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► To cite this version:

Michael M. Rey. Group-theoretical formulation of an Eckart-frame kinetic energy operator in curvilinear coordinates for polyatomic molecules. *Journal of Chemical Physics*, 2019, 151 (2), pp.024101. 10.1063/1.5109482 . hal-03563205

HAL Id: hal-03563205

<https://hal.science/hal-03563205>

Submitted on 9 Feb 2022

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Group-theoretical formulation of an Eckart-frame kinetic energy operator in curvilinear coordinates for polyatomic molecules

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(Dated: 19 June 2019)

A new procedure is presented for building a general kinetic energy operator expressed as a polynomial series expansion of symmetry-adapted curvilinear coordinates for semirigid polyatomic molecules. As a starting point, the normal-mode Watson kinetic energy part is considered and then transformed into its curvilinear counterpart. An Eckart molecular fixed-frame is thus implicitly used. To this end, we exploit symmetry at all stages of the calculation and show how group-theoretically based methods and Γ -covariant tensors help to properly invert nonlinear polynomials for the coordinate changes. Such a *linearization* procedure could be also useful in different contexts. **Unlike the usual normal mode approach, the potential part initially expressed in curvilinear coordinates is not transformed in this work, making convergence of the Hamiltonian expansion generally faster.** For dimensionality reduction, the final curvilinear kinetic and potential parts are expanded in terms of irreducible tensor operators when doubly and triply degenerate vibrations are involved. The procedure proposed here is general and can be applied to arbitrary Abelian and non-Abelian point groups. Illustrative examples will be given for the H_2S (C_{2v}), H_2CO (C_{2v}), PH_3 (C_{3v}) and SiH_4 (T_d) molecules.

Keywords: Kinetic energy operator; curvilinear coordinates; Semirigid molecules; Symmetry; Irreducible tensor operators; Eckart frame .

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I. INTRODUCTION

The derivation of the exact quantum kinetic energy operator (KEO) expressed in an appropriate set of coordinates adapted to various types of nuclear motions still remains an active field of research^{1–23}. Accurate determination of the energy levels and associated wave functions is of primary importance, both in spectroscopy and quantum molecular dynamics, and requires two main ingredients: (i) *ab initio* potential energy surfaces (PES) built on a wide range of nuclear configurations and (ii) compact expressions of the KEO that may be applicable to general polyatomic molecules. Assuming the PES known hereafter, we will focus only on the construction of the KEO. To this end, it is common to start with space-fixed Cartesian coordinates $\mathbf{X}_k \equiv (X_k, Y_k, Z_k)$, with $k = 1, \dots, N$, allowing the KEO of a N -atom molecule to take a particularly simple form. But in practice, a set of $(3N - 6)$ orthogonal or non-orthogonal coordinates \mathbf{R} and of three Euler angles is generally preferred. The derivation of the KEO is then accomplished either by two applications of the chain rule²⁴ or by the alternative procedure proposed by Podolsky²⁵. To further simplify calculations, a set of symmetry-adapted coordinates $\mathbf{S} = \{S_{k\sigma}^{(\Gamma)}\}$ may also be introduced, where Γ is the irreducible representation (irrep) of a group G for a mode k and σ is a component to distinguish degenerate vibrations. Using for example the projection operator method, these coordinates are expressed as a linear combination of internal coordinates usually denoted as $\mathbf{S}^{(\Gamma)} = \mathbf{U}\mathbf{R}$. The use of symmetry—apart from allowing block-diagonalization of the Hamiltonian matrix—is of primary importance in the quantum-mechanical description of molecular spectra because it allows a complete and unambiguous labelling of the rotation-vibration states, to predict allowed transitions *via* selection rules and may be used to determine the nuclear spin statistical weights. It will be shown in Section III how symmetry can also help to properly invert a set of polynomial equations.

At this stage, it is of major importance to choose a relevant system of axes tied to the molecule. The Eckart frame (EF) has the advantage of minimizing the Coriolis coupling terms. Several methods have been proposed to solve the Eckart equations^{26–32}. The maximum separation between vibration and rotation generally makes calculations less demanding and as mentioned in Ref.³³ allows more unambiguous assignments in spectra compared to other embeddings. The Eckart frame ro-vibrational KEO for nonlinear molecules derived by Watson³⁴ using $(3N - 6)$ rectilinear normal coordinates \mathbf{q} has a particularly simple, compact

