2} = X$ is unique (see appendix) and is given in algorithmic way by

$$O_+ = \lim_{v\to\infty} O_v \tag{20}$$

where

$$O_{v+1} = O_v + \frac{1}{2}[g(r)^{-1} - O_v^2] \tag{21}$$

On the other hand, since $g(r)$ is symmetric and positive definite, it is diagonalizable by a proper orthogonal matrix ρ

$$\rho g(r)\rho^t = \Lambda = \mathrm{diag}(\lambda_1,\ldots,\lambda_n) \tag{22}$$

If X is to be the positive solution of the equation

$$X = g(r)^{-1/2} \tag{23}$$

then

$$O_+ = g(r)^{-1/2} = \rho^t\Lambda^{-1/2}\rho \tag{24}$$

Apart from being a symmetric orthonormalization of the basis $\{r^1,\ldots,r^n\}$, O_+ commutes with any permutation matrix $p(\gamma)$ representing exchange of identical particles. Yhis property is a direct consequence of

the polynomial form of O_+ given by equation (21). Actually there exists another solution for X commuting with $p(\gamma)$ (see below).

3. Analytic Expression of the Positive Solution

The eigenvalues of g(r) are easily determined by solving the secular equation. The results are

$$\lambda_1 = \alpha^2(1-a) \tag{25}$$

$$\lambda_2 = \alpha^2[1-a(1-n)] \tag{26}$$

where λ_1 is (n–1)–fold degenerate and λ_2 is not degenerate.

It is easily shown that the eigenvector corresponding to λ_2 is

$$p^1 = n^{-1/2}(1,1,...,1) \tag{27}$$

since

$$(\rho_{11} \dots \rho_{1n})g(r) = \alpha^2[1-a(1-n)](\rho_{11} \dots \rho_{1n})$$

$$\Rightarrow \quad \Sigma_i \rho_{1i} - n\rho_{1j} = 0 \qquad \text{for any } j$$

$$\Rightarrow \quad \rho_{1j} = \rho_{1k} \qquad \text{for any couple } (j,k)$$

$$\Rightarrow \quad \rho_{1j} = n^{-1/2} \qquad \text{for any } j = 1,...,n$$

The eigenvectors corresponding to the degenerate eigenvalue λ_1 are defined up to an (n–1) dimensional proper orthogonal matrix of the degenerate eigenspace.

By using the $\frac{n(n+1)}{2}$ orthogonality relations

$$\Sigma_k \rho_{ik}\rho_{kj} = \delta_{ij} \tag{28}$$

one obtains the (n–1) independent relations characterizing any matrix ρ diagonalizing g(r)

$$\Sigma_k \rho_{ik} = 0 \quad \text{for } i = 2,...,n \tag{29}$$

Taken with the orthogonality relations, this leaves $\frac{(n-1)(n-2)}{2}$ arbitrary relations among the ρ_{ik}.

On the other hand, the set of matrices of the type g(r) forms an abelian group for both multiplication and addition hence, any polynomial in g(r) belongs to the group; in particular $g(r)^{-1/2}$. By using these properties it is easy to evaluate the matrix elements of the positive solution O_+. The results are

$$[O_+]_{ii} = \lambda_1^{-1/2} + n^{-1}(\lambda_2^{-1/2} - \lambda_1^{-1/2}) \tag{30}$$

$$[O_+]_{ij} = n^{-1}(\lambda_2^{-1/2} - \lambda_1^{-1/2}) \tag{31}$$

4. Other Solutions

We demonstrate hereafter that there exists an other solution for X having the property (17).

Let $\{C_n(a:b)\}$ be the set of nxn matrices having a on the diagonal and b elsewhere: g(r) belongs to this set. $\{C_n(a:b)\}$ forms an abelian group Γ_n,. for matrix multiplication, the identity is $C_n(1:0) = I_n$.

Let O be an orthonormalization for g(r) = C(a:b) satisfying

$$O^t = O \tag{32}$$

$$\Rightarrow \qquad Og(r)O = I_n \tag{33}$$

$O \epsilon \Gamma_n$ since $O^{-2} = g(r) \epsilon \Gamma_n$ therefore

$$[O,g(r)] = 0 \tag{34}$$

Since O is an orthonormalization, it satisfies

$$O = UO_+ \tag{35}$$

where U is an n–dimensional orthogonal matrix

$$U^{-1} = U^t \tag{36}$$

Since O and O_+ belong to Γ_n, U belongs to the group. Moreover, U is symmetric since $OU^t = UO = O_+U$)

$$U^t = U \tag{37}$$

It follows that U is a square root of the unit n–dimensional matrix I_n

$$U^2 = I_n \tag{38}$$

Apart from the trivial solutions

$$U = I_n \quad \text{and} \quad U = -I_n \tag{39}$$

the equation (38) has the solutions *

$$U = \pm C_n(\tfrac{2-n}{n}, \tfrac{2}{n}) \tag{40}$$

Let us denote by O_* the solution

$$O_* = +C_n(\tfrac{2-n}{n}, \tfrac{2}{n})O_+ \tag{41}$$

and let $O_s = C_n(\alpha;\beta)$ then O_* is given by

$$O_* = C_n(\alpha';\beta') \tag{42}$$

where

$$\alpha' = n^{-1}[(2-n)\alpha + 2(n-1)\beta] \tag{43}$$

$$\beta = n^{-1}[2\alpha + (n-2)\beta] \tag{44}$$

In particular, for $g(r) = C_n(2;1)$ then

$$O_+ = C_n(\eta+1;\eta) \tag{45}$$

$$O_* = C_n(\eta'-1;\eta') \tag{46}$$

where

$$\eta = \frac{1}{n}[(n+1)^{-1/2} - 1] \tag{47}$$

$$\eta' = \frac{1}{n}[(n+1)^{-1/2} + 1] \tag{48}$$

Remark

O_+ and O_* both commute with all the $p(\gamma)$:

$$[p(\gamma),O_*] = [p(\gamma),UO_+] = [p(\gamma),U]O_+ + U[p(\gamma),O_*]$$
$$=0$$

Recall that any permutation is expressible as the composition of a transposition $P_\times$ and the the cycle $P_/$:

$$P_\times = \begin{pmatrix} 1 & 2 & \cdots & i & \cdots & j & \cdots & n \\ 1 & 2 & \cdots & j & \cdots & i & \cdots & n \end{pmatrix}$$

$$P_/ = \begin{pmatrix} 1 & 2 & \cdots & n \\ n & 1 & \cdots & n-1 \end{pmatrix}$$

$P_\times$ commutes with U and $P_/$ belongs to Γ_n hence commutes with U. It follows that $[p(\gamma),U] = 0$ for any γ.

5. Derived Descriptions

From the degeneracy of the eigenvalue λ_1, there exists an infinity of ways to diagonalize g(r). Following the discussion of section 3, let ρ_P be a particular choice. By pre– and post–multiplyinf equation (22) by $\Lambda^{-1/2}$, we obtain

$$\Lambda^{-1/2}\rho_P = O_P \qquad (49)$$

where O_P is the orthonormalization matrix corresponding to the choice ρ_P

For example, one can take $\frac{(n-1)(n-2)}{2}$ elements ρ_{ik} equal to zero. This defines uniquely an orthonormalization matrix for g(r). Of course this choice does not lead to a symmetric orthogonal basis.

