Derivation of ρ -dependent coordinate transformations for nonrigid molecules in the Hougen-Bunker-Johns formalism

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In this paper, we report a series of transformations for the construction of a Hamiltonian model for nonrigid polyatomic molecules in the framework of the Hougen-Bunker-Johns formalism (HBJ). This model is expressed in normal mode coordinates for small vibrations and in a specific coordinate ρ to describe the large amplitude motion. For the first time, a general procedure linking the “true” curvilinear coordinates to ρ is proposed, allowing to express the potential energy part in the same coordinate representation as the kinetic energy operator, whatever the number of atoms. A Lie group-based method is also proposed for the derivation of the reference configuration in the internal axis system. This work opens new perspectives for future high-resolution spectroscopic studies of nonrigid, medium-sized molecules using HBJ-type Hamiltonians. Illustrative examples and computation of vibrational energy levels on semirigid and nonrigid molecules are given to validate this method.

Keywords: Hougen-Bunker-Johns Hamiltonian, nonrigid molecules, large amplitude motions, ρ , $\bar{\rho}$, normal coordinates, coordinate transformations, internal axis system

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I. INTRODUCTION

The astronomical observations based on new generation of space telescopes, satellites and exploratory missions provide exciting information about molecular universe¹. In this context, the analyses of astronomical spectra are vital for the determination of chemical abundances and temperature conditions. There is an increasing interest in the investigation of molecular systems detected in both cold (Titan², interstellar media³) and hot atmospheres (exoplanets, brown dwarfs, and cool stars⁴⁻⁷), requiring the development of accurate theoretical models for the modelling, analysis and interpretation of spectra. One of the challenging problems in computational molecular spectroscopy³ is the study of nonrigid "floppy" molecules characterized by one or several large amplitude motions (LAMs). The use of adapted vibrational coordinates is thus required to describe LAMs such as internal rotation (e.g. C₂H₆, HNO₃, HONO)⁸⁻¹¹, floppy bending (e.g. C₃, CH₂)¹²⁻¹⁴ or inversion (e.g. NH₃)^{15,16}. Because the study of high-lying LAM vibrational states lies in the frontier between spectroscopy and chemical dynamics, floppy molecules have attracted much attention from both theoretical and experimental sides. As stated by Bačić and Light in a review paper¹⁷, "*studying floppy molecules is challenging because it forces us to reexamine, modify, and often abandon many of the basic concepts, formalisms, and computational methods applicable to small amplitude vibrations*". These past few decades, a large number of theoretical studies^{10,18-28} has been devoted to the investigations of LAMs using different kinds of vibrational coordinates implemented in various computer codes (see Section III.).

The present work essentially focuses on the approach proposed in 1970 by Hougen, Bunker and Johns (HBJ)²⁹. The HBJ model can be considered as the nonrigid counterpart of the semirigid Watson formalism³⁰ which over the years became the standard toolbox in high-resolution molecular spectroscopy^{31,32}. The conceptual difference with the commonly-used curvilinear nonrigid models is this similarity with the Watson formalism, augmented by an efficient combination of rectilinear, normal-mode coordinates to describe the small vibrations with curvilinear $\bar{\rho}$ ("real") and ρ ("effective") LAM coordinates and including their couplings with the rotational motion.

Here, the geometrically-defined $\bar{\rho}$ coordinate is used to build the potential energy function while ρ is involved in the kinetic energy operator (KEO). Although the link between $\bar{\rho}$ and ρ must be clearly established in order to express both the KEO and PES in the same

set of coordinates, the combination of Q with $(\bar{\rho}, \rho)$ is threefold. (i) It turns out quite natural because each all the vibration characterized by Q will be small along the reference configuration defined by ρ . (ii) It allows fast analytical computation of the matrix elements in variational calculations. (iii) It could further serve to derive “polyad” spectroscopic effective Hamiltonians for high-resolution analyses of nonrigid, medium-sized molecules. So far, explicit relations between $\bar{\rho}$ and ρ were derived only for triatomic molecules by Jensen³³.

A generalization to an arbitrary number of atoms through a series of transformations is the purpose of the present paper that will be structured as follows. The strategy of the proposed approach as well as its main potential advantages are summarized in Sec. II. An overview of relevant theoretical studies devoted to nonrigid molecules using or not the HBJ philosophy is given in Sec. III. In the next section, we will recall general definitions about LAM coordinates and propose a method for the construction of the ρ -dependent reference configuration in the internal axis system. The procedure for all coordinate transformations as well as the construction of the HBJ Hamiltonian will be presented in Sections V. and VI. As numerical validations, the computation of vibrational energy levels for some 3- and 4-atomic semirigid and nonrigid molecules will be given in Section VII. This is a necessary step before considering larger nonrigid systems like CH_3OH , C_2H_6 , etc. detected in many astrophysical environments (*e.g.* giant planets, Titan^{2,34}) and for which the computation of highly-excited ro-vibrational states is still challenging.

II. KEYS OF THE PROPOSED APPROACH

Based on a series of coordinate transformations, our strategy consists in converting the *ab initio* curvilinear potential V naturally expressed in the geometrically-defined $\bar{\rho}$ and internal (or symmetry) coordinates to a function of $3N - 7$ normal coordinates Q and of ρ . The construction scheme of HBJ-type Hamiltonians for the nuclear motions in molecules can be outlined as

$$H^{HBJ} = T^{HBJ}(\rho, Q; -id/d\rho, -id/dQ; J_x, J_y, J_z) + [V(\bar{\rho}, R) \rightarrow V(\rho, Q)],$$

where J_α are the components of the total angular momentum in the molecular frame and T^{HBJ} is the original kinetic energy operator derived by Hougen *et al.*²⁹ Let us summarize the main potential advantages of an extension of this approach for polyatomic molecules:

- Contrary to most of the KEO expressions in curvilinear coordinates, the form and complexity of T^{HBJ} remain the same whatever the number of atoms. Similarly to the Watson KEO for semirigid molecules, a unique and simple implementation of T^{HBJ} in a computer code would allow one to tackle the problem in the general case of nonrigid polyatomic molecules.
- The use of the normal mode Q and effective ρ coordinates in T^{HBJ} allows an optimal separation between the small and large amplitude nuclear motions. This is achieved by the Sayvetz condition³⁵.
- A polynomial expansion in Q and ρ in appropriate elementary functions for both KEO and PES may lead to an efficient algebraic solution of Schrödinger equation with the HBJ Hamiltonian, making thus possible the use of our reduction-compression tools^{36–38} initially designed for variational nuclear motion calculations of semirigid molecules. A full account of symmetry *via* the use of irreducible tensor operators^{36,39,40} can be also implemented.
- The algebraic formulation of the HBJ model could allow us to derive an *ab initio* effective model by applying a series of contact transformations^{41,42}. In this context, an empirical optimisation of only a small set of Hamiltonian parameters will be sufficient to match high-resolution observed spectra⁴³.

We expect that a systematic development and computer implementation of such an approach could pave the way for the computation of highly-excited states involved in the construction of complete lists of rovibrational transitions in high-temperature conditions. This is in spirit of the ongoing work on the construction of theoretical spectroscopic databases^{44–46} for new molecular species relevant for astrophysical applications.