and quite general form. These coordinates also transform as the irreps of the point group, that is $\mathbf{q} = \{q_{k\sigma}^{(\Gamma)}\}$, and in the linear approximation we write $\mathbf{q} = \mathbf{L}^{-1}\mathbf{S}$ where L_{ij} are the eigenvectors of the Wilson \mathbf{GF} matrix³⁵. In contrast, the implementation of the Eckart frame kinetic energy operator (EF-KEO) employing curvilinear coordinates is somewhat more involved when increasing the number of atoms, though the use of symbolic computational packages may help to simplify expressions³⁶. In order to overcome limitations, an alternative numerical method has been developed to build general KEOs, even when sophisticated coordinates are involved³⁷. Numerical procedures have been proposed to get EF-KEO when employing curvilinear coordinates (see *e.g.* Lauvergnat *et al.*³⁸, Wang & Carrington²⁰, Fábri *et al.*²¹ and Yachmenev & Yurchenko²⁹).

Here, we propose to derive a general expression of an N -atom EF-KEO using curvilinear coordinates and group-theoretical transformations. For a full account of symmetry, the final kinetic energy and potential parts will be expressed in terms of irreducible tensor operators for arbitrary Abelian or non-Abelian point groups. A recent study has been devoted to the classification of point-group symmetric orientational ordering tensors³⁹. In this work, we will focus on semirigid molecules having a nonlinear reference configuration **and a single potential well**. It is thus quite natural to consider the normal-mode Watson KEO as a starting point because the EF is implicitly included in that case. The philosophy of this work closely follows that of V. Szalay who introduced a *gateway Hamiltonian*^{40,41} but our methodology is probably more intuitive and symmetry is exploited at all stages. The present work aims at obtaining a general expression of the ro-vibrational EF KEO in curvilinear as well as its matrix elements for an N -atom semirigid molecule using group-theoretical tools. **Though expressed in curvilinear coordinates this model is not fully designed in its current form for molecules having a large amplitude motion or for studying states near a linearity barrier, as done for example by the MORBID approach⁴².**

The strategy of the present approach as well as its main advantages are summarized in Section II. The procedure for the derivation of the symmetry-adapted KEO is described in Section III while Section IV will be devoted to the construction of a curvilinear Hamiltonian and to the computation of matrix elements using irreducible tensor operators generally encountered in normal mode effective spectroscopic models. Illustrative example calculations will be presented for the H_2S , H_2CO , PH_3 and SiH_4 molecules.

II. STRATEGY AND METHODOLOGY

A. Advantages of the proposed formulation

Unlike the usual normal mode approach for which the KEO is expressed in q_i and the *ab initio* PES $V(S)$ is transformed as $V(q)$ following Hoy, Mills and Strey⁴³, we follow a different strategy here. It consists in the conversion of the normal mode Eckart-Watson vibrational KEO part into its curvilinear counterpart while keeping the rotational and potential $V(S)$ parts unchanged. This is summarized as

$$H^{E-W} = [T(q, d/dq, J_\alpha) \rightarrow T(S, d/dS, J_\alpha)] + V(S), \quad (1)$$

where J_α ($\alpha = x, y, z$) are the components of the total angular momentum in the molecular Eckart frame. Considering the transformation (1) instead of the commonly used procedure $T(q, d/dq, J_\alpha) + [V(S) \rightarrow V(q)]$ may present a series of advantages that can be itemized as follows:

- The kinetic energy part in curvilinear coordinates is constructed naturally in the Eckart-frame and as the original Watson KEO³⁴, its form remains the same whatever the number of atoms.

- The mass-independent potential part comes directly from the analytical function $V(S)$ fitted on a grid of *ab initio* points. Though $V(q)$ is generally well adapted near the bottom of the well, our approach avoids the usual $V(S) \rightarrow V(q)$ conversion which is one the main drawbacks of the normal mode formalism. Indeed, high order polynomial Taylor expansions in q are usually required for describing high energy states but (i) may suffer from a lack of convergence over the whole range of nuclear configurations and (ii) may lead to artefacts and spurious minima that are very difficult to control in the full $(3N - 6)$ -dimensional space. Here we assume that the PES is expressed as linear combination of symmetrized powers in the S coordinates as

$$V(S) = \sum_{\{\mathbf{p}\}} \mathbf{F}_{\mathbf{p}} \prod_{i=1}^M \prod_{\sigma}^{[\Gamma]} \left(S_{i\sigma}^{(\Gamma_i)} \right)^{p_{i\sigma}}, \quad (2)$$

where M is the number of vibrational modes, $\mathbf{F}_{\mathbf{p}}$ are the force constants, $[\Gamma]$ is the dimension of the irrep Γ and the set $\mathbf{p} = \{p_{1\sigma_1}, p_{2\sigma_2}, \dots\}$ stands for all powers.