As another example, observe that the number of $\frac{(n-1)(n-2)}{2}$ relations is precisely the number of relations characterizing a symmetric matrix of dimension (n–1)x(n–1) that is $\rho_{ik} = \rho_{ki}$ for i and k = 2,...,n.

By imposing these constraints, the matrix ρ is itself symmetric

which implies that

$$\rho_{i1} = n^{-1/2} \tag{50}$$

Moreover the diagonal elements ρ_{ii} $(i \neq 1)$ are all equal. Let us call these solutions ρ_t. They are orthogonal and symmetric matrices hence square roots of the unit matrix.

6. Construction of "Irreducible Symmetric" Descriptions

The n–dimensional rotation matrix ρ_t transforming O_+ into a particular orthonormalization O_t is such that

$$\rho_t O_+ = O_t \tag{52}$$

A particular frame defined by the orthonormalization matrix O_t is obtained from the ES frame by a rotation ρ_t uniquely defined by the prescription of $\frac{(n-1)(n-2)}{2}$ relations among the elements ρ_{ik}. In particular if ρ_t is symmetric

$$\rho_t O_+ = \Lambda^{-1/2}\rho_t \tag{53}$$

Every vector orthogonal to p^1 (defined in equation 27) is an actual eigenvector of the degenerate eigenvalue and every linear combination of such vectors are still eigenvectors. In particular, every vector of the form (1,...,–1,...) is orthogonal to p^1 but are not orthogonal among them. The (n–1)x(n–1) metric tensor has the form

$$g' = C_{n-1}(2;1) \tag{54}$$

. By following the same procedure as above, g' is diagonalized by an (n–1)(n–1) real, proper orthogonal matrix ρ' whose eigenvalues are

$$\lambda'_1 = 1 \quad \lambda'_2 = n \tag{55}$$

where λ'_1 is (n–2)–fold degenerate while λ'_2 is not degenerate. The

eigenvectors corresponding to λ_2' is

$$p^{1'} = (n-1)^{-1/2}(1,...,1) \qquad (56)$$

The procedure can be carried out by successively diminishing the dimension of the eigenspace by one unit. The construction is as follows.

From the ES_+ orthonormal basis $\{s^k\}$, one can construct the "totally irreducible basis" as follows.

Observe that the vector $n^{-1/2}\Sigma_i s^i$ is precisely the vector p^1 of the previous section. In the degenerate eigensubspace orthogonal to p^1 one can choose the basis formed by the (n–1) vectors $t^k = s^1 - s^k$ (k=2,...,n). This transformation is achieved by the matrix Z_t:

$$Z_t = \begin{bmatrix} n^{-1/2} & \cdots & & & n^{-1/2} \\ 1 & -1 & 0 & \cdots & 0 \\ 1 & 0 & -1 & \cdots & 0 \\ & \cdots & & & \end{bmatrix} \qquad (57)$$

The basis $\{t^2,...,t^n\}$ is not orthogonal, the associated (n–1)x(n–1) metric tensor $g_r(t)$ is not diagonal:

$$g_r(t) = C_{n-1}(2;1) \qquad (58)$$

and the new metric tensor is now

$$g'(t) = \begin{bmatrix} 1 & 0 \\ 0^t & g_r(t) \end{bmatrix} \qquad (59)$$

where $\overline{O}$ is the (n–1) column of zeroes. The basis $\{t^2,...,t^n\}$ may now be orthonormalized by either the ES_+ or the ES_* matrices for the (n–1) dimensional space.

For example, one can use the (n–1)x(n–1) matrix $\overline{O}_+$ given analytically by equations (30–31):

$$\overline{O}_+ = \begin{bmatrix} 1+\eta & \eta & \dots & \eta \\ \eta & 1+\eta & \dots & \eta \\ & \dots & & \\ \eta & \eta & \dots & 1+\eta \end{bmatrix}_{(n-1)} \quad (n-1) \qquad (60)$$

where

$$\eta = \frac{n^{1/2} - n}{n(n-1)} \qquad (61)$$

The transformation of the orthonormal basis {s} into the orthonormal basis {p} is achieved by $\tilde{O}_+ Z_t$ where $\tilde{O}_+$ is the nxn matrix

$$\tilde{O}_+ = \begin{bmatrix} 1 & 0 \\ 0^t & \overline{O}_+ \end{bmatrix} \qquad (62)$$

$\rho_+ = \tilde{O}_+ Z_t$ is orthogonal (hence $\tilde{O}_+ Z_t O_+$ is an orthonormalization of {r}) and is symmetric hence is a square root of I_n.

The same procedure can be carried out with O_* instead of O_+ leading to ρ_*. The results are as follows $n^{-1/2}$

$$\rho_+ = \begin{bmatrix} n^{-1/2} & n^{-1/2} & n^{-1/2} & \dots & n^{-1/2} \\ n^{-1/2} & -1-\eta & -\eta & \dots & -\eta \\ & \dots & & & \\ n^{-1/2} & -\eta & -\eta & \dots & -1-\eta \end{bmatrix} \qquad (63)$$

$$\rho_* = \begin{bmatrix} n^{-1/2} & n^{-1/2} & n^{-1/2} & \dots & n^{-1/2} \\ n^{-1/2} & 1-\eta' & -\eta' & \dots & -\eta' \\ \dots & & & & \\ n^{-1/2} & -\eta' & -\eta' & \dots & 1-\eta' \end{bmatrix} \qquad (64)$$

where η and η' are given by (47–48).

Example: n=4

$$\rho_+ = \frac{1}{6}\begin{bmatrix} 3 & 3 & 3 & 3 \\ 3 & -5 & 1 & 1 \\ 3 & 1 & -5 & 1 \\ 3 & 1 & 1 & -5 \end{bmatrix}$$

$$\rho_* = \frac{1}{2}\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{bmatrix}$$

and ρ_* corresponds to the "totally irreducible representation".

APPENDIX 7

POLAR DECOMPOSITION OF AN OPERATOR IN EUCLIDEAN SPACE

Theorem

Every linear operator A acting in a euclidean space is representable in the form of a product

$$A = SQ \tag{1}$$

$$A = Q'S' \tag{2}$$

where S, S' are positive–semidefinite symmetric and Q, Q' are orthogonal operators; here $S = \sqrt{(AA^t)} = g(AA^t)$, $S' = \sqrt{(A^tA)} = h(A^tA)$, where $g(\lambda)$ and $h(\lambda)$ are real polynomials.

A is a normal operator if and only if S and Q (S' and Q') are permutable.

Similar statements hold for matrices.