III. OVERVIEW OF THEORETICAL STUDIES FOR NUCLEAR MOTION CALCULATIONS IN NONRIGID MOLECULES

1. *Methods based on the HBJ approach*

The study of nonrigid systems is a long-standing topic which started in 1939 with the work of Sayvetz³⁵. He was the first to introduce the notion of “anomalous” molecules with one or several vibrational LAM requiring a specific treatment that goes beyond conventional “semirigid” approach. However, no advanced calculations were carried out until the pioneering work by Hougen, Bunker and Johns²⁹ in 1970 who derived a prototype Hamiltonian and applied it mostly to triatomic molecules. In their approach, the LAM is treated as part of the rotational problem using a specific coordinate ρ . A so-called reference configuration playing the role that has the equilibrium configuration in a standard scheme is introduced. It is chosen to minimize the coupling between LAMs and the small vibrations, achieved by the Sayvetz condition³⁵. These past five decades, the HBJ model inspired a substantial number of studies aimed at the derivation of effective Hamiltonians using perturbation theory. A part of them can be divided into 3 classes, namely: the *rigid bender* (1970-1972), the *semirigid bender* (1977-1983) and the *nonrigid bender* (1982 and later) models. The first two ones are simple models based on some crude approximations while the development of the more elaborate nonrigid bender Hamiltonian was motivated by the needs of interpretation of experimental CH₂ spectra in its ground electronic state. The rigid bender Hamiltonian was used in the original HBJ paper²⁹ for the calculation of HCN and DCN vibrational levels and later by Bunker and Stone^{47,48} for studying H₂O, HCN and their deuterated isotopologues. An extension to the four-atomic ammonia molecule was reported out by Špirko and co-workers^{49–55} in *nonrigid inverter* model. See table I for more detailed bibliographic references. An extension of the Contact Transformation method for nonrigid water and ammonia-type molecules has been considered in Refs.^{56–58}. More recently, the BELGI computer code has been developed by Kleiner *et al.*^{59–64} to study inversion or internal rotation of methyl groups and to compute both line positions and line intensities of nonrigid molecules.

Variational calculations, taking advantage of increasing computational resources, were performed for 3-atomic molecules^{65–71} using the MORBID computer program developed by Jensen²¹. More recently, Yurchenko *et al.* have developed the TROVE code²⁰ based on the

Sorensen’s approach⁷² and designed for general polyatomic molecules. The use of TROVE led to the construction of extensive ammonia line lists^{73,74} from accurate *ab initio* potential energy surfaces^{15,20,75–77}.

Contrary to the computer codes like MORBID or TROVE employing curvilinear internal coordinates, even for the description of the small vibrations, we adopt here the original HBJ formulation based on the use of both rectilinear and curvilinear coordinates. This makes possible an algebraic formulation of the HBJ Hamiltonian for each point of the numerical grid in ρ .

2. *Other types of approach*

There exist other approaches to compute energy levels of nonrigid molecules without using the HBJ “philosophy”. As stated above, the HBJ approach allows a maximum separation between the different types of molecular motions but in turn requires to truncate power series expansion in Q . This can be avoided by using exact KEO built in terms of curvilinear coordinates that are a natural choice for the description of floppy systems, combined with variational calculations (see for example Carter, Handy^{78,79}, Schwenke, Huang *et al.*^{18,80–83}, Csaszar *et al.*^{19,22,23,84}, Lauvergnat *et al.*^{9,24,85}, studies in the framework of MCTDH^{10,11,25,86–89}, Carrington, Wang^{90–92}, etc.). In such numerical calculations, no specific representation as *e.g.* Taylor expansion of the actual PES is required. A review of some earlier works can be found in Refs.^{93–96}. *Ab initio* effective rotational and rovibrational Hamiltonians for nonrigid systems *via* curvilinear second order vibrational Møller–Plesset perturbation theory was considered in Ref.⁹⁷.

To summarize, we give in Tab. I a non-exhaustive list of studies devoted to the treatment of nonrigid molecules, using or not the HBJ formalism.

IV. DEFINITIONS OF THE LAM COORDINATES–REFERENCE CONFIGURATION

As already mentioned, the HBJ approach inspired a series of works (see Tab. I). Their common element is the use of two classes of coordinates: large amplitude coordinates ρ_i and normal mode coordinates Q_k for the description of the small vibrations. The major difference

TABLE I. Non-exhaustive list of contributions and computer codes devoted to nonrigid molecules.

Contributor or computer code [†]	Coordinates	Type	Ref.
Rigid Bender	Normal [†]	E	29,47,48
SemiRigid Bender	Normal [†]	E	48,98–104
NonRigid Bender	Normal [†]	E	33,105–113
NonRigid Invertor	Normal [†]	E	49–55,114–117
Contact Transformations	Normal	E	56,58,118,119
Sorensen	Curvilinear [†]	E	72
Szalay	Normal [†]	E	120,121
Wang & Carrington	Curvilinear	V	90–92
Marquardt <i>et al.</i>	Curvilinear	V	122,123
MORBID [‡]	Curvilinear [†]	V	21,65–71,124
TROVE [‡]	Curvilinear [†]	V	20,73–76,125
Schwenke <i>et al.</i>	Curvilinear	V	18,80–82,126
Makarewicz	Curvilinear	V	127,128
GENIUSH [‡]	Curvilinear	V	19,23,84,129
BELGI [‡]	Normal [†]	E	59–64
Pearson <i>et al.</i>	Normal [†]	E	130–132
Coudert <i>et al.</i>	Curvilinear	E	133–137
ELVIBROT-TNUM [‡]	Curvilinear	V	9,24,85,135,138
TANA [‡]	Curvilinear	V	139
MCTDH [‡]	Curvilinear	V	10,11,25,86–89
DVR3D [‡]	Curvilinear	V	140
MULTIMODE [‡]	Normal	V	27,28,141,142
Tensor ^{‡,a}	Normal [†]	V	This work

[†] Based on the HBJ or similar idea; E $\equiv$ Effective Hamiltonian, V $\equiv$ Variational calculations.

^a Extension of the TENSOR computer code initially designed for semirigid molecules^{37,39}

between the semirigid and HBJ approaches lies in the introduction of a so-called reference configuration $\mathbf{a}(\rho_i)$ following LAMs instead of the fixed, equilibrium geometry $\mathbf{a}_e$. If we

FIG. 1. Schematic representation of a 3-atomic nonlinear molecule in its reference configuration (defined by ρ, r_{21}^e and r_{23}^e coordinates) and in its instantaneous configuration (defined by $\bar{\rho}, r_{21}, r_{23}$ coordinates).

consider a molecule with L large amplitude motions, the vibrational part will be described as follows:

Small amplitude motions $\leftrightarrow$ $(3N - 6 - L)$ -like normal coordinates Q_k

Large amplitude motions $\leftrightarrow$ $\rho_i, \bar{\rho}_i$ with $i = 1, \dots, L$

In this paper, we will limit ourself to only one LAM ($L = 1$) associated with 2 specific coordinates, namely $\rho_1 \equiv \rho$ and $\bar{\rho}_1 \equiv \bar{\rho}$ but the strategy would be similar for $L > 1$. As stated by Szalay¹⁴³, ρ can be considered as a kind of “effective” mass-dependent coordinate for which all other coordinates are kept fixed. The HBJ kinetic energy operator depends explicitly on this variable while the potential function is built from the geometrically defined angle $\bar{\rho}$ (*i.e.* bond angles, torsional/dihedral angles, inversion angle) that will differ from ρ beyond the reference configuration (see Fig. 1 in the case of triatomic molecules). As a simple illustration, Papoušek and Špirko¹⁴⁴ have determined for NH_3 the dependence of $\bar{\rho}$ on ρ when all instantaneous bond lengths and valence angles are equal, but different from the reference configuration. Here, ρ is the angle subtended by the NH bond of the reference configuration and the C_3 axis (see Fig. 4 of Ref.¹⁴⁴). In this particularly case, the following simple relation holds

$$\cos(\rho) = \frac{r}{r_e} \cos(\bar{\rho}), \quad (1)$$

and we can easily notice that ρ and $\bar{\rho}$ coincide at the reference configuration.

