

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

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"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

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## 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.



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## 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<sup>1</sup>). The use of normal coordinates (Brester<sup>2</sup> and Wigner<sup>3</sup>) for the description of these motions was investigated thoroughly by Wilson<sup>4</sup>. It was, however, only in 1934 and 1935 that Eckart<sup>5,6</sup> 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<sup>7,8</sup>.

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<sup>5</sup> 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<sup>9</sup>). 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<sup>10</sup> 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<sup>11</sup>. A further simplification was proposed later by Watson<sup>12</sup> whereas Louck and Galbraith<sup>13,14</sup> 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*<sup>15</sup> 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<sup>10,16</sup> 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<sup>17</sup> (using valence coordinates) and by Smith and co-workers<sup>18-22</sup> (using hyperspherical coordinates). Lately, Johnson<sup>23-25</sup> reviewed the results for three-body systems and Ohn<sup>26-28</sup> used hyperspherical coordinates for the description of four-bodies. Buck and co-workers<sup>29</sup> 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*<sup>30</sup> 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*<sup>31</sup> 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<sup>32</sup> to bound state problems incorporating the (orthogonal) Jacobi vectors description ("mobiles"<sup>33-35</sup>) 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 primarily 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 attributable to the source potential function itself. Assume that a

potential (source potential) can be set up from spectroscopic data<sup>41-46</sup> 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:

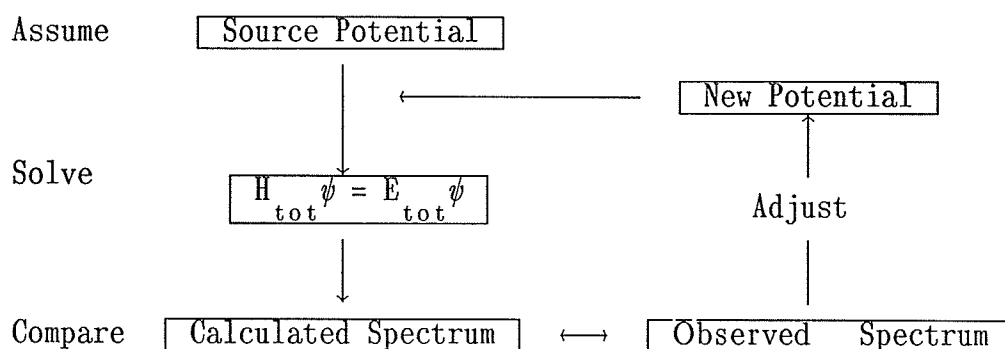


Figure 1

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<sup>38-39</sup> 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<sup>40</sup> (lengths  $Q_i$  and angles  $\theta_{ij}$  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  $\theta_{ij}$  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<sup>1</sup> 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 describe 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<sup>2-5</sup> or, in the case of the

three-body system, by hyperspherical polar coordinates<sup>6,7</sup>. 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 ordinarily met by generalized Jacobi coordinates but these may be symmetrized as originally suggested by Hirschfelder<sup>5,8</sup> 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.<sup>9</sup>) 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<sup>2-4</sup> 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<sup>9</sup>. 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  $x = (x_1, x_2, \dots, x_n)$  be a column vector constructed from the set of  $n = N-1$  bond vectors. The bilinear form defined by the (symmetric) Gram matrix,

$$G = xx^t$$

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

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

$$Q = O x \quad (2.2)$$

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  $i, j, \dots$  denote particle identification labels, and  $\alpha, \beta, \gamma$  denote cartesian components. An arbitrary configuration in the 3N-dimensional configuration space,  $\Omega_{3N}$ , can be denoted by a vector

$$X = \sum_{i, \alpha} x^{i\alpha} e_{i\alpha} \quad (2.3)$$

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

$$g(\Omega) = \begin{bmatrix} \mathbf{D}_N & 0 & 0 \\ 0 & \mathbf{D}_N & 0 \\ 0 & 0 & \mathbf{D}_N \end{bmatrix} \quad (2.4)$$

where

$$D_N = \text{diag}(m_1, m_2, \dots, m_n) \quad (2.5)$$

The trace of  $D_N$  is the total mass  $M$ . The configuration space can be regarded as a direct product of a "label space",  $\Lambda_N$ , and a "physical space"  $E_3$ :

$$\Omega_{3N} = \Lambda_N \otimes E_3 \quad (2.6)$$

Likewise the base vectors of the configuration space can be expressed

$$e_{i\alpha} = e_i \otimes d_\alpha \quad (2.7)$$

where  $e_i$  are the label space base vectors and  $d_\alpha$  are the "physical" three-dimensional-space base vectors.

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

$$e' = Ae, \quad e = A^{-1}e' \quad (2.8)$$

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

$$X = x^t e = x'^t e' = x'^t A e \quad (2.9)$$

Hence

$$x' = (A^{-1})^t x \quad (2.10)$$

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

$$g' = e' \cdot e'^t = A e \cdot e^t A^t = A g A^t \quad (2.11)$$

The center-of-mass coordinate in  $\Lambda_N$  is conventionally defined as follows:



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

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  $N$ -dimensional label space is a direct sum,

$$\Lambda_N = \Lambda_{\text{rel}} \oplus \Lambda_G \quad (2.17)$$

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

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

One seeks those linear transformations,  $O$ , in the space  $\Lambda_{\text{rel}}$  which will diagonalize  $g'$ . All such transformations define orthogonal coordinates in  $\Lambda_{\text{rel}}$ .

### 3. Orthonormalization procedures in $\Lambda_{\text{rel}}$ .

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

$$E' = Oe \quad (3.1)$$

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

$$E'E'^t = 1 \quad (3.2)$$

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