Let us point out the geometrical content of these formulas. We let the vectors of an n–dimensional euclidean space issue from the origin of the coordinate system. Then every vector is the radius vector of some point of the space. The orthogonal transformation realized by the operator Q (or Q') is a "rotation" in this space, because it preserves the euclidean metric and leaves the origin of the coordinate system fixed. For $|Q| = 1$ this is a proper rotation; but for $|Q| = -1$ it is a combination of a rotation and a reflection in a coordinate plane. The symmetric operator S (or S') represents a "dilatation" of the n–dimensional space (i.e., a

"stretching" along n mutually perpendicular directions with "stretching factors" $\rho_1, \rho_2, \ldots, \rho_n$ that are in general distinct ($\rho_1, \rho_2, \ldots, \rho_n$ are arbitrary non–negative numbers). According to formula (1) and (2), every linear homogeneous transformation of an n–dimensional euclidean space can be obtained by carrying out in succession some rotation and some dilatation (in any order).

APPENDIX 8

PSEUDOINVERSE OF A MATRIX

For an arbitrary m×n matrix A there exists an n×m matrix A^+, the so–called *pseudoinverse* (or *Moore–penrose inverse*). It is associated with A in a natural fashion and agrees with the inverse A^{-1} of A in case $m = n$ and A is nonsingular.

Consider the range space R(A) and the null space N(A) of A,

$$R(A) = \{Ax \in \mathbb{R}_m \mid x \in \mathbb{R}_n \} \tag{1}$$

$$C(A) = \{x \in \mathbb{R}_n \mid Ax = 0 \} \tag{2}$$

together with their orthogonal complement spaces $R(A)^{\perp} \subset \mathbb{R}_m$ and $N(A)^{\perp} \subset \mathbb{R}_n$ }. Further, let P be the n×n matrix which projects $\mathbb{R}_n$ onto $N(A)^{\perp}$ and let $\bar{P}$ be the m×n matrix which projects $\mathbb{R}_m$ onto R(A):

$$P = P^h = P^2,\ Px = 0 \Leftrightarrow x \in N(A) \tag{3}$$

$$\bar{P} = \bar{P}^h = \bar{P}^2,\ \bar{P}y = y \Leftrightarrow y \in R(A) \tag{4}$$

For each $y \in R(A)$ there is a uniquely determined $x_1 \in N(A)^{\perp}$ satisfying $Ax_1 = y$ i.e., there is a well–defined mapping $f: R(A) \to \mathbb{R}_n$ with

$$Af(y) = y,\ f(y) \in N(A)^{\perp} \text{ for all } y \in R(A) \tag{5}$$

For, given $y \in R(A)$, there is an x which satisfies $y = Ax$; hence $y = A[Px + (I - P)x] = APx = Ax_1$, where $x_1 = Px \in N(A)^{\perp}$, since (I–P)x $\in N(A)$. Further, if $x_1, x_2 \in N(A)^{\perp}$, $Ax_1 = Ax_2$, it follows that

$$x_1 - x_2 \in N(A) \cap N(A)^{\perp} = \{0\} \tag{6}$$

which implies that $x_1 = x_2$, f is obviously linear.

The composite mapping $f: \bar{P}: y \in \mathbb{R}_m \to f(\bar{P}y) \in \mathbb{R}_n$ is well–defined and linear, since $\bar{P}y \in R(A)$; hence it is represented by an $n \times m$ matrix, which

is precisely A^+, the pseudeoinverse of A; $A^+y = f(\bar{P}(y))$ for all $y \in \mathbb{R}_m$.

A^+ has the following properties:

(1) $A^+A = P$ is the orthogonal projector $P: \mathbb{R}_m \to N(A)^{\perp}$ and $AA^+ = \bar{P}$ is the orthogonal projector $\bar{P}: \mathbb{R}_m \to R(A)$

(2) The following formula hold

a) $A^+A = (A^+A)^h$ (7)

b) $AA^+ = (AA^+)^h$ (8)

c) $AA^+A = A$ (9)

d) $A^+AA^+ = A^+$ (10)

(3) If Z is a matrix satisfying

a) $ZA = (ZA)^h$ (11)

b) $AZ = (AZ)^h$ (12)

c) $AZA = A$ (13)

d) $ZAZ = A^+$ (14)

then $Z = A^+$ (15)

(4) For all matrices A

$A^{++} = A$, $(A^+)^h = (A^h)^+$ (16)

APPENDIX 9

PERMUTATIONS OF IDENTICAL PARTICLES.

Let γ be a permutation of the identical particles B. γ is represented schematically by:

$$\gamma = \begin{pmatrix} 1 & 2 & \dots & n \\ i_1 & i_2 & \dots & i_n \end{pmatrix} \qquad (1)$$

We recall hereafter some definitions and properties of the group of permutations of n elements: the symmetric group $\mathscr{S}_n$.

A transposition is a permutation leaving all but two elements unchanged:

$$\tau_{jk} = \begin{pmatrix} 1 & 2 & \dots & j & \dots & k & \dots & n \\ i_1 & i_2 & \dots & k & \dots & j & & i_n \end{pmatrix} \qquad (2)$$

Of course, $\tau_{jk}^{-1} = \tau_{kj}$ hence $\tau_{jk}^{2} = I$, the identity.

A cycle (ijk...) is the permutation of $m \leq n$ elements:

$$\begin{pmatrix} \alpha_1 & \alpha_2 & \dots & \alpha_{m-1} & \alpha_m & \alpha_{m+1} & \dots & \alpha_n \\ \alpha_2 & \alpha_3 & \dots & \alpha_m & \alpha_1 & \alpha_{m+1} & \dots & \alpha_n \end{pmatrix}$$

m is the length of the cycle => a transposition is a cycle of length 2.

The "general shift" is the cycle of length n:

$$\tau_{\times} = \begin{pmatrix} 1 & 2 & \dots & n \\ n & 1 & & n-1 \end{pmatrix}$$

Any permutation can be expressed as:

(1) a product of commuting cycles (no elements in common), this decomposition is unique.

(2) a product of transpositions (with common elements), this decomposition is not unique.

(3) some combinations of the only two permutations τ_{12} and $\tau_{\times}$

Representations.

The (relative) label space plays the role of carrier space for a representation of $\mathscr{S}_n$: to an element γ of $\mathscr{S}_n$ there corresponds an (n×n) permutation matrix $p(\gamma)$ acting in label space such that $p(\gamma)p(\gamma') = p(\gamma\gamma')$. Let $\{r^1,\dots,r^n\}$ be the contravariant basis :

$$(r^1,\dots,r^n)^t \xrightarrow{\gamma} p(\gamma)(r^1,\dots,r^n)^t = (r^{i_1},\dots,r^{i_n})^t = (r'^1,\dots,r'^n)^t \qquad (3)$$

In matrix notation,

$$p(\gamma)\underset{\sim}{r} = \underset{\sim}{r}' \qquad (4)$$

The group $\mathscr{P}_n$ of matrices $\{p(\gamma)\}$ is a representation in label space of the symmetric group $\mathscr{S}_n$ and the matrices $p(\gamma)$ are orthogonal since

$p(\gamma)^{-1} = p(\gamma)^t$. Unless n=1 or 2, these groups are not abelian. $\mathscr{P}_n$ is a subgroup of the orthogonal group $\mathcal{O}_n$.

A matrix A acting in label space is invariant under the group $\mathscr{P}_n$ if $[A,p(\gamma)] = 0$ for all γ.

If A commutes with all $p(\gamma)$, any polynomial in A is invariant under $\mathscr{P}_n$, in particular A^{-1}.