- As it will be shown in Section IV C, the EW “ S ” model will converge more rapidly than the EW “ q ” model because only the KEO is Taylor expanded in this new approach and it

generally converges quite well with respect to the reciprocal μ tensor expansion for semirigid molecules (see Ref.⁴⁴ for a discussion). At low order, our “ S ” model gives better results than the “ q ” model because $V(q)$ is not converged yet (see Fig. 1 for H_2S ; the behaviour being similar for other species). Typically, $V(S)$ contains $\sim 10\text{--}20$ terms for triatomic molecules while $V(q)$ should contain $\sim 500\text{--}1000$ terms to reach the same accuracy. For XY_4 molecules, the ratio between the number of terms in $V(S)$ and $V(q)$ is $\sim 1000 \div 200000$.

- Working with isotopic-independent quantities (PES or DMS) avoids to perform non-linear normal-mode transformations (see Ref.⁴⁵) when studying isotopic substitutions.
- Using the $\{S, -id/dS\}$ representation, the Heisenberg-Weyl algebra is conserved so that we may easily transpose all our existing compression-reduction tools^{45–48}—initially designed for normal coordinates—to this curvilinear tensor model. As a direct consequence, our normal-mode and curvilinear models will share the same variational computer code for the prediction of energy levels and for spectra calculations.

B. Comparison with other approaches

Mathematically speaking and by analogy with the so-called $\mathbf{X}(\mathbf{R})$ and $\mathbf{R}(\mathbf{X})$ approaches⁴⁹, Eq. (1) requires to derive the $\mathbf{q}(\mathbf{S})$ and $\mathbf{S}(\mathbf{q})$ relations. Starting from $\mathbf{S}(\mathbf{q})$ whose derivation is known since the seminal work of Hoy, Mills and Strey⁴³, the main difficulty of the present approach will be to determine $\mathbf{q}(\mathbf{S})$. This step, sometimes tedious and rather involved, is mandatory to convert the Jacobian matrix $\mathbf{J}_{S \rightarrow q} = \partial S_i / \partial q_j$ and the Jacobian determinant $\mathcal{J}_{q \rightarrow S} = \mathcal{J}_{S \rightarrow q}^{-1}$ into S -dependent functions. In the framework of the Sørensen’s formulation⁵⁰, the TROVE approach¹⁶ proposes a numerical procedure to inverse the Jacobian matrix. Similarly, the GENIUSH approach⁵¹ also proposes a numerical implementation to solve this problem. Here, we propose (see Section III) a general procedure based on group theory and on the construction of so-called Γ -covariant tensors to algebraically derive polynomial series $q_i(S)$ whose expansion coefficients will be numerically exact to a given order. Finally, the approach we propose is nothing but the inverse procedure proposed in Ref⁴³ since it is based on the transformation of the KEO as $T(q \rightarrow S)$ while the usual manner to proceed in normal mode calculations is to convert the potential part to $V(S \rightarrow q)$.

The final form of our sum-of-product Taylor-expanded KEO will contain thousands of terms but in turn will allow a fast and analytical computation of the matrix elements using

the Wigner-Eckart theorem and Clebsch-Gordan (CG) coupling coefficients. In all other formulations the KEO generally contains only few terms, except in the TROVE approach also based on power series in terms of internal coordinates²⁹, but all matrix elements are evaluated numerically. As stated in Ref.⁵², the numerical calculation of both the KEO and matrix elements can be time-consuming. Typically, it takes ~ 9 days to calculate a 12D Hamiltonian and the huge number of grid points (\sim billion) cannot be stored in memory (hundreds of Gb required) against only few minutes to build our 12D ethylene algebraic Hamiltonian, few hours to compute its matrix elements and only few Mb to store our reduced vibrational eigenfunctions. In this context, Nauts & Lauvergnat⁵² proposed a numerical on-the-fly implementation to accelerate numerical calculations. Recently, Nikitin *et al.*^{22,53} have proposed an algorithm to compute KEO matrix elements for XY₄-type molecules using the six (redundant) angles for symmetry considerations, but only for vibration.