A. Determination of the reference configuration in the Internal Axis System

By definition, the reference configuration depends explicitly on ρ and is defined with respect to a specific molecular axis system. It is common to use the Internal Axis System (IAS) for which the internal angular momentum due to ρ vanishes and where the zero-order cross terms $I_{\alpha\rho}^{(0)}$ ($\alpha = x, y, z$) of the 4×4 generalized inertia matrix $\mathbf{I}$ are zero. This condition of vanishing implies

$$\mathbf{I}_{\text{Rot-LAM}} = \sum_{i=1}^N m_i \mathbf{U}(\rho) \mathbf{a}_i \times \frac{d\mathbf{U}(\rho) \mathbf{a}_i}{d\rho} = \mathbf{0}, \quad (2)$$

where N denotes the number of atoms. $\mathbf{U}(\rho)$ is a LAM-dependent rotation matrix that will transform the position vectors $\mathbf{a}_i$ defined in an initial molecular axis system (MF_1) to those in the IAS for each value of ρ . In the standard HBJ derivation, the initial reference configuration was defined in the literature for 3 and 4-atomic nonrigid molecules as a function of an auxiliary angle $\epsilon(\rho)^{33,116}$ that must satisfy Eq. (2). This angle is generally defined as the angle between the z -axis and one of the equilibrium bond length (see *e.g.* Fig. 1 of Ref.³³ or Fig. 5 of Ref.¹⁴⁴). Szalay and Ortigoso¹⁴⁵ proposed a way to derive the rotation matrix from the Floquet theory¹⁴⁶. Recently, an alternative method to determine $\mathbf{U}(\rho)$ was considered¹⁴⁷. It consists in integrating the kinematic equation

$$\frac{d\mathbf{U}(\rho)}{d\rho} = \mathbf{U}(\rho) \boldsymbol{\Omega}(\rho), \quad (3)$$

using methods by Lie group and Lie algebra where $\boldsymbol{\Omega}(\rho)$ is a skew-symmetric matrix involving the LAM dependent angular velocity vector components $(\omega_x, \omega_y, \omega_z)$ defined by $\boldsymbol{\omega}(\rho) \equiv \boldsymbol{\omega}^{\text{exact}} = -\mathbf{I}_{\text{Rot-Rot}} \mathbf{I}_{\text{Rot-LAM}}$ with $\mathbf{I}_{\text{Rot-Rot}}(\rho)$ the rotational tensor of inertia. To exemplify these techniques, we would like to show here how to define a reference configuration without knowing an explicit analytic $\epsilon = f(\rho)$ relation. The asymmetric deuterated substitutions of water and ammonia molecules (HDO and NH_2D) as well as HNO_3 are chosen as illustrative examples.

Using the skew symmetric matrix $\mathbf{P} = \sum p_\alpha S_\alpha$ where $S_\alpha = (S_x, S_y, S_z)$ are the generators of the $so(3)$ Lie algebra, the elements of the rotation Lie-group $SO(3)$ can be obtained *via* the exponential mapping^{148,149} $\mathbf{U} = \exp(\mathbf{P})$. Here, the three components (p_x, p_y, p_z) of $\mathbf{P}$ are to be determined. At this stage, it can be shown that the problem (3) reduces to solve

FIG. 2. Variation of $I_{\alpha\rho}$ (left) and ω_α (right) as function of the LAM coordinate ρ for HNO_3 .

a set of three differential equations given by (see Appendix B of Ref.¹⁴⁷)

$$\frac{d\mathbf{P}}{d\rho} = \frac{1}{2}(\mathbf{P} \times \boldsymbol{\omega}) \cdot \mathbf{S} + \frac{\boldsymbol{\omega} \cdot \mathbf{S}}{2} \|p\| \cot\left(\frac{\|p\|}{2}\right) - \frac{(\mathbf{P} \cdot \boldsymbol{\omega})(\mathbf{P} \cdot \mathbf{S})}{2\|p\|^2} \left[\|p\| \cot\left(\frac{\|p\|}{2}\right) - 2 \right], \quad (4)$$

where $\|p\|$ is the Euclidean norm. From the initial reference configuration of asymmetric ABC molecules (see Fig. 2 of Ref.¹²⁰), the condition (2) for HDO is not fulfilled. For NH_2D (see Fig. 5 of Ref.¹⁴⁴ for the definition of MF_1), the condition (2) is not satisfied as well. For example, we obtain the following rotation matrices (evaluated here at $\rho = \pi/4$) after solving (4)

$$\mathbf{U}^{\text{HDO}}(\pi/4) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0.9607 & 0.2776 \\ 0 & -0.2776 & 0.9607 \end{pmatrix}, \quad \mathbf{U}^{\text{NH}_2\text{D}}(\pi/4) = \begin{pmatrix} 0.9792 & 0 & 0.2030 \\ 0 & 1 & 0 \\ -0.2030 & 0 & 0.9792 \end{pmatrix}. \quad (5)$$

which are nothing but rotations of angle $\epsilon(\pi/4)$ (see Eqs. (2.7) and (3.28) of Refs.^{33,144}) about the x and y axes, respectively. Note that no rotation is required for H_2O and NH_3 when using the axis system of Ref.^{120,144}. Another interesting example is nitric acid (HNO_3) possessing one internal rotation where $\boldsymbol{\omega}(\rho)$ changes of direction (see Fig. 2) and for which no analytical solution exists for the IAS rotation matrix. This nonrigid molecule exhibits a torsional motion (corresponding to the ν_9 band) of the O(3)-H bond (called top) with respect to the much heavier group (called frame) characterized by the ρ angle between the plane containing H-O(3) bond and another one containing O(3)NO(2)O(1) (see Fig. 3). As

FIG. 3. HNO₃ in its reference configuration defined in the MF₁ and the definition of ρ .

an illustration, Eqs. (6) show the rotation matrices evaluated at $\rho = \pi/8$ et $\rho = 3\pi/2$

$$\mathbf{U}^{\text{HNO}_3}\left(\frac{\pi}{8}\right) = \begin{pmatrix} 0.9998 & 0.0164 & -0.0014 \\ -0.0164 & 0.9998 & 0.0100 \\ 0.0016 & -0.0100 & 0.9999 \end{pmatrix}, \quad \mathbf{U}^{\text{HNO}_3}\left(\frac{3\pi}{2}\right) = \begin{pmatrix} 0.9805 & 0.1948 & -0.0259 \\ -0.1954 & 0.9804 & -0.0265 \\ 0.0203 & 0.0310 & 0.9993 \end{pmatrix}. \quad (6)$$

Our strategy for the derivation of the ρ -dependent reference configuration in the IAS can be summarized as follows: (i) determination of the angular velocity vector $\boldsymbol{\omega}(\rho)$ in the MF₁, (ii) integration of Eq. (4) leading to the determination of the (p_x, p_y, p_z) components, (iii) calculation of the ρ -dependent rotation matrix $\mathbf{U}$ and (iv) computation of $a_i^{\text{IAS}}(\rho) = \mathbf{U}(\rho)a_i^{\text{MF}_1}(\rho)$. Convergence of rovibrational energy levels computed in both IAS and MF₁ will be discussed in Section VII for the asymmetric HDS molecule.

V. CONSTRUCTION OF THE HBJ HAMILTONIAN: PHILOSOPHY OF THE PRESENT APPROACH

We describe in this part the strategy to build the HBJ Hamiltonian in a convenient form in order to transpose our tools of variational calculations initially designed for the treatment of rigid molecules^{36–38}. The reference configuration $\mathbf{a}(\rho)$ defined in the IAS as well as the relation linking the coordinates $\bar{\rho}$ and ρ are key elements for the success of the proposed approach. A general procedure for the derivation of the relation $\bar{\rho} = f(\rho)$ will be proposed in

the next section but for the time being it will be assumed known. Note that unless specified otherwise, all running indices $i, j, k, \dots$ will take values $1, \dots, 3N - 7$, while Greek letters $\alpha, \beta, \dots$ will run over x, y , or z .

A. Resolution of the GF problem—strategy

One of the major difficulties in the polyatomic extension of the HBJ approach is to transform the *ab initio*-based curvilinear potential part into normal and ρ coordinates in a systematic manner. To this end, we define a set of $3N - 7$ normal coordinates Q_k by solving numerically the GF problem¹⁵⁰ on a grid of points $\rho_m \in [\rho_{min}, \rho_{max}]$ where the values ρ_{min} and ρ_{max} will depend on the type of LAM. As already mentioned in Introduction, the main drawback of the HBJ approach lies in the fact that the kinematic $\mathbf{G}$ matrix, defined from the reference configuration $\mathbf{a}(\rho)$, is thus ρ -dependent while the force constant $\bar{\mathbf{F}}$ matrix is determined from the potential function initially expressed in terms of $3N - 7$ internal coordinates and of $\bar{\rho}$. In short, we have $\mathbf{G} = \mathbf{G}(\rho)$ and $\bar{\mathbf{F}} = \bar{\mathbf{F}}(\bar{\rho})$ making it necessary to find the transformation $\bar{\mathbf{F}}(\bar{\rho}) \rightarrow \mathbf{F}(\rho)$ to express both the potential and KEO parts in the same set of coordinates, namely of (Q_k, ρ) . In other words, this requires deriving the relation $\bar{\rho} = f(\rho, \mathbf{S})$ to compute the elements $F_{ij}(\rho_m) \equiv \partial^2 V(\rho_m) / \partial S_i \partial S_j$ where $\{S\}$ is a set of symmetry-adapted curvilinear coordinates. In more details, these coordinates should be denoted as $S_{r\sigma_r}^{(\Gamma_r)}$ where Γ_r is the irreducible representation for a mode r and σ_r stands for a component to distinguish degenerate vibrations.