A subspace S of the label space is invariant under $\mathscr{P}_n$ if for any γ and any vector x of S, $\gamma x \epsilon S$.

The action of $p(\gamma)$ in physical space is then to transform the set $\{\vec{q}\}$ into a new set $\{\vec{q}'\}$. Actually, there exists another representation of $\mathscr{S}_n$ of interest: let $\{\vec{q}_e\}$ be the set of Jacobi vectors at equilibrium; $\{\vec{q}'_e\}$ is obtained by the orthogonal transformation $R(\gamma)$ (in physical space) such that $R_{\alpha\beta}(\gamma) = (\vec{\ell}''_\alpha, \gamma\vec{\ell}''_\beta)$. The inversion ι of the physical space is defined by $\iota\vec{r} = -\vec{r}$ and is represented by $-I_3$. Thus the two correspondences:

$$\gamma \longrightarrow p(\gamma) \qquad \text{and } \gamma \longrightarrow R(\gamma) \qquad \text{any } \gamma \epsilon \mathscr{S}_n \tag{5}$$

are representations of the symmetric group $\mathscr{S}_n$.

The two representations are intertwined by the (3×n) matrix A_e:

$$A_e = \begin{bmatrix} q_e^{11} & \cdots & q_e^{n1} \\ q_e^{12} & \cdots & q_e^{n2} \\ q_e^{13} & \cdots & q_e^{n3} \end{bmatrix} \tag{6}$$

that is:

$$R(\gamma)A_e = A_e p(g) \tag{7}$$

Obviously, the cartesian components with respect to the inertial frame will follow the same invariance pattern whereas the invariance of

the cartesian components in an noninertial frame will depend upon the invariance of the frame itself. This will be treated rigorously in the next chapter. Actually, a frame defined from all the GJV's is invariant under any permutation γ whereas "locally" defined frames are not.

In this chapter, we show that the sets of GJV's invariant under $\mathscr{S}_n$ are the E.S. Jacobi vectors $\{\vec{q}_s(i)\}$ and $\{\vec{q}_{s'}(i)\}$ obtained by the positive square root and a particular negative square root of $g(r)^{-1}$ respectively. Nevertheless, accounting to the above discussion, we shall consider derived systems obtained from the E.S. by label rotations and reflecting some other symmetries of interest in the relative configuration space.

Actually, since all $p(\gamma)$ are orthogonal matrices ($p(\gamma)^{-1} = p(\gamma)^t$), their action in label space is a change of basis.the group of permutation matrices $p(\gamma)$ is a representation of the symmetric group S(n) (n! elements) and is obviously not a faithful representation of G. For example, the point group of SF_6 contains 48 elements whereas S(6) contains 720 elements.

APPENDIX 10

REVIEW

1.Parameterization of the Relative Configuration.

a) General procedure

To an instantaneous configuration of the system, one associates a point M of a point affine 3N–dimensional vector space. The metric (euclidean) is diagonal and has the form:

$$g = \mathrm{diag}(D_n, D_n, D_n)$$

where

$$D_n = \mathrm{diag}(m_1, \ldots, m_n)$$

m_i is the mass of particle (i).

The covariant metric tensor is simply

$$g^{-1} = \mathrm{diag}(D_n^{-1}, D_n^{-1}, D_n^{-1})$$

so that the quantum kinetic energy operator has the usual form

$$2T_{qm} = -\hbar^2 \sum_n m_n^{-1} \nabla_n^2$$

where ∇_n^2 is the laplacian in cartesian coordinates

$$\nabla_n^2 = \sum_\Upsilon \frac{\partial^2}{\partial (x^{n\beta})^2}$$

By introducing generalized coordinates $\zeta^p = \zeta^p\ (x^{i\Upsilon})$, the kinetic energy becomes (appendix I)

$$2T_{qm} = -\hbar^2\, g^{pq} \frac{D^2}{D\zeta^p D\zeta^q}$$

where g^{pq} are the contravariant metric tensor elements and $D/D\zeta^p$ are the covariant derivatives. The diagonalization of T_{qm} amounts then to diagonalizing the covariant metric tensor together with "assigning" three coordinates to the translational motion, three coordinates to the rotational motion and the remaining 3N–6 coordinates to translation/rotation invariant motion. This method is actually untracktable for systems constituted of more than two bodies and alternate techniques have to be cosidered.

In the present approach, the configuration space is interpreted as a tensor product of a "*label*" N dimensional space with a 3–dimensional "*physical*" space (this is justified by the block–diagonal form of the metric tensor). The (dual, contravariant) label basis is orthogonal though not normed while the "physical" basis is orthonormal. The separation of the CM motion is achieved by introducing the CM vector as base vector. The N–1 dimensional space orthogonal to x^{cm} is the relative label space and it can be spanned by many bases.

b) Separation of the translational motion: Jacobi Vectors.

The viewpoint and the procedures of the derivation come within the scope of the previous works of Wallace[27] where the formalism developed by Biedenharn[25] has been adapted. Once the motion of the c.m. has been removed, the relative configuration of the system is described by a set of bond distance vectors $\{\vec{r}\}$ invariant under permutation of identical particles. The corresponding cartesian coordinates with respect to an inertial frame centered at the c.m. of the molecule do not lead to a

diagonal kinetic energy operator. In order to recover the orthogonality, the bond vectors are transformed into Jacobi vectors $\{\vec{q}\}$ by means of a *label* orthonormalizing transformation **O**. The transformation **O** may be chosen in order to reflect the symmetry and the "topology" of the system. This was not the case for the previous version of Jacobi vectors which were obtained from a Gram–Schmidt orthonormalization of the bond vectors. The procedure is presented schematicaly in the following diagram

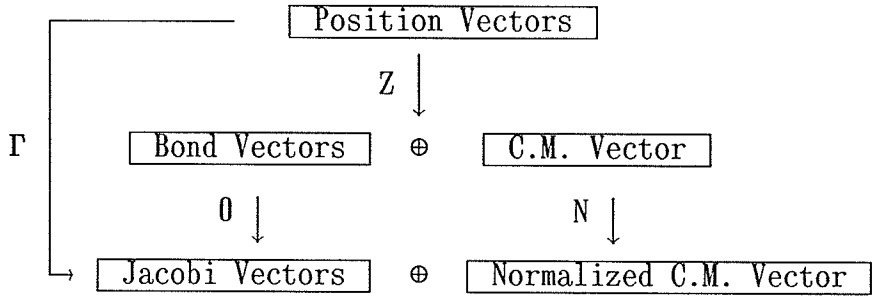


Figure 2.

The resulting kinetic energy operator is diagonal in the same fashion than once expressed in the cartesian coordinates $x^{i\beta}$ of the position vectors $(\vec{x})$

$$\frac{1}{2}\sum_{i,\beta}\frac{(P_{i\beta})^2}{m_i} \xrightarrow{\Gamma} \frac{1}{2}\sum_{k,\beta}(p_{k\beta})^2 + T_{cm}$$

$$T_{tot} \xrightarrow{\Gamma} T_{rel} + T_{cm}$$

where $P_{i\beta}$ and $p_{k\beta}$ are the linear momenta conjugate to the cartesian coordinates of the position vectors $\{\vec{x}\}$ and $\{\vec{q}\}$ respectively.