One of the crucial points when expanding the KEO is the computation of the successive derivatives. To circumvent the round-off errors problem encountered in the finite difference method, Yachmenev & Yurchenko²⁹ introduced an automatic differentiation (AD) technique. Similarly, we have implemented in our TENSOR code a modified version of the computer program COSY Infinity⁵⁴ allowing high-order multivariate AD without almost no loss of accuracy.

Last but not least, the algebraic nature of our S model could allow to apply a series of contact transformations⁵⁵. To our knowledge, a first non-empirical effective curvilinear Hamiltonians could be thus used for high-resolution analysis and spectra data reduction.

III. PROCEDURE FOR THE DERIVATION OF THE RO-VIBRATIONAL ECKART-EMBEDDED KEO

Hereafter, dimensionless coordinates and momenta will be considered and all quantities in front of them will be expressed in wavenumber units (cm^{-1}). For the sake of simplicity, we will omit in Section III A the symmetry labels in all coordinates and conjugate momenta that will simply be denoted by $q_j(\equiv q_{k\sigma}^{(\Gamma)})$, $p_j(\equiv p_{k\sigma}^{(\Gamma)}) = -id/dq_j$, S_j and $P_j = -id/dS_j$. Unless specified otherwise, all running indices i, j, k, \dots will take values $1, \dots, 3N - 6$ while Greek letters α, β, \dots will equal x, y or z . The elements of the Jacobian matrix $\mathbf{J}_{S \rightarrow q}$ will be denoted by $J_j^i = \partial S_i / \partial q_j$ and its determinant $|\text{Det}(\mathbf{J}_{S \rightarrow q})|$ by \mathcal{J} , with the

well-known property $\mathcal{J} = (|\text{Det}(\mathbf{J}_{q \rightarrow S})|)^{-1}$. Note that our conventions differ from those of the literature where \mathcal{J} generally corresponds to the determinant of $\mathbf{J}_{q \rightarrow S}$. In order to work with “usual” conventions, we would need to change the sign of each individual term containing \mathcal{J} only once in Eqs. (10) and (11) below.

A. General expression of the KEO

The philosophy of the present approach, as already outlined in the Introduction part, is very simple to understand and lies in the transformation of the normal mode Eckart-Watson KEO to curvilinear coordinates. The two coordinate changes, namely $\mathbf{q}(\mathbf{S})$ and $\mathbf{S}(\mathbf{q})$, will be determined in Sections IIIB and IIID but are assumed known for the time being. In order to handle compact algebraic expressions and to compute more easily all matrix elements, it is convenient to put the Watson’s KEO part into a better suited *normally ordered* form $u(q)v(p)w(J_\alpha) =: (\boldsymbol{\pi} - \mathbf{J})\boldsymbol{\mu}(\boldsymbol{\pi} - \mathbf{J}) :$ where the symbol “ $::$ ” denotes normal ordering and u and v are not necessarily commuting functions. After some algebra, it is straightforward to show that

$$\begin{aligned} 2T^{E-W} = & \sum_{jl} f_{jl}(q)p_j p_l + \sum_l g_l(q)p_l \\ & + \sum_{\beta l} t_{l\beta}(q)p_l J_\beta + \sum_\beta h_\beta(q)J_\beta \\ & + \sum_{\alpha\beta} \mu_{\alpha\beta}(q)J_\alpha J_\beta - \frac{1}{4} \sum_\alpha \mu_{\alpha\alpha}(q), \end{aligned} \quad (3)$$

where $\mu_{\alpha\beta}$ are the components of the reciprocal inertia tensor expanded in Taylor series in normal coordinates and

$$\begin{aligned} f_{jl}(q) = & \sum_{\alpha\beta ik} \zeta_{ij}^\alpha \zeta_{kl}^\beta q_i q_k \mu_{\alpha\beta}(q) + \omega_j \delta_{jl}, \\ g_l(q) = & -i \sum_{\alpha\beta ijk} \zeta_{ij}^\alpha \zeta_{kl}^\beta q_i q_k \left(\frac{\partial \mu_{\alpha\beta}(q)}{\partial q_j} \right) \\ & -i \sum_{\alpha\beta ij} \zeta_{ij}^\alpha \zeta_{jl}^\beta q_i \mu_{\alpha\beta}(q), \\ h_\beta(q) = & i \sum_{\alpha ij} \zeta_{ij}^\alpha q_i \left(\frac{\partial \mu_{\alpha\beta}(q)}{\partial q_j} \right), \\ t_{l\beta}(q) = & -2 \sum_{\alpha i} \zeta_{il}^\alpha q_i \mu_{\alpha\beta}(q), \end{aligned} \quad (4)$$