As a starting point, we assume that the potential function can be developed in power series of small-amplitude vibrational displacements

$$V = V_0(\bar{u}(\bar{\rho})) + \sum_i \bar{F}_i(\bar{u}(\bar{\rho}))S_i + \frac{1}{2} \sum_{ij} \bar{F}_{ij}(\bar{u}(\bar{\rho}))S_i S_j + \frac{1}{6} \sum_{ijk} \bar{F}_{ijk}(\bar{\rho})S_i S_j S_k + \dots, \quad (7)$$

where $\bar{F}_i, \bar{F}_{ij}, \bar{F}_{ijk}$ are $\bar{\rho}$ -dependent linear, quadratic and cubic force constants. The first term in Eq. (7)

$$V_0(\bar{\rho}) \equiv V_0(\bar{u}(\bar{\rho})) = \sum_r g_r [\bar{u}(\bar{\rho})]^r, \quad (8)$$

is the 1D LAM potential defined at the reference configuration ($V_0(\bar{\rho}) = V_0(\rho)$ if all $S_i = 0$). The notation $\bar{u}$ stands for appropriate elementary functions of LAM $\bar{\rho}$ coordinate *i.e.* $\bar{u}(\bar{\rho}) = \bar{\rho} - \bar{\rho}_e, \sin \bar{\rho}_e - \sin \bar{\rho}$, etc. which will be used for the modelling of the potential energy

surface. In order to properly solve the GF problem, it is quite straightforward to show from Eqs. (7) and (8) that $\bar{u}(\bar{\rho})$ takes necessarily the form

$$\bar{u}(\bar{\rho}) = u(\rho) + \sum_i C_i(u(\rho))S_i + \sum_{ij} C_{ij}(u(\rho))S_iS_j \quad (9)$$

where the ρ -dependent $C_i(u(\rho))$ and $C_{ij}(u(\rho))$ coefficients are to be determined (see Section VI) and u is not necessarily the same function as $\bar{u}$. We can note that only terms of degree 2 in S in (9) are required to fully determine a set of normal coordinates. This is in contrast with the MORBID approach where higher-order coefficients C_{ijk} , C_{ijkl} , *etc.*, are needed²¹ and have been determined analytically for triatomic molecules up to the fourth order (see Tab. 1 of Ref.³³). Assuming the C_i and C_{ij} coefficients known in this section, we can substitute Eq. (9) into (7) and solve the eigenequation

$$\mathbf{GF}(\rho_m)\mathbf{L}(\rho_m) = \lambda(\rho_m)\mathbf{L}(\rho_m) \quad (10)$$

to finally obtain the eigenvalues $\lambda_i(\rho_m)$ ($\equiv \omega_i(\rho_m)$) as well as the elements $L_{ij}(\rho_m)$ of the corresponding eigenfunctions. This is done in the same fashion as in the Born-Oppenheimer approximation (separation of “slow” and “fast” motions) where the electronic equation is solved on a grid of nuclear geometries. The elements of the $3N \times 3N - 7$ orthogonal transformation $\mathbf{I}(\rho_m)$ linking the mass-weighted Cartesian displacements to the normal coordinates are simultaneously computed using the same grid of points.

At this stage, it is shown that both the normal-mode KEO and the potential parts of the HBJ Hamiltonian can be completely determined from $\mathbf{I}(\rho_m)$. In order to further express the Hamiltonian as a power series in the $(Q_k, u(\rho))$ coordinates, our strategy consists in fitting the $3N \times 3N - 7$ elements $l_{s\alpha,k}(\rho_m)$ to n th order polynomial functions as

$$l_{s\alpha,k}(\rho) = \sum_{r=0}^n \tilde{l}_r^{s\alpha,k}[u(\rho)]^r, \quad (s = 1, \dots, N). \quad (11)$$

The Coriolis parameters can be either computed directly from $\mathbf{I}(\rho)$ or empirically-adjusted from the same grid. We thus write

$$\zeta_{ij}^\Theta(\rho) = \sum_{r=0}^n \tilde{\zeta}_{ij,r}^\Theta[u(\rho)]^r, \quad (\Theta = x, y, z, \rho). \quad (12)$$

Generally, $n=8, 10$ or 12 in Eqs. (11) and (12) is sufficient to obtain reasonably accurate root-mean-squares fit. This fitting procedure, though numerical, will make possible analytical computation of the matrix elements.

B. Transformation of the potential energy surface

In order to build an extended HBJ Hamiltonian, the initial PES (7) needs to be conveniently transformed to the normal mode and LAM coordinates. Unfortunately, the use of Eq. (9) is only valid for the solution of the GF problem within the quadratic approximation. In this context, and by analogy with the Hoy, Mills and Strey formalism¹⁵¹, all quantities are expressed in Cartesian displacements making possible the use of the orthogonal transformation $\mathbf{l}(\rho) \equiv \mathbf{l}(u(\rho))$ defined in Eq. (11). We finally write

$$\bar{u}(\bar{\rho}) = f(\mathbf{S}, u(\rho)) \xrightarrow{\text{Cartesian}} \bar{u}(\bar{\rho}) = f(\mathbf{S}(\mathbf{d}), u(\rho)) \xrightarrow{\mathbf{d}=\mathbf{M}^{-\frac{1}{2}}\mathbf{l}(\mathbf{u}(\rho))\mathbf{Q}} \bar{u}(\bar{\rho}) = g(\mathbf{Q}, u(\rho)). \quad (13)$$

From this expression, we can easily convert the potential function as :

$$V(\mathbf{S}, \bar{u}(\bar{\rho})) \xrightarrow{\text{Cartesian, } g(\mathbf{Q}, u(\rho))} V(\mathbf{S}(d), g(u(\rho), \mathbf{Q})) \xrightarrow{\mathbf{d}=\mathbf{M}^{-\frac{1}{2}}\mathbf{l}(\mathbf{u}(\rho))\mathbf{Q}} V(\mathbf{Q}, u(\rho)). \quad (14)$$

The passage (14) from the *ab initio* potential $V(\mathbf{S}, \bar{u}(\bar{\rho}))$ to $V(\mathbf{Q}, u(\rho))$ can be made from two different manners. The first way to proceed is to perform a Taylor-series expansion of all quantities around $Q = u = 0$. However, this procedure may suffer from a lack of convergence and thus fail to describe accurately the LAM if the form of the elementary function u is not appropriately chosen. Another route consists in performing this transformation numerically by generating a grid of points (Q_h, ρ_m) from $a(\rho_m)$ and $l(\rho_m)$ and fitting a potential function in the full $3N - 6$ -dimensional nuclear space. These two approaches will be discussed and compared in Section VI.

C. Formulation of the Hougen-Bunker-Johns Hamiltonian

Though only applied to tri- and tetra-atomic molecules^{33,49,50} so far, a general and compact expression of the KEO has been proposed by Hougen, Bunker and Johns²⁹ in 1970. It is given by

$$T = \frac{1}{2}\mu^{1/4} \sum_{\alpha, \beta=x,y,z,\rho} (J_\alpha - \pi_\alpha)\mu_{\alpha\beta}\mu^{-1/2}(J_\beta - \pi_\beta)\mu^{1/4} + \frac{1}{2}\mu^{1/4} \sum_{k=1}^{3N-7} P_k\mu^{-1/2}P_k\mu^{1/4}, \quad (15)$$

where $P_k = -i\hbar\partial/\partial Q_k$ is the conjugate momentum of the normal coordinates Q_k and J_α ($\alpha = x, y, z$) and $J_\rho = -i\hbar d/d\rho$ are the components of the total angular momentum and LAM coordinate, respectively. All other terms are well-described elsewhere^{29,33,144}. It is

important to note that according to Eqs. (11) and (12), all quantities involved in (15) will be ρ -dependent.