If the potential is translationally invariant (as it is the case in this

context), the wave function $\Psi(x)$ of the total configuration is expressible as the product

$$\Psi(x) = f(q_{cm})\psi(q^{k\beta})$$

of a function f of the coordinates of the c.m. and a function ψ of the set of 3N–3 coordinates $q^{k\beta}$ specifying the configuration relative to the c.m.

The total hamiltonian is separable into a translational and a rovibrational part

$$H_{tot} = H_{tr} + H_{rovib}$$

that is

$$H_{tr} f(q_{cm}) = E_{tr} f(q_{cm})$$
$$H_{rovib} \psi(q^{k\beta}) = (E_{tot} - E_{tr}) \psi(q^{k\beta})$$

where E_{tot} and E_{tr} are respectively the total and the translational energies.

c. Separation of the rotational motion: Noninertial Frames.

At this point the system can be considered as equivalently represented by a set of (unit mass) fictitious particles (1 for the c.m. and N–1 for the relative motion) and the procedure of constructing a rotating frame can be carried out using an orthonormalization procedure of a set of three vectors $\vec{F}_\alpha$ (so–called Eckart vectors) obtained from independent linear combinations of the Jacobi vectors:

$$\vec{F}_\beta = \sum_k A_{k\beta} \vec{q}_k$$

If all the Jacobi vectors are involved, the frame is referred as "global", otherwise, the frame is "local" (i.e., tied to the configuration of a fragment of the molecule). The subset of Jacobi vectors serving to

define the frame is refered to as the D–fragment (D for defining) whereas the remaining vectors constitute the I–fragment (I for internal).

The frame $\{\vec{F}_\beta\}$ is then orthonormalized (in 3–d. space) by a transformation O so that the overall 3×(N–1) matrix B=OA defines uniquely an orthonormal frame $\{\vec{f}_\beta\}$

The particular choice of the Jacobi vectors $\vec{q}_k$ as well as the choice of the orthonormalization O permit to adapt the frame to a specific physical problem.

The matrix B serves to define in an elegant way the two tensors G and $\mathcal{I}$ playing a key role in the derivation of the kinetic energy operator

$$G^{-1} = B^t B$$

$$\mathcal{I}^{-1} = BB^t$$

respectively the reciprocal Gram matrix of the Jacobi vectors and their tensor of inertia with respect to the inertial frame. The rotational invariance of G (under R, B transforms into RB) is expressed by imposing three liaisons among the cartesian coordinates of the Jacobi vectors of the D–fragment with respect to the noninertial frame defined by B. The separation of the variables is explicitly achieved in

$$q^{i\beta} = \Sigma_\Upsilon R_{\beta\Upsilon}(\theta_s) y^{i\Upsilon}(\rho_\varsigma)$$

where R is the orthogonal matrix representing the rotation carrying the inertial frame centered at the c.m. to the noninertial frame and ρ_ς are some set of (3N–6) internal coordinates parameterizing the cartesian coordinates $y^{i\Upsilon}$ accounting to the three liaisons defining the frame.

The relative wave function is factorized in the standard way[26] into a sum of products of functions of the rotational coordinates θ_s and the

internal coordinates ρ_ς

$$\psi^J_M(q^{i\beta}) = \sum_K D^{J\,*}_{MK}(\theta_s)\chi^J_{iK}(\rho_\varsigma)$$

This method enhances the distinct character of the internal and external parameters (traditionally, internal coordinates and rotating frames are intimately related: normal coordinates/Eckart molecular frame, hyperspherical coordinates/Principal axes frame,...) and the two issues have to be treated separately.

d. Expression of the linear and angular momenta in Cartesian Coordinates.

The total angular momentum $\vec{L}$ has components $\vec{L}^o$ and $\vec{L}'$, respectively for the D and the I–fragments. Their components with respect to the inertial frame are the generators of the rotations of the whole molecule, the D–fragment and the I–fragment respectively. With respect to the noninertial frame, the components of the total angular momentum are

$$(\vec{L},\vec{f}_\beta) = K^o_\beta + P'_\beta$$

where P'_β are the generators of the rotations of the I–fragment with respect to the noninertial frame.

The transformation of the linear momenta $p_{i\beta}$ is achieved in

$$p_{i\beta} = \Sigma_\Upsilon R_{\beta\Upsilon}(\theta_s)\mathcal{O}_{i\Upsilon}$$

where $\mathcal{O}_{i\Upsilon}$ is defined by

$$\mathcal{O}_{i\Upsilon} = \pi_{i\Upsilon} + \Sigma_\varsigma I^i_{\Upsilon\varsigma}(K^o_\varsigma + P^o_\varsigma + P'_\varsigma)$$

respect to the noninertial frame.

The transformation of the linear momenta $p_{i\beta}$ is achieved in

$$p_{i\beta} = \Sigma_{\Upsilon} R_{\beta\Upsilon}(\theta_s) \mathcal{O}_{i\Upsilon}$$

where $\mathcal{O}_{i\Upsilon}$ is defined by

$$\mathcal{O}_{i\Upsilon} = \pi_{i\Upsilon} + \Sigma_{\varsigma\,\Upsilon\varsigma} I^i (K^o_\varsigma + P^o_\varsigma + P^{\prime}_\varsigma)$$

where

$\pi_{i\Upsilon}$ is the linear momentum component in the noninertial frame

P^o_ς is the *vortex* angular momentum (generators of the rotations in label space)

I^i is a matrix defined by the specification of the frame.

2.The Kinetic Energy Operator In BRI Coordinates.

a. Rovibrational kinetic energy operator.

In a preliminary version, the kinetic energy operator is expressed in terms of the (3N–3) rotational invariant cartesian coordinates $y^{i\beta}$ of the Jacobi vectors with respect to the noninertial frame. These coordinates are not independent: there exist three liaisons (constraints) among them that can be used to describe the noninertial frame. For example, the specification of a diagonal tensor of inertia leads to the three liaisons

$$\Sigma_i y^{i\beta} y^{i\Upsilon} = \delta_{\beta\Upsilon}$$

The cartesian coordinates together with the three constraints can be parameterized in many ways in agreement with the definition of the frame. According to a well–known result of the vector invariant theory,

any internal coordinate (rotation invariants) may be expressed as polynomials in the scalar products of the Jacobi vectors (Basic Rotational Invariant). These can be used as a basic parameterization of the cartesian coordinates and are, from their definition, precursors for any other set of internal coordinates. The final version of the kinetic energy operator is expressed in terms of the BRI coordinates and the coefficients of the various operators are expressed in terms of some simple functions of the reciprocal tensor of inertia associated with the rotating frame.

The derivation of the kinetic energy operator is achieved in adding the squares of the linear momenta conjugate to the coordinates $q^{i\beta}$.

b. "Internal" kinetic energy operator.