with the corresponding volume element of integration

$$d\tau = \sin\theta d\theta d\phi d\chi dq_1 dq_2 \cdots dq_{3N-6}. \quad (5)$$

A brief inspection of Eq. (3) shows that the last three terms are converted in S coordinates by using only $\mathbf{q}(\mathbf{S})$, *e.g.* $h_\beta(q) \rightarrow h_\beta(q(S))$, while the first three terms are transformed from one or two applications of the chain rule. In that case, knowledge of the Jacobian $\mathbf{J}_{S \rightarrow q}$ is required. The transformed linear momentum simply reads

$$p_j = -i \sum_k \left(\frac{\partial S_k}{\partial q_j} \right) \frac{\partial}{\partial S_k} = \sum_k J_j^k P_k \quad (6)$$

where P_k is the conjugate momentum of S_k with the commutation rule $[S_j, P_k] = i\delta_{jk}$. Concerning the crossed term $p_i p_j$, two applications of the chain rule are necessary to make the transformation. We thus write

$$\begin{aligned} p_i p_j &= - \sum_k \left\{ \left(\frac{\partial^2 S_k}{\partial q_i \partial q_j} \right) \frac{\partial}{\partial S_k} \right. \\ &\quad \left. + \left(\frac{\partial S_k}{\partial q_i} \right) \sum_l \left(\frac{\partial S_l}{\partial q_j} \right) \frac{\partial^2}{\partial S_k \partial S_l} \right\} \\ &= -i \sum_{kr} J_i^r \left(\frac{\partial J_j^k}{\partial S_r} \right) P_k + \sum_{kl} J_i^k J_j^l P_k P_l \end{aligned} \quad (7)$$

where the term containing the second derivative with respect to q has been rearranged because $J_i^k \equiv J_i^k(q(S))$ is now a function of S . It is shown in the appendix how Eq. (7) can be reformulated using tensor calculus. The Jacobian \mathcal{J} also depends on S and the new volume element reads

$$d\tau_S = \sin\theta d\theta d\phi d\chi \mathcal{J}^{-1}(S) dS_1 dS_2 \cdots dS_{3N-6}. \quad (8)$$

In many situations, this volume element is not adapted to the basis set requiring to define a new one as $d\tau'_S = \sin\theta d\theta d\phi d\chi \rho(S) dS_1 dS_2 \cdots dS_{3N-6}$ where $\rho(S)$ is a weight function. The KEO is modified accordingly as $(\rho(S)\mathcal{J}(S))^{-1/2} T^{E-W} (\rho(S)\mathcal{J}(S))^{1/2}$ but in order to closely follow the normal-mode formalism, with the possibility of using the same computer codes, we choose to work with the non-Euclidean normalization which occurs for $\rho = 1$ (also called Wilson convention⁴⁹). In that case, the standard harmonic oscillator basis functions defined on the space spanned by S as $\phi_i(S_i) \sim H_v(\kappa_i^2 S_i) \exp(-\kappa_i^2 S_i^2/2)$, can be used to compute analytically all matrix elements (see Section IV B). The final form of the normally-ordered transformed KEO is thus given by

$$\begin{aligned} \tilde{T}_S^{E-W} &=: [\mathcal{J}(S)]^{-\frac{1}{2}} T^{E-W} [\mathcal{J}(S)]^{\frac{1}{2}} : \\ &= \tilde{K}_S + \tilde{W}_S \end{aligned} \quad (9)$$

where

$$\begin{aligned}
\tilde{K}_S = & \frac{1}{2} \sum_{kl} g_l J_l^k P_k + \frac{1}{2} \sum_{k\beta l} t_{l\beta} J_l^k P_k J_\beta + \frac{1}{2} \sum_{\beta} h_\beta J_\beta \\
& - \frac{i}{4} \sum_{k\beta l} t_{l\beta} J_l^k \left(\frac{\partial \ln \mathcal{J}}{\partial S_k} \right) J_\beta + \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} J_\alpha J_\beta \\
& - \frac{i}{2} \sum_{kjlr} f_{jl} J_j^r \left(\frac{\partial J_l^k}{\partial S_r} \right) P_k + \frac{1}{2} \sum_{kjlr} f_{jl} J_j^k J_l^r P_k P_r \\
& - \frac{i}{4} \sum_{kjlr} f_{jl} J_j^k J_l^r \left\{ \left(\frac{\partial \ln \mathcal{J}}{\partial S_k} \right) P_r + \left(\frac{\partial \ln \mathcal{J}}{\partial S_r} \right) P_k \right\}
\end{aligned} \tag{10}$$