Finally, using Eqs. (14) and (15), the extended HBJ Hamiltonian can be written as

$$H(\mathbf{Q}, \mathbf{P}, \rho, J_\rho, J_\alpha) = T(\mathbf{Q}, \mathbf{P}, \rho, J_\rho, J_\alpha) + [V(\mathbf{S}, \bar{u}(\bar{\rho})) \rightarrow V(\mathbf{Q}, u(\rho))]. \quad (16)$$

Contrary to the previously published HBJ-based studies (see Tab. I) where a numerical treatment for the LAM coordinate was usually required (*e.g.* numerical integration using Numerov-Cooley), this Hamiltonian is written as a polynomial expansion in Q_k and $u(\rho)$ making thus possible the use of tensor operators for a full account of symmetry and computation of matrix elements from the Wigner-Eckart theorem. To this end, it is convenient to put the Hamiltonian (16) in a better suited normally-ordered form where each term is expressed as $f(Q, \rho)g(P)J_\rho w(J_\alpha)$. Here f and g are not necessarily commuting functions and $f(Q, \rho)$ does not commute with J_ρ . In order to apply our reduction technique³⁹ for efficient variational calculations previously developed for semirigid molecules, creation and annihilation operators of vibrational modes could be also introduced.

VI. GENERAL PROCEDURE FOR THE DERIVATION OF $\bar{u}(\bar{\rho}) = f(\mathbf{S}, u(\rho))$

At this stage, the key relation (9) linking the effective and “real” LAM coordinates allowing the construction of the matrix $\mathbf{F}(\rho_m)$ on a grid, remains undetermined. We propose in this section a general method for computing the $C_i(\rho)$ and $C_{ij}(\rho)$ coefficients through a two-step procedure.

A. Transformations between quadratic forms in internal and Cartesian coordinates

The first step is the determination of a set of equations $\mathbf{d} = \mathbf{d}(\mathbf{S}, u(\rho))$ relating the Cartesian displacements to the $3N - 7$ curvilinear and LAM coordinates. In other words, we have to invert the following set of nonlinear equations

$$S_i = \sum_r B_{i;r\alpha}^v(\rho) d_{r\alpha} + \frac{1}{2} \sum_{rs} B_{i;r\alpha,s\beta}^v(\rho) d_{r\alpha} d_{s\beta} + \cdots \quad (r, s = 1, \dots, N), \quad (17)$$

where the $B_{i;r\alpha}^v(\rho) \equiv B_{i;r\alpha}^v(u(\rho))$ and $B_{i;r\alpha,s\beta}^v(\rho) \equiv B_{i;r\alpha,s\beta}^v(u(\rho))$ coefficients depend on ρ *via* the reference configuration $\mathbf{a}(\rho)$. Bearing in mind that in the linear approximation, the $\mathbf{B}^v(\rho)$

$$\begin{aligned}
& \underbrace{\begin{pmatrix} R_1^2 \\ R_1 R_2 \\ \vdots \\ R_1 R_{3N-7} \\ R_1 T_x \\ R_1 T_y \\ \vdots \\ R_2^2 \\ T_x^2 \\ \vdots \\ R_z S \\ S^2 \end{pmatrix}}_{\frac{(3N)(3N+1)}{2} \text{ Quadratic terms}} = \mathbf{B}_{quad}(\rho_m) \underbrace{\begin{pmatrix} R_1 \\ R_2 \\ \vdots \\ R_{3N-7} \\ T_x \\ T_y \\ T_z \\ R_x \\ R_y \\ R_z \\ S \end{pmatrix}}_{(3N) \text{ Linear terms}} \\
& \mathbf{B}_{quad}(\rho_m) = \frac{9N(N+1)}{2} \times \frac{9N(N+1)}{2}
\end{aligned}$$

FIG. 4. Schematic representation of the $\mathbf{B}_{quad}$ matrix defined in Eq. (20) for each value $\rho_m \in [\rho_{min}, \rho_{max}]$.

matrix is of dimension $(3N - 7) \times 3N$, supplementary 7 constraints have to be introduced to properly define the inverse relation $d = d(S)$. These are the six translational and rotational Eckart conditions complemented by the Sayvets condition $\mathcal{S}$ defined by

$$\begin{aligned}
\mathcal{T}_\alpha &= \frac{1}{\sqrt{M}} \sum_{i=1}^N m_i d_{i\alpha} = 0, \\
\mathcal{R}_\alpha &= \frac{1}{\sqrt{I_{\alpha\alpha}^{ref}(\rho)}} \sum_{i=1}^N m_i \epsilon_{\alpha\beta\gamma} a_{i\beta}(\rho) d_{i\gamma} = 0, \\
\mathcal{S} &= \frac{1}{\sqrt{I_{\rho\rho}^{ref}(\rho)}} \sum_{i=1}^N m_i \frac{\partial a_{i\alpha}(\rho)}{\partial \rho} d_{i\alpha} = 0.
\end{aligned} \tag{18}$$

Here, M is the total mass of system, ϵ corresponds to the Levi-Civita tensor and $I_{\alpha\alpha}^{ref}$, $I_{\rho\rho}^{ref}$ are the diagonal elements of 4×4 inertia matrix²⁹. Finally, the new matrix $\mathbf{B}_{lin}(\rho_m)$ of dimension $3N \times 3N$ defined such as $(\mathbf{S}, \mathcal{T}_\alpha, \mathcal{R}_\alpha, \mathcal{S})^t = \mathbf{B}_{lin}(\rho_m) \mathbf{d}$ can be numerically computed on the grid of points and inverted. We thus write

$$\mathbf{d} = \mathbf{B}_{lin}^{-1}(\rho_m) (\mathbf{S}, \mathcal{T}_\alpha = 0, \mathcal{R}_\alpha = 0, \mathcal{S} = 0)^t. \tag{19}$$

However, quadratic terms $S_i S_j$ are also involved in Eq. (9) making insufficient the use of Eq. (19). To properly compute $C_i(\rho)$ and $C_{ij}(\rho)$, we have to construct all the quadratic forms

$\mathbf{X.Y}$ with $X_i = \{S_i, \mathcal{T}_\beta, \mathcal{R}_\beta, \mathcal{S}\}$ and $Y_j = \{S_j, \mathcal{T}_\beta, \mathcal{R}_\beta, \mathcal{S}\}$ from Eqs. (17) and (18), each of these forms being expanded at order 2 in Cartesian displacements to get a linear system of equations. This strategy closely follows the “linearisation” procedure proposed in Ref.⁴⁰ to invert the set of nonlinear equations $S = S(Q)$. This leads to

$$(\mathbf{S}, \mathcal{T}_\alpha, \mathcal{R}_\alpha, \mathcal{S}, \mathbf{X.Y})^t = \mathbf{B}_{quad}(\rho_m) (\mathbf{d}, \mathbf{d.d})^t, \quad (20)$$

where the new matrix $\mathbf{B}_{quad}(\rho_m)$ is of dimension $\frac{9N(N+1)}{2} \times \frac{9N(N+1)}{2}$. We have thus transformed the initial nonlinear problem (17) to a linear one. This transformation is schematically represented on Fig. 4 where $\mathbf{B}_{quad}(\rho_m)$ is numerically evaluated for each value $\rho_m \in [\rho_{min}, \rho_{max}]$. For example, this matrix will be of dimension 54×54 , 90×90 and 189×189 for 3-, 4- and 8-atomic molecules.