After having integrated over the rotations in the manner of Curtiss *et al*, the kinetic energy operator is obtained in a form dependent only upon the "internal" coordinates, the rotational quantum numbers and the step–up/step–down operators $\sigma_{\pm}$ mixing the internal states of different rotational quantum numbers. The resulting expression is partitioned into pure internal terms T_{int}, a centrifugal potential terms V_c, pure rotational terms T_{rot} and terms representing the rovibrational couplings T_{coup}. The part (T^{o}_{int}) of T_{int} corresponding to the BRI coordinates associated with the Jacobi vectors entering in the construction of the frame is invariant under a change of frame involving the same Jacobi vectors. It contains a diagonal radial part, a diagonal angular part and coupling terms between the angular variables only. The internal part (T'_{int}) corresponding to the BRI coordinates of the remaining Jacobi vectors is expressed (through the

elements of the reciprocal tensor of inertia $\mathcal{I}^{-1}$) in a more or less complicated way depending of the choice of the frame. The coupling terms (T_{ic}) between the two fragments are equally dependent upon the choice of the frame. For frames defined irrespective to the lengths of the Jacobi vectors (for example, an axis of quantization along the bisector of two Jacobi vectors), this term reduces to coupling terms between angular variables. The centrifugal potential V_c is a function of the rotational quantum numbers (as parameters) and the diagonal elements of $\mathcal{I}^{-1}$. It represents the rotational contribution to the oscillators associated with the Jacobi vectors defining the frame. The "pure rotational" term T_{rot} is expressed as a function of the step–up/step–down operators, the rotational quantum numbers and the elements of the $\mathcal{I}^{-1}$. Finally, the rovibrational interaction is expressed by expressions coupling the operators $\sigma_{\pm}$ with the linear momenta conjugate to the BRI coordinates of the Jacobi vectors defining the frame (T_c^o) and the components P'_{α} of the (internal) angular momentum of the remaining Jacobi vectors (T'_c). Of course, for a global frame (i.e., involving the totality of the Jacobi vectors), the terms T'_{int}, T_{ic} and T'_c are zero.

3.The Schroedinger Equation in BRI coordinates.

a. Potential energy.

In order to obtain an expression for the hamiltonian, the source potential function V is firstly re–expressed in terms of the BRI coordinates of the Jacobi vectors defining the frame and an appropriate

parameterization for the internal coordinates describing the remaining Jacobi vectors. Actually, the potentials available in the literature (see for example Carter *et al* [32]) from spectroscopic data (and *ab initio* calculations) are expressed in valence coordinates (mixture of bond lengths and bond angles) which are not in general orthogonal (leading to cross terms in the kinetic energy). The effective potential V_{eff} is obtained by adding the centrifugal potential V_c to the source potential V. In general, the effective potential is expressible (numerically) as a sum of a separable part $V_{eff}^{(s)}$ and a non–separable part $V_{eff}^{(ns)}$, the former being the summation $\Sigma_j V(\xi_j)$ over all the internal coordinates ξ_j of the parts of the effective potential function of a single internal coordinate, the remaining being hold at equilibrium. Formally,

$$V_{eff} = \Sigma_i V_{eff}^{(s)}(Q_i) + \Sigma_{i,j} V_{eff}^{(s)}(\theta_{ij}) + V_{eff}^{(ns)}$$

b. Zero–order hamiltonian.

A zero–order hamiltonian H^o is obtained from the diagonal elements of the kinetic energy together with the separable parts of the effective potential.

This leads to a set of N–1 radial and 2N–5 angular operators having respectively the form:

Radial equations:

$$R(Q_i) = -\frac{\hbar^2}{2}\left[\frac{\partial^2}{\partial Q_i^2} + \frac{2}{\theta_i}\frac{\partial}{\partial Q_i}\right] + V_{eff}(Q_i) \quad (i=1,\ldots,N-1)$$

Angular equations:

$$A(\theta_{ij}) = -\frac{\hbar^2}{2} F_{ij}\left[\frac{\partial^2}{\partial \theta_{ij}^2} + \cot\theta_{ij}\frac{\partial}{\partial \theta_{ij}} - F_{ij}^{-1} V_{eff}(\theta_{ij})\right]$$

where i and j are labeling the Jacobi vectors defining the frame and F_{ij} is some function of the radial coordinates.

The angular equations corresponding to the remaining Jacobi vectors have a form depending upon the choice of the frame and the parameterization itself.

The corresponding angular eigenvalue equations are solved numerically by the renormalized Numerov method[33,34] (RNM) leading to eigenvalues once multiplied by the radial factor F_{ij} are re–introduced into the radial equations which can be solved numerically by the RNM. This is actually a generalization of the well–known procedure used in the solution of the hydrogen atom.

c. Coupling terms.

The zero–order basis can finally be used for the evaluation of the coupling terms by a standard perturbation theory. It is worth mentioning that in the RNM, the values of the eigenfunctions and their derivatives are stored for each grid–point of the integration. This particular feature of the method makes easier (and faster) the evaluation of the coupling matrix elements.

d. Alternate choices for the internal coordinates.

The choice of an appropriate parameterization (internal coordinates and noninertial frame) appears clearly as essential in the treatment of the coupling terms (these have of course to be small) as well as in the

separability of the potential. Although the radial BRI coordinates are orthogonal irrespective to the choice of the frame, the angular BRI parameterization leads to angular–angular and (for certain frames) radial–angular couplings.

The metric tensor has the form

$$g = \begin{bmatrix} g_r & 0 & C \\ 0 & g_i & E \\ C^t & E^t & g_e \end{bmatrix}$$

where g_r, g_i and g_e are respectively the metric subtensors of the radial, internal angular and external angular coordinates. C and E represent respectively the radial–external angular and internal–external angular couplings. A proper (infinitesimal) orthonormalization of the BRI angles is a necessary subject to be investigated in order to reduce the angular–angular interactions.

APPENDIX 11

GRAM MATRIX AND MASS QUADRUPOLE

In the derivation of generalized Jacobi vectors, the concept of *label space* plays a major role: the transformation of position vectors into GJV is actually generated by a change of basis in label space.

The instantaneous configuration of a set of N particles is formulated by a set {x} of N position vectors $\vec{x}_i$ with repect to a fixed origin O. These N vectors are linearly independent, they span therefore a N dimensional vector space: the *label space* Λ_N.

Once an orthonormal, fixed basis $\{\vec{\ell}_\alpha; \alpha=1,2,3\}$ with common origin at O is defined in the usual physical space (3 dimensional euclidean space E_3), the position vector $\vec{x}_i$ is expressed as:

$$\vec{x}_i = \Sigma_\alpha x^{i\alpha} \vec{\ell}_\alpha \qquad (1)$$

where $x^{i\alpha}$ is the usual component of $\vec{x}_i$ with respect to $\vec{\ell}_\alpha$.

To the position vector description of the configuration, there corresponds in label space a unique covariant basis whose metric tensor is $\mathrm{diag}(m_1,\ldots,m_N)$, m_i being the mass of particle described by position vector $\vec{x}(i)$. To a GJV description of the relative configuration, there corresponds in relative label space an orthonormal basis (covariant metric tensor is I_n; where n=N–1). Any orthogonal transformation in label space generates an other GJV description, the metric tensor being unaltered.