contains the rotation-vibration coupling terms and

$$\begin{aligned}
\tilde{W}_S = & -\frac{1}{8} \sum_{\alpha} \mu_{\alpha\alpha} - \frac{i}{4} \sum_{kl} g_l J_l^k \left(\frac{\partial \ln \mathcal{J}}{\partial S_k} \right) \\
& - \frac{1}{4} \sum_{kjlr} f_{jl} J_j^r \left(\frac{\partial J_l^k}{\partial S_r} \right) \left(\frac{\partial \ln \mathcal{J}}{\partial S_k} \right) \\
& - \frac{1}{4} \sum_{kjlr} f_{jl} J_j^k J_l^r \left(\frac{\partial^2 \ln \mathcal{J}}{\partial S_k \partial S_r} \right) \\
& - \frac{1}{8} \sum_{kjlr} f_{jl} J_j^k J_l^r \left(\frac{\partial \ln \mathcal{J}}{\partial S_k} \right) \left(\frac{\partial \ln \mathcal{J}}{\partial S_r} \right)
\end{aligned} \tag{11}$$

is the extra-potential term. The associated volume element is $d\tau'_S = \sin\theta d\theta d\phi d\chi dS_1 dS_2 \cdots dS_{3N-6}$.

In Eqs. (10) and (11), the polynomial functions g , t , h , f , μ , J and \mathcal{J} are all S -dependent so that \tilde{T}_S^{E-W} may be considered as the curvilinear counterpart of the well-known Eckart-Watson KEO initially expressed in normal coordinates. Below, we explain the procedure to determine all these functions from the coordinate transformation $S \rightarrow q$ and its inverse $q \rightarrow S$.

B. Computation of the Jacobian matrix $\mathbf{J}_{S \rightarrow q}$

This task is by far the most direct and the methodology is well-established since decades. The only possible limitation probably lies in the computation of high-order Taylor series expansions when many vibrational degrees of freedom (say > 10) are involved. In few words, the simplest way consists in first starting from Cartesian coordinates and their link with the q 's through the l matrix. Then a set of curvilinear internal coordinates \mathbf{R} can be expressed as a function of the q 's for arbitrary N -atomic systems (see *e.g.* Eq. (7) of Ref.⁵⁶). Applying the group symmetry transformation \mathbf{U} and expanding all quantities in Taylor series about the equilibrium configuration (all $q_i = 0$), the symmetry-adapted coordinates are expressed

in terms of q_i as⁴³

$$S_{i\sigma}^{(\Gamma)} = L_{i,j}^{\sigma,\sigma'} q_{j\sigma'}^{(\Gamma)} \delta_{\sigma\sigma'} + \frac{1}{2} L_{i,jk}^{\sigma,\sigma'\sigma''} q_{j\sigma'}^{(\Gamma')} q_{k\sigma''}^{(\Gamma'')} + \frac{1}{6} L_{i,jkl}^{\sigma,\sigma'\sigma''\sigma'''} q_{j\sigma'}^{(\Gamma')} q_{k\sigma''}^{(\Gamma'')} q_{l\sigma'''}^{(\Gamma''')} + \dots, \quad (12)$$

with the symmetry condition $\Gamma(q_j) \times \Gamma(q_k) \times \dots \times \Gamma(q_l) \supset \Gamma$, or in a more compact form as

$$\mathbf{S} = \mathbf{L}\mathbf{q} + \mathcal{L}(\mathbf{q}), \quad (13)$$

where \mathcal{L} is a nonlinear function. Due to symmetry, the \mathbf{L} matrix has a block diagonal form where each block is of dimension $[\Gamma_i]$. Computation of the elements $J_k^l = \partial S_l / \partial q_k$ turns out to be a trivial task

$$J_k^l \equiv J_k^l(q) = L_{l,k} + \mathcal{L}'(q), \quad (14)$$

but at this stage these functions are still q -dependent.