B. Computation of the linear Cartesian displacements and determination of Eq. (9)

From Eq. (20), we are now able to express the linear and quadratic Cartesian displacements for each ρ_m as a linear combination of $\mathbf{X}$ and $\mathbf{X.Y}$ as

$$(\mathbf{d}, \mathbf{d.d})^t = \mathbf{B}_{quad}^{-1}(\rho_m) (\mathbf{S}, \mathcal{T}_\alpha = 0, \mathcal{R}_\alpha = 0, \mathcal{S} = 0, X.Y)^t, \quad (21)$$

with $X.Y = 0$ if X or Y equals $\mathcal{T}_\alpha$, $\mathcal{R}_\alpha$ or $\mathcal{S}$. At this stage, we are finally able to define the $3N$ linear Cartesian displacements by extracting $3N$ lines and $\frac{(3N-7)(3N-4)}{2}$ columns from $\mathbf{B}_{quad}^{-1}(\rho_m)$ to give $\mathbf{A}_{quad}^{inv}(\rho_m)$ such that

$$\mathbf{d} = \mathbf{A}_{quad}^{inv}(\rho_m) (\mathbf{S}, \mathbf{S.S})^t. \quad (22)$$

This transformation is represented schematically in Fig. 5 where the red and green colours highlight the extracted parts from $\mathbf{B}_{quad}^{-1}(\rho_m)$.

From Eq. (22), the link between $\bar{\rho}$ and ρ can be clearly established by means of geometry considerations. For example, in the case of triatomic molecules like H_2O or C_3 for which $\bar{\rho}$ is a complementary angle to $\angle 123$ (see Fig. 1), we have

$$\cos(\bar{\rho}) = -\frac{\mathbf{r}_{21} \cdot \mathbf{r}_{23}}{\|\mathbf{r}_{21}\| \|\mathbf{r}_{23}\|}, \quad (23)$$

with $\mathbf{r}_{21} = \mathbf{a}_1(\rho_m) + \mathbf{d}_1 - \mathbf{a}_2(\rho_m) - \mathbf{d}_2$ and $\mathbf{r}_{23} = \mathbf{a}_3(\rho_m) + \mathbf{d}_3 - \mathbf{a}_2(\rho_m) - \mathbf{d}_2$. By Taylor-expanding (23) in Cartesian coordinates and by substituting (22) in the resulting polynomial,

FIG. 5. Extracted part of $\mathbf{B}^{quad}$ and schematic representation of $\mathbf{A}_{quad}^{inv}$ defined in Eq. (22).

we directly obtain the numerical coefficients $C_i(\rho_m)$ and $C_{ij}(\rho_m)$ for the function $\bar{u}(\bar{\rho}) = \cos(\bar{\rho})$. For pyramidal XY_3 molecules, $\bar{\rho}$ corresponds to the angle between the C_3 axis and the bond X–Y and can be defined by the relation

$$\sin(\bar{\rho}) = \frac{2}{\sqrt{3}} \sin[(\alpha_1 + \alpha_2 + \alpha_3)/6] \quad (24)$$

where α_i is the angle between $r_j \equiv \text{NH}_j$ and $r_k \equiv \text{NH}_k$ with $(ijk) = (123)$, (213) and (312)

$$\alpha_i = \cos^{-1} \left[\frac{\mathbf{r}_j \cdot \mathbf{r}_k}{r_j r_k} \right], \quad (25)$$

with $\mathbf{r}_j = \mathbf{a}_j(\rho) + \mathbf{d}_j - \mathbf{a}_4(\rho) + \mathbf{d}_4$. Similarly, we easily obtain the numerical coefficients $C_i(\rho_m)$ and $C_{ij}(\rho_m)$ for the function $\bar{u}(\bar{\rho}) = \sin(\bar{\rho})$. As an illustrative example, Fig. 6 displays the behaviour of these coefficients for NH_3 as a function of $u(\rho) = \Delta\rho = \rho - \pi/2$.

C. Comparison with existing expressions for 3-atomic molecules

In order to validate our approach, we considered analytical expressions available in the literature and derived by Jensen³³ for 3-atomic molecules. These latter were transformed to symmetry adapted coordinates and applied to H_2S , SO_2 and O_3 ^{152–154}. We have shown that our numerical coefficients C_i and C_{ij} evaluated at different values of ρ were all in excellent agreement (errors $< 10^{-8}$) with those obtained from the tabulated analytical expressions³³.

FIG. 6. C_i et C_{ij} Coefficients of Eq. (9) for NH_3 as a function of $\Delta\rho = \rho_m - \pi/2$ with $\rho_m \in [0.68, 2.50]$ rad.

Another source of validation has consisted in comparing our results for the ozone PES¹⁵⁴ to those provided by P. Jensen from the MORBID code²¹. All the coefficients in front of Δr_1 , Δr_3 , Δr_1^2 , Δr_3^2 and $\Delta r_1 \Delta r_3$ obtained from both methods were identical, whatever the value of ρ .

VII. NUMERICAL VALIDATION: COMPUTATION OF VIBRATIONAL ENERGY LEVELS

The final validation is the computation of vibrational energy levels obtained from the extended HBJ Hamiltonian (16) and more generally from the procedure described in Sections V and VI. As a first step, we consider 3-atomic and 4-atomic semirigid molecules (H_2S , SO_2 , O_3 , PH_3), for which numerically exact benchmark results are available using the well established Eckart-Watson formalism and potential energy surfaces from Refs.^{152–155}. This permits checking all algebraic transformations described above with high precision at the

TABLE II. Selected vibrational energy levels for H₂S, SO₂ and O₃ computed from the HBJ model (E^{HBJ} , this work) and comparison to those obtained from the Watson-Eckart Hamiltonian. Here, $\Delta E = E^{WE} - E^{HBJ}$ (cm⁻¹).

Band, Sym	H ₂ S		SO ₂		O ₃	
	E^{HBJ} (cm ⁻¹)	ΔE (cm ⁻¹)	E^{HBJ} (cm ⁻¹)	ΔE (cm ⁻¹)	E^{HBJ} (cm ⁻¹)	ΔE (cm ⁻¹)
ν_2 (A_1)	1182.893	0.0 ^a	517.913	0.0 ^a	700.909	0.0 ^a
$2\nu_2$ (A_1)	2354.126	0.0 ^a	1035.171	0.0 ^a	1399.285	0.0 ^a
ν_1 (A_1)	2614.359	0.0 ^a	1151.693	0.0 ^a	1103.112	0.0 ^a
ν_3 (B_1)	2628.765	0.0 ^a	1362.066	0.0 ^a	1042.057	0.0 ^a
$3\nu_2$ (A_1)	3513.801	0.0 ^a	1551.681	0.0 ^a	2094.965	0.0 ^a
$\nu_1 + \nu_2$ (A_1)	3778.999	0.0 ^a	1666.340	0.0 ^a	1796.235	0.0 ^a
$\nu_2 + \nu_3$ (B_1)	3789.137	0.0 ^a	1875.797	0.0 ^a	1726.543	0.0 ^a
$4\nu_2$ (A_1)	4661.522	-0.0002	2067.348	0.0 ^a	2787.779	0.0 ^a
$\nu_1 + 2\nu_2$ (A_1)	4932.395	0.0 ^a	2180.352	0.0 ^a	2486.597	0.0 ^a
$2\nu_2 + \nu_3$ (B_1)	4938.604	0.0 ^a	2388.934	0.0 ^a	2407.977	0.00004
$\nu_1 + \nu_3$ (B_1)	5147.214	0.0 ^a	2499.852	0.0 ^a	2110.836	0.00001
$2\nu_3$ (A_1)	5243.477	0.0 ^a	2713.401	0.0 ^a	2110.836	0.00001
$5\nu_2$ (A_1)	5796.561	-0.0019	2582.071	0.0 ^a	3477.564	-0.001
$\nu_1 + 3\nu_2$ (A_1)	6074.625	0.0002	2693.640	0.0 ^a	3173.898	-0.0005

^a Error below 10⁻⁶ cm⁻¹.

level of experimental accuracy. As the second step, we apply our formalism to the nonrigid ammonia molecule possessing large amplitude inversion motion and compare the calculations with the recent results in the literature using the potential energy surface of Refs.^{15,77}. In the case of NH₃, an updated and optimized version of the TENSOR computer code^{37,156} initially designed for rigid systems, was used.