As well, the proper way to introduce noninertial frames in physical space is to define in label space a set of three independent linear

combinations of the label base vectors. There corresponds in the physical space a set of three vectors $\vec{F}_\lambda$ which can be orthonormalized (in physical space) to provide an orthonormal noninertial frame tied to the configuration of the GJV involved in the linear combinations.

Let $\{\vec{e}_i\}$ be the label basis corresponding to a particular representation in terms of GJV. Define the label vectors:

$$\vec{\zeta}_\lambda = \Sigma_k A_{\lambda k} \vec{c}_k \qquad (\lambda=1,2,3) \tag{2}$$

The corresponding (3×3) Gram matrix is:

$$G(\zeta) = AA^t \tag{3}$$

To the three vectors $\vec{\zeta}_\lambda$, there corresponds in physical space three vectors $\vec{\varphi}_\lambda$:

$$\vec{\varphi}_\lambda = \Sigma_k A_{\lambda k} \vec{q}_k \tag{4}$$

whose Gram matrix is:

$$G(\varphi) = AG(q)A^t \tag{5}$$

Orthonormalizing the set $\{\vec{\varphi}_\lambda\}$ by a standard procedure O yields the desired noninertial frame $\{\vec{f}_\mu\}$:

$$\vec{f}_\mu = \Sigma_\lambda O_{\mu\lambda} \vec{F}_\lambda \tag{6}$$

where:

$$OG(\varphi)O^t = I_3 \tag{7}$$

$$= OAG(q)A^tO^t = BG(q)B^t \tag{8}$$

with $B \equiv OA$.

Let $\varphi^{\lambda\mu}$ be the component of $\vec{\varphi}_\lambda$ with respect to $\vec{f}_\mu$ and F be the (3×3) matrix of the components $\varphi^{\lambda\mu}$: $O = F^{-1}$ and (7) can be written as well as:

$$FG(q)^{-1}F^t = I_3 \tag{9}$$

For a given A, this system is not independent and there exists 3

liaisons among the $\varphi^{\lambda\mu}$ and consequently, by using (4), among the components of the GJV's $y^{k\mu} = (\vec{q}_k, \vec{f}_\mu)$.

Corresponding to the matrix B, equations (1–4) become:

$$\vec{z}_\lambda = \Sigma_k B_{\lambda k} \vec{c}_k \tag{10}$$

$$G(z) = BB^t = OAA^tO^t \tag{11}$$

$$\vec{f}_\lambda = \Sigma_k B_{\lambda k} \vec{q}_k \tag{12}$$

$$G(f) = BG(q)B^t = I_3 \tag{13}$$

In short, to any set of three independent linear combinations of the base vectors of label space, there corresponds in physical space a unique noninertial frame. The frame is orthonormal if the (3×n) matrix B representing the set satisfies (6). This condition imposes 3 constraints on the elements of the matrix B and consequently on the 3n components $y^{k\lambda}$. The way the frame is tied to the configuration of the GJV is entirely defined by the matrix B.

It is interesting to observe that the same frame can be obtained from an infinity of procedures:

let A and A′ be two different linear combination matrices; there exists a transformation $\mathscr{A}$ such that :

$$A' = \mathscr{A}A$$

The corresponding Gram matrices are

$$G(\varphi) = AG(q)A^t$$

$$G(\}') = A'G(q)A'^t$$

$$\rightarrow \quad G(\varphi) = \mathscr{A}^{-1}A'G(q)A'^t(\mathscr{A}^{-1})^t = \mathscr{A}^{-1}G(\varphi')(\mathscr{A}^{-1})^t$$

Let O and O′ be the orthonormalization matrices providing the same frame {f} from the different sets $\{\varphi\}$ and $\{\varphi'\}$:

$$\rightarrow \quad OG(\varphi)O^t = O'G(\varphi')O'^t = O\mathscr{A}^{-1}G(\varphi')(\mathscr{A}^{-1})^tO^t = I_3$$

$$\rightarrow \qquad O' = O\mathscr{A}^{-1} \tag{14}$$

Note: two orthonormalization matrices O and O′ of the same set of vectors $\{\varphi\}$ are related by $O' = \mathscr{R}O$ where $\mathscr{R}$ is orthogonal since $O'G(\varphi)O'^{t} = \mathscr{R}OG(\varphi)O^{t}\mathscr{R}^{t} = \mathscr{R}I_3\mathscr{R}^{t} = I_3$. O and O′ in equation (2.5"") do not obey this rule since they are not orthonormalizations of the same set of vectors

This result is quite interesting since it permits to simplify the construction of a frame using an easier orthonormalization procedure. For instance, analytically, the E.S. procedure of three vectors is quite cumbersome and it is easier to construct the desired frame in using a Gram–Schmidt procedure for two vectors obtained by the appropriate transformation $\mathscr{A}$. Actually, any frame can be constructed in using two vectors and a planar orthonormalization; the third vector is automatically defined by their vector product.

On the other hand, the vectors $\vec{q}_i$ are expressible in a unique way in terms of the base vectors $\vec{f}_\lambda$:

$$\vec{q}_k = \Sigma_\lambda y^{k\lambda}\vec{f}_\lambda \tag{15}$$

where $y^{k\lambda}$ are the components of $\vec{q}_k$ with respect to the frame $\{\vec{f}\}$.

Dot (2.3′) with $\vec{f}_\alpha$ to obtain the matrix equation:

$$BY = I_3 \tag{16}$$

where Y is the n×3 matrix whose elements are the components $y^{k\lambda}$. The uniqueness of the expansion (8) allows us to define Y as the unique pseudo–inverse of B (Penrose–Moore inverse): $Y = B^{\dagger}$.

Dot (5) with $\vec{\ell}_\alpha$ to obtain the matrix equation:

$$R = BQ \tag{17}$$

where R is the orthogonal matrix whose elements are the direction cosines

of $\vec{f}_\lambda$ with respect to $\vec{\ell}_\alpha$ hence the matrix representing the rotation transforming the inertial frame into the noninertial frame defined by B; Q is the n×3 matrix whose elements are $q^{k\lambda}$, components of $\vec{q}_k$ along the inertial frame vectors $\vec{\ell}_\lambda$. Under the rotation R, Q transforms into Y (dot equation 2.6 with $\vec{\ell}_{\alpha'}$):

$$Y = QR \tag{18}$$

The invariance of the Gram matrix G(q) under R is easily shown: $G'(q) = YY^t = QRR^tQ^t = QQ^t = G(q)$.

With the same notation, we define the (3×3) mass quadrupole tensor in the inertial frame:

$$\mathcal{M} = Q^tQ \tag{19}$$

Actually, the mass quadrupole is related to the more conventional tensor of inertia $\mathcal{I} = \mathrm{Tr}\mathcal{M}I_3 - \mathcal{M}$ whose elements are the usual moments of inertia $\mathcal{I}_{\alpha\beta}$.

Under the rotation R, $\mathcal{M}$ transforms into

$$\mathcal{M}' = Y^tY = R^t\mathcal{M}R \tag{20}$$

and is of course not invariant under physical orthogonal transformations. It is now easy to show that the Gram matrix of the label vectors $\vec{z}_\lambda$ is actually the inverse of the mass quadrupole:

$$G(z) = BB^t = \mathcal{M}^{-1} \tag{21}$$

Otherwise stated, $(\vec{z}_\lambda, \vec{z}_\mu) = (\mathcal{M}^{-1})_{\lambda\mu}$.