C. Computation of the Jacobian determinant \mathcal{J}

The next step is the computation of the determinant \mathcal{J} . A number of studies has already been devoted to the determination of the Jacobians (see *e.g.* Refs.^{10,23}), but they are not adapted to the present work. Though each element J_j^i may contain thousands of terms, it is desirable to work with power series expansions so that optimized methods for computing the Jacobians are strongly required. Different methods are available in literature, some of them are based on the Leibniz formula or on Laplace's cofactor expansions. But after some trial tests, these commonly used methods are costly and time prohibitive when performing algebraic calculations, even for triatomic molecules. We thus explored another route for expanding the Jacobian determinant in Taylor series. A method involving the discriminant and the trace of matrix has been preferred for this work. Following Ref.⁵⁷, it is shown that the discriminants of $\mathbf{J}_{S \rightarrow q}$ can be computed iteratively as

$$\mathcal{I}(k) = \frac{1}{k} \sum_{i=1}^k (-1)^{i-1} \mathcal{I}(k-1) \text{Tr}(\mathbf{J}_{S \rightarrow q})^i, \quad (15)$$

with $\mathcal{I}(0) = 1$ and $k = 1, \dots, 3N - 6$ and that the determinant is nothing but

$$\mathcal{J}(q) = |\mathcal{I}(3N - 6)|. \quad (16)$$

Such a recursive scheme is computationally convenient, quite easy to implement and allows fast calculations of Jacobians without using too much resources. The power series expansion

of the logarithm of \mathcal{J} has a form similar to (12) with the only exception that $\ln\mathcal{J}(q) \equiv \ln\mathcal{J}^{(\Gamma_0)}(S)$ where Γ_0 is the totally symmetric irrep of the group.

D. Solving the inverse problem $\mathbf{q}(\mathbf{S}) = [\mathbf{S}(\mathbf{q})]^{-1}$ from symmetry

Last but not least, we propose in this section a new procedure to derive the inverse relation of Eq. (13), namely $\mathbf{q} = \mathbf{q}(\mathbf{S})$. To that end, a linearization algebraic method will be introduced where once again the use of symmetry will be crucial. As is well-known, group-theoretical methods are of great help in molecular physics and are commonly used to generate symmetry-adapted basis functions and classify energy levels according to the irreps. They may also be used to build all symmetry-allowed invariant polynomials⁵⁸ of symmetry Γ_0 (A_1 , A' or A_{1g}) of a group G . More general polynomials transforming as the irrep Γ (not necessarily Γ_0), the so-called Γ -covariant polynomials with $\Gamma = \{\Gamma_1, \dots, \Gamma_m\}$, can be generated, m being the number of classes of G . We show in this section how such polynomials may serve to compute $\mathbf{q}(\mathbf{S})$ from $\mathbf{S}(\mathbf{q})$ of Eq. (13). This latter equation can be considered as Γ -covariant polynomials in q .

For Abelian point groups (C_n , C_{nh} , S_{2n}) and also for D_n , C_{nv} and D_{nh} groups for which the order of the symmetry axis does not exceed $n = 2$ (otherwise they are non-Abelian), no degenerate vibrations are involved, that is $\text{Dim}(\Gamma)=1$. This is a trivial case because matrix and character coincide and we simply deal with multiplications of numbers to form symmetry-adapted polynomials and basis-sets. The treatment of non-Abelian groups (D_n , C_{nv} , D_{nh} with $n \geq 3$ and D_{nd}) is somewhat more challenging because of the two- and three-fold degenerate irreps (the icosahedral I_h group is omitted here). In that case, sophisticated symmetrization methods have to be considered (see below).

1. Construction of Γ -covariant polynomials

If Ω_{tot} denotes the maximum degree in the symmetry-adapted q or S polynomials then the dimension of the space spanned by these polynomials increases very rapidly with Ω_{tot} . One way to circumvent the problem is to consider an integrity basis for Γ -covariant polynomials from two partitions: the so-called denominator (or primary polynomials) that are invariant polynomials and the numerator (or secondary polynomials) that transform as Γ .

All the Γ -covariant polynomials are thus generated from the polynomials of the small integrity basis^{59,60}. It can be shown that these polynomials are nothing but Molien series⁵⁸ $M^G(\Gamma, \Gamma^{ini}; t) = c_0 + c_1 t + c_2 t^2 + \dots$ where $\Gamma^{ini} = \Gamma_1 \oplus \Gamma_2 \oplus \dots \oplus \Gamma_M$ with M the number of vibrational modes of symmetry Γ_i (see Eq. (2)). Cassam-Chenai *et al.*⁵⁹ proposed a recursive scheme to build the generating functions by decomposing the initial representation as $\Gamma^{ini} = (\Gamma_1 \oplus \Gamma_2 \oplus \dots \oplus \Gamma_{M-1}) \oplus \Gamma_M$ and by making iterations until no more decomposition of the representations is possible. However, to be consistent with our previous studies^{44,45,56}, we have chosen to follow a different route based on successive tensor products and coupling CG coefficients for the construction of linearly independent polynomials.