Hydrogen sulfide, sulfur dioxide, ozone: For these three molecules, both the kinetic energy and the potential parts were expanded in Taylor series at order 18 in Q_k and in the variable $u(\rho) = \rho - \rho_e$. To ensure a convergence better than 0.001 cm⁻¹ in variational calculations, the $F(20)$ basis set (see Eq. (A1) of Ref.¹⁵⁶ for the notation), composed of 911 vibrational functions of symmetry A_1 and 791 vibrational functions of symmetry B_1 in the

C_{2v} point group, was employed. The “HBJ” calculated vibrational energy levels were compared directly to those obtained in the framework of the normal-mode Watson formalism, taken as benchmark calculations. For consistent comparisons, the Watson Hamiltonian was also expanded at the same order and the same number of basis functions was used. Selected energy levels for H_2S , SO_2 and O_3 are given in Tab. II. We can see the excellent agreement between the calculations obtained from the HBJ model expanded according to Eq. (16) and the Watson model. Here, the internal axis system defined by the transformation of the initial reference configuration $a_i^{\text{MF}_1}(\rho)$ to $a_i^{\text{IAS}}(\rho)$ has been used (see Section IV. A). In order to prove that IAS ensures a better convergence of rovibrational energy levels compared to MF_1 , we have considered the HDS molecules of symmetry C_s and computed the $J = 5$,

FIG. 8. Impact of the linear approximation (see Eq. (9)) on the vibrational levels of PH_3 . Results obtained from the Watson-Eckart (W-E) Hamiltonian are taken as reference values.

10, 15 and 20 energy levels up to 4000 cm^{-1} . The molecular frame MF_1 was chosen such that the y axis bisects the bending angle of H_2S before attaching the axis system in the center of mass of HDS. By definition, $\text{IAS} \mu_{x\rho}^{(0)} = 0$ while in MF_1 the non-vanishing coupling term $\text{MF}_1 \mu_{x\rho}^{(0)} = -4.6733 + 0.00069u(\rho) - 0.0084u(\rho)^2 + \dots$ arises. For both calculations, the HBJ Hamiltonian was expanded at order 14 and the $F(6)$, $F(10)$ and $F(12)$ basis sets were employed. The $F(6)$ basis set is composed of (315, 378), (693, 630), (945, 1008) and (1323, 1260) rovibrational functions of symmetry (A', A'') for $J = 5, 10, 15$ and 20, respectively. The $F(10)$ and $F(12)$ basis sets contain ~ 4 and ~ 6 times more functions than $F(6)$. As illustrated in Fig. 7, the non-zero term $\text{MF}_1 \mu_{x\rho}^{(0)}$ makes convergence of highly-excited ro-vibrational energy levels slower, in particular when using small basis sets. In that case, the rotational errors between IAS and MF_1 calculations may reach few wavenumbers. Though these errors are drastically reduced when increasing the number of basis function, we can see that the ro-vibrational energy levels are always better converged in IAS.

Phosphine: Though semirigid, this molecule is also a good candidate because it belongs to the non-Abelian point group C_{3v} and possesses two doubly degenerate irreducible repre-

TABLE III. Selected vibrational energy levels (in cm^{-1}) for PH_3 obtained from the HBJ model (16) (this work) and comparison with those computed from the Watson-Eckart (W-E) Hamiltonian.

Band (Sym.)	E^{W-E}	E^{HBJ}	$\Delta(W-E) - HBJ$
$\nu_2 (A_1)$	992.136	992.136	0.000
$\nu_4 (E)$	1118.308	1118.308	0.000
$2\nu_2 (A_1)$	1972.533	1972.532	0.000
$\nu_2 + \nu_4 (E)$	2108.267	2108.266	0.001
$2\nu_4 (A_1)$	2226.920	2226.919	0.001
$2\nu_4 (E)$	2234.972	2234.971	0.001
$\nu_1 (A_1)$	2321.126	2321.131	-0.005
$\nu_3 (E)$	2326.865	2326.870	-0.005
$3\nu_2 (A_1)$	2940.751	2940.758	-0.007
$2\nu_2 + \nu_4 (E)$	3085.855	3085.857	-0.002
$\nu_2 + 2\nu_4 (A_1)$	3215.231	3215.231	-0.001
$\nu_2 + 2\nu_4 (E)$	3222.776	3222.776	0.000
$\nu_1 + \nu_2 (A_1)$	3307.673	3307.675	-0.002
$\nu_2 + \nu_3 (E)$	3311.929	3311.933	-0.004
$3\nu_4 (E)$	3333.762	3333.764	-0.002
$3\nu_4 (A_2)$	3349.375	3349.376	-0.001
$3\nu_4 (A_1)$	3349.852	3349.850	0.002
$\nu_3 + \nu_4 (A_2)$	3424.614	3424.614	0.000
$\nu_1 + \nu_4 (E)$	3424.882	3424.882	0.000
$\nu_3 + \nu_4 (E)$	3435.671	3435.674	-0.003
$\nu_3 + \nu_4 (A_1)$	3440.339	3440.343	-0.003

sentations of type E . We have used the PES from Ref.¹⁵⁵ expressed as a power series in the S_i and $\bar{u}(\bar{\rho}) = \cos\bar{\rho} - \cos\rho_e$ coordinates. The HBJ Hamiltonien (16) was developed at order 18 in Q_k and in $u(\rho) = \rho - \rho_e$ before making the reduction at order 10 (see Refs.^{36,39} for more details). For the basis set, 9651, 8451 and 18081 vibrational functions of symmetry A_1 , A_2 and E , respectively, have been used in the variational calculations. Convergence of

calculation is estimated to be better than 0.001 cm^{-1} . Again, the energy levels obtained from the Watson Hamiltonian were taken as reference benchmark values. All vibrational levels up to the octad are given in Tab. III showing the validity of our extended HBJ-type calculations. In Fig. 8, the strong deviation of the energy levels from the full calculation is displayed in case of simplified linear approximation ($C_{ij} = 0$). This shows the necessity of including all terms in the expansion (9) proving once again that the $\bar{\rho}$ and ρ coordinates have essentially different nature.

Ammonia: Calculations on semirigid molecules partly proved that the methodology presented in Section VI was correct but a validation on a nonrigid system remains the ultimate proof of the concept. Using the refined NH_3 PES of Refs.¹⁵ and ⁷⁷, the vibrational energy levels obtained from the computer codes GENIUSH^{16,84} and TROVE¹²⁵ for nuclear motion calculations were taken as reference values. In order to properly describe the tunnelling splitting due to the inversion motion, appropriate basis functions had to be introduced in the TENSOR code for a rapid convergence. For the resolution of the GF problem (10), a grid of points ρ_m has been generated in the range $[0.75, 2.39]$ by step of $\pi/1000$. For both PESs, a reduced $(Q_k, u(\rho))$ -kinetic energy operator $16 \rightarrow 10$ was built using the the simplest linear $u(\rho) = \rho - \pi/2$ coordinate before converting to $D_{3h}(\text{M})$ tensor operators. Concerning the potential part, the S_i and $\bar{u}(\bar{\rho}) = \sin \rho_e - \sin \bar{\rho}$ representation was considered before performing a 18th-order series expansion in Q_k and $u(\rho)$ to ensure a good reproducibility of the 1D double-well curve. The presence of spurious minima in such high order polynomial expansions makes the use of the reduction technique of Ref.³⁹ absolutely necessary. After several trial tests, it turned out that only the $18 \rightarrow 10$ reduced potential had no holes, preventing from some spurious states. Unfortunately, this reduction does not allow to reproduce conveniently the vibrational energy levels for which the inversion mode ν_2 is involved. We thus followed the strategy explained below Eq. (14) that consists in directly fitting the $V(Q_k, \rho)$ potential.

To consider a lower order polynomial expansion, the variable $u(\rho) \equiv u^{(A'_1)} = \sin \rho_e - \sin \rho$ was preferred to $u(\rho) \equiv u^{(A''_2)} = \rho - \pi/2$. In order to fit a grid composed of 90000 points up to 7000 cm^{-1} generated from Eqs. (13) and (14), the maximum degrees involved in the $D_{3h}(\text{M})$ potential tensor operator of symmetry A'_1 are 6, 6 and 8 in the $(Q_1^{(A'_1)}, Q_{3a,b}^{(E')}, u^{(A'_1)}(\rho))$ and $Q_{4a,b}^{(E')}$ coordinates, respectively. Using a nonlinear fitting procedure, we have obtained a rms error of 0.022 cm^{-1} . For the variational calculation, 6945, 5985 and 12915 functions of

TABLE IV. Selected vibrational energy levels for NH_3 using the extended HBJ Hamiltonian model using the PES¹⁵ and comparison with GENIUSH¹⁶. Δ_{lin} , Δ_{Taylor} and Δ_{fit} stand for the difference between GENIUSH and the linear approximation (see Eq. (9)), the Taylor potential and the fitted potential (see text), respectively. All values are in cm^{-1} .