We can consider in a similar way label orthogonal transformations ρ. This corresponds to a change of representation of the same configuration: a set of GJV's {q} is transformed into a new set of GJV's {q'}. Under ρ, G(q) transforms into G(q'):

$$G(q') = \rho G(q)\rho \tag{22}$$

whereas the mass quadrupole remains invariant:

$$\mathscr{M}' = Q^t \rho^t \rho Q = Q^t Q = \mathscr{M} \tag{23}$$

Let Q(r) be the 3×n matrix of the components of a set of interparticle vectors with respect to the inertial frame.

Under an arbitrary label transformation τ, Q(r) transforms into Q(r′) according to:

$$Q(r') = \tau Q(r) \tag{24}$$

where Q(r′) is the matrix of the components of a set {r′} of linearly independent physical vectors representing the same configuration with repect to the inertial frame.

Under a physical orthogonal transformation R, Q(r) transforms into Q′(r) according to:

$$Q'(r) = Q(r)R \tag{25}$$

where Q′(r) is the matrix of the components of the interparticle vectors with respect to a new frame obtained from the inertial frame.

Combining the two procedures gives the matrix Q′(r′) of the components of the new representation in a new frame:

$$Q'(r') = \tau Q(r)R \tag{26}$$

The Gram matrix for the new representation is:

$$G'(r') = \tau Q(r)\tau' = G(r') \tag{27}$$

The mass quadrupole for the representation {r′} in the new frame is :

$$\mathscr{M}'(r') = R^t Q^t(r) \tau^t \tau Q(r) R \tag{28}$$

If τ is orthogonal, i.e., change of a set of interparticle vectors into another set of linearly independent interparticle vectors, the mass quadrupole remains the same. Of particular interest are the

orthonormalizing transformations O: in such cases, $\tau^t\tau = g(r)$, the metric tensor of the label basis associated with the representation {r}.

Consider the orthogonal transformation diagonalizing $\mathscr{M}$:

$$R\mathscr{M}R^t = \Lambda \tag{29}$$

The resulting frame is constituted by the principal axes of inertia of the GJV's. This frame does not correspond to the principal axes of inertia of the interparticle vectors, the latter being not obtained from a GJV description by an orthogonal transformation but rather by an orthonormalization procedure O transforming the non orthonormal representation {r} into {q}.

REFERENCES

1. M. Born and J. Oppenheimer, Ann. Physik, 84 (1927) 457
2. J.C. Brester, Z. Physics, 24 (1924)
3. E.P. Wigner, Gottinger Nachrichten (1930) 133. A translation and discussion of this paper among others appears in the monograph by A.P. Cracknell, *Applied Group Theory*, Pergamon, New York, 1968
4. E. B. Wilson, J. Chem. Phys. 2 (1934) 432
5. C. Eckart, Phys. Rev. 46 (1934) 383
6. C. Eckart, Phys. Rev. 47 (1935) 552
7. H.B.G. Casimir, Koninckl. Ned. Akad. Wetenshap Proc. 34 (1931) 844
8. "Rotation of a Rigid Body in Quantum Mechanics", H.B.G. Casimir (Walters, Groningen, Netherlands, 1931)
9. J.O.Hirschfelder and E. P. Wigner, Proc. Nat. Acad. Sci. 21 (1935) 113
10. J.H. Van Vleck, Phys. Rev. 47 (1935) 487
11. B.T. Darling and D.M. Dennison, Phys. Rev. 57 (1940) 128
12. J.K.G. Watson, Mol. Phys. 15 (1968) 479
13. J.D. Louck and H.W. Galbraith, Rev. of Mod. Phys. 48 (1976) 69
14. H.H. Nielsen, Rev. Mod. Phys., 23 (1951) 90
15. "Encyclopedia of Mathematics, Angular Momentum in Quantum Physics", J.D. Louck and L.C. Biedenharn (Addison–Wesley,1981)
16. J.H. Van Vleck, Phys. Rev. 47 (1935) 487
17. K.F. Freed and J.R. Lombardi, J. Chem. Phys., 45 (1966) 591
18. F.T. Smith, Phys. Rev. 120 (1960) 1058
19. F.T. Smith, J. Math. Phys. 3 (1962) 75

20. R. C. Whitten and F.T. Smith, J. Math. Phys. 9 (1968) 1103

21. R. C. Whitten, J. Math. Phys. 10 (1969) 1631

22. R. C. Whitten and J.C. Sims, Phys. rev. A. 9 (1974) 1586

23. B.R. Johnson, J. Chem. Phys. 73 (1980) 5051

24. B.R. Johnson, J. Chem. Phys. 79 (1983) 1906

25. B.R. Johnson, J. Chem. Phys. 79 (1983) 1916

26. M. Mishra and J. Linderberg, Mol. Phys. 50 (1983) 91

27. J. Linderberg and Y. Ohrn, Int. J. Quantum Chem. 27 (1985) 273

28. Y. Ohrn and J. Linderberg, Mol. Phys. 49 (1983) 53

29. B. Buck, L.C. Biedenharn and R.Y. Cusson, Nucl. Phys., A317

30. O.L. Weaver, R.Y. Cusson and L.C. Biedenharn, Ann. Phys. 102 (1976) 493

31. C.F. Curtiss, J.O. Hirschfelder and F.T. Adler, J. Chem. Phys. 18 (1950) 1638

32. R. Wallace, Chemical Physics, 88 (1984) 247

33. J.O. Hirschfelder and J.S. Dahler, Physics 42 (1956) 363

34. J.O. Hirschfelder, Int. J. Quantum Chem. 3S (1969) 17

35. D.W. Jepsen and J.O. Hirschfelder, Physics 45 (1959) 249

36. D.J. Rowe, Nuclear Phys. A152 (1970) 273

37. P. Gushani and D.J. Rowe, Can. J. Phys. 54 (1976) 970

38. H.M. Pickett, J. Chem. Phys., 56 (1972) 1715

39. B.T. Sutcliffe, Molecular Physics 48 (1983) 561

40. "The Classical Groups", H. Weyl, Princeton University Press, Princeton, 1946

41. S. Carter, N.C. Handy and B.T. Sutcliffe, Molecular Physics, 49 (1983) 745

42. A.J.C. Varandas and J.N. Murrell, J. Chem. Soc. Faraday Trans. II 73 (1977) 939

43. S. Carter, I.M. Mills and J.N. Murrell, Molec. Phys. 39 (1980) 455

44. V. Spirko, J. Molec. Spect., 101 (1983) 30

45. S. Carter, I.M.Mills, J.N. Murrell and A.J.C. Varandas, Mol. Phys. 45 (1982) 1053

46. "Molecular Potential Energy Functions", J.N. Murrell, S. Carter, S.C. Farantos, P. Huxley and A.J.C. Varandas, John Wiley & Sons (1984)

47. F.T. Smith, Phys. Rev. Letters 45 (1980) 1157