Band (Sym.)	This work	Ref. ¹⁶	Δ_{lin}	Δ_{Taylor}	Δ_{fit}
ZPE	7436.80	7436.82			
GS (A_2'')	0.79	0.79	-0.01	0.00	0.00
ν_2 (A_1')	932.40	932.41	5.98	0.08	0.01
ν_2 (A_2'')	968.13	968.15	6.26	0.08	0.02
$2\nu_2$ (A_1')	1597.28	1597.26	9.09	0.27	-0.02
ν_4 (E_1')	1625.62	1625.62	-1.61	-0.48	0.00
ν_4 (E_1'')	1626.73	1626.73	-1.62	-0.48	0.00
$2\nu_2$ (A_2'')	1882.14	1882.18	11.72	-0.09	0.04
$3\nu_2$ (A_1')	2384.16	2384.20	14.77	-0.06	0.04
$\nu_2 + \nu_4$ (E_1')	2539.58	2539.60	2.86	-1.28	0.02
$\nu_2 + \nu_4$ (E_1'')	2585.33	2585.38	2.66	-1.60	0.05
$3\nu_2$ (A_2'')	2895.68	2895.74	18.66	-0.89	0.06
$2\nu_2 + \nu_4$ (E_1')	3189.09	3189.11	5.88	-1.60	0.02
$2\nu_4$ (A_1')	3214.49	3214.45	-8.50	-1.43	-0.04
$2\nu_4$ (A_2'')	3216.18	3216.14	-8.44	-1.35	-0.04
$2\nu_4$ (E_1')	3238.54	3238.55	-3.29	-1.11	0.01
$2\nu_4$ (E_1'')	3240.04	3240.05	-3.34	-1.12	0.01
ν_1 (A_1')	3335.75	3335.77	-16.07	-0.62	0.02
ν_1 (A_2'')	3336.80	3336.83	-15.93	-0.64	0.03
ν_3 (E_1')	3443.92	3443.91	4.11	-0.05	-0.01
ν_3 (E_1'')	3444.26	3444.26	2.02	-0.02	0.00
$4\nu_2$ (A_1')	3462.94	3463.00	20.74	-1.38	0.06
$2\nu_2 + \nu_4$ (E_1'')	3502.29	3502.44	6.22	-3.64	0.15
$4\nu_2$ (A_2'')	4062.46	4062.47	26.89	-3.24	0.01
$\nu_2 + 2\nu_4$ (E_1')	4133.20	4133.20	-0.08	-3.20	0.00
$\nu_1 + \nu_2$ (A_1')	4294.14	4294.12	-7.54	-1.02	-0.02
$\nu_1 + \nu_2$ (A_1'')	4319.75	4319.76	-7.06	-1.43	0.01
$\nu_2 + \nu_6$ (E_1')	4417.01	4416.93	9.45	-0.26	-0.08
$\nu_2 + \nu_6$ (E_1'')	4435.62	4435.57	10.41	-0.24	-0.05
$2\nu_2 + 2\nu_4$ (E_1')	4772.17	4772.16	2.12	-4.70	-0.01
$3\nu_4$ (E_1')	4796.03	4795.89	-12.43	-1.07	-0.14
$3\nu_4$ (E_1'')	4798.32	4798.17	-12.48	-0.92	-0.15
$3\nu_4$ (A_1')	4838.70	4838.55	-4.98	-1.11	-0.15
$3\nu_4$ (A_2'')	4838.84	4838.77	-4.83	-2.02	-0.07
$\nu_3 + \nu_4$ (E_1')	4953.97	4954.07	-15.71	-0.47	0.10
$\nu_3 + \nu_4$ (E_1'')	4955.24	4955.33	-15.57	-0.57	0.09
rms (cm^{-1})			9.69	1.82	0.07

symmetry (A_1', A_2''), (A_1'', A_2') and (E', E''), respectively, were used. Again convergence was

TABLE V. Selected vibrational energy levels for NH_3 using the extended HBJ Hamiltonian model using the PES⁷⁷ without the diagonal Born-Oppenheimer correction (DBOC) and comparison with TROVE given in Tab. 3.8 of Ref.¹⁵⁷. All values are in cm^{-1} .

Band (Sym.)	This work (TW)	Δ (TW)-TROVE
GS (A_2'')	0.775	0.000
ν_2 (A_1')	934.561	0.031
ν_2 (A_2'')	969.566	0.011
$2\nu_2$ (A_1')	1601.735	0.073
ν_4 (E_1')	1626.524	-0.031
ν_4 (E_1'')	1627.596	-0.023
$2\nu_2$ (A_2'')	1884.248	-0.021
$3\nu_2$ (A_1')	2386.461	-0.075
$\nu_2 + \nu_4$ (E_1')	2542.976	0.062
$\nu_2 + \nu_4$ (E_1'')	2587.766	0.004
$3\nu_2$ (A_2'')	2897.189	-0.171
$2\nu_2 + \nu_4$ (E_1')	3193.604	0.157
$2\nu_4$ (A_1')	3216.397	-0.033
$2\nu_4$ (A_2'')	3217.976	-0.001
$2\nu_4$ (E_1')	3240.644	-0.040
$2\nu_4$ (E_1'')	3242.015	-0.014
rms (cm^{-1})		0.068

estimated to $\sim 0.001 \text{ cm}^{-1}$ up to 5000 cm^{-1} .

A comparison of the first NH_3 energy levels up to 5000 cm^{-1} between HBJ (this work) and GENIUSH¹⁶ is given in Tab. IV. As expected, the linear approximation ($C_{ij} = 0$ in Eq. (9), fourth column of Tab. IV) gives poor results. The 5th and 6th columns show deviations from GENIUSH using the Taylor and fitted potentials. As mentioned above, the biggest discrepancies arise for $n\nu_2$ -type levels when using the Taylor expansion while the agreement with GENIUSH becomes quite good using the potential function fitted on the grid; our precision being limited by the quality of the fit. Finally, we have considered the refined potential of Ref.⁷⁷, but without the diagonal Born-Oppenheimer correction (DBOC)

for convenience of benchmark calculations, because the DBOC part have been expressed in a set of coordinates different from that of the Born-Oppenheimer part. In Tab. V, we compare our results obtained from the fitted potential to those given in Tab. 3.8 of Ref.¹⁵⁷.

VIII. CONCLUSION

In this paper, we have proposed a general procedure for the series of transformations involving LAM coordinates required for the construction of the generalized Hougen-Bunker-Johns Hamiltonian. First, a combination of algebraic/numerical method is described to build an internal axis system through a ρ -dependent rotation matrix. Illustrative examples are given for HDO, NH₂D and HNO₃. Most importantly, we have developed a general procedure for expressing an *ab initio* curvilinear potential energy surface in the same coordinate system as the HBJ kinetic energy operator. Explicit relations relating the “true” and effective $(\bar{\rho}, \rho)$ internal coordinates have been derived. In order to validate the proposed formalism, 3- and 4-atomic semirigid and nonrigid molecules were considered. Good agreements with results obtained from the Watson Hamiltonian on the one side, and from the nuclear motion computer programs GENIUSH and TROVE, on the other side, confirm the validity of the proposed approach.

In the near future, an hybrid tensor/numerical approach will be considered to avoid fitting potential functions in the full nuclear space. This work can be thus considered as a first insight into future applications of more complex nonrigid species. This project aims at contributing to the construction of the theoretical spectroscopic databases of molecules possessing a strong astrophysical and planetological interest and to the extension of our TheoReTS Reims-Tomsk information system⁴⁴ to ethane-like molecules.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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