The right-hand side of Eq. (12) are polynomials of order Ω_{tot} in q while its left-hand side only contains $3N - 6$ linear terms in S , thus calling for a relevant “regularization” method to invert these equations. To solve this ill-posed problem, our approach follows two steps summarized as:

Step 1: The first step in the determination of the $\mathbf{q}(\mathbf{S})$ relation is to form a set of Γ -covariant polynomials up to order Ω_{tot} in S .

$$T_{\sigma}^{\{\Omega_{\alpha}\Theta\}(\Gamma)} = \left(\left(\mathcal{S}_1^{\Omega_1(\alpha_1\Theta_1)} \otimes \mathcal{S}_2^{\Omega_2(\alpha_2\Theta_2)} \right)^{(\Theta_{12})} \otimes \dots \otimes \mathcal{S}_M^{\Omega_M(\alpha_M\Theta_M)} \right)_{\sigma}^{(\Gamma)}, \quad (17)$$

with the symmetrized powers

$$\begin{aligned} \mathcal{S}_{i\sigma_i}^{\Omega_i(\alpha_i\Theta_i)} &= \underbrace{[S_i^{(\Gamma_i)} \otimes S_i^{(\Gamma_i)} \otimes \dots \otimes S_i^{(\Gamma_i)}]_{i\sigma_i}^{\Omega_i(\alpha_i\Theta_i)}}_{\Omega_i \text{ times}}, \\ &= \otimes_{i=1}^{\Omega_i} S_i^{(\Gamma_i)} \end{aligned} \quad (18)$$

where α_i are all intermediate quantum numbers and symmetry labels and $\sum_i \Omega_i = \Omega_{tot}$ is the total polynomial degree. We have the non-vanishing selection rules $\Theta_1 \times \dots \times \Theta_M \supset \Gamma$, or equivalently $\Theta_{12\dots M-1} \times \Theta_M \supset \Gamma$ where $\{\Theta_{12}, \Theta_{123}, \dots, \Theta_{12\dots M-1}\}$ are the symmetry labels of the inner coupling scheme. In Eq. (18), powers of representations imply $(\Gamma_i)^{\Omega_i} \supset \Theta_i$. The formulation (17) ensures that all possible linearly-independent polynomials in S are properly built at a given order. The other advantage of using the irreducible tensor operator formalism lies in its compact and unified formulation since Eqs. (17) and (18) remain the same whatever the symmetry point group. For Abelian point groups admitting only one dimensional irreps (asymmetric top molecules), the σ_i index can be omitted and, most

importantly, the symmetrized powers simply read as

$$\text{Dim}(irreps) = 1, \quad \mathcal{S}_i^{\Omega_i(\alpha_i \Theta_i)} = \begin{cases} (S_i^{\Omega_i})^{(\Gamma_0)} & \text{if } \Omega_i \text{ even} \\ (S_i^{\Omega_i})^{(\Gamma_i)} & \text{if } \Omega_i \text{ odd} \end{cases} \quad (19)$$

For non-Abelian point groups admitting E - and F -type irreps (symmetric or spherical top molecules), Eq. (18) requires much more attention. An algebraic and unified treatment in the framework of the $u(2)$ and $u(3)$ Lie theory and boson representation has been proposed in Refs.^{61–64} to build symmetrized powers for all point groups admitting two and three dimensional irreps. Another tensorial formalism has been reviewed in Ref.^{65,66} but it was elaborated only for spectroscopic effective models and implemented for few point groups. It is not as computationally efficient as the formalism proposed by Nikitin *et al.*⁶⁷, initially designed for effective Hamiltonians of symmetry C_{3v} , T_d and O_h but recently extended to *ab initio* models^{44,56,68} and to arbitrary Abelian and non-Abelian point groups⁶⁹. A link between this formalism and that based on the $u(2)$ Lie theory has been clearly established (See Section 3.2 of Ref.⁶³). In any cases, orientation into G can be realized through a transformation \mathcal{G} as

$$\text{Dim}(irreps) > 1, \quad \mathcal{S}_{i\sigma_i}^{\Omega_i(\alpha_i \Theta_i)} = \sum_{\alpha_i} \mathcal{G}_{\alpha_i \sigma_i}^{\Theta_i} \prod_{\beta_i}^{[\Gamma_i]} \left(S_{i\beta_i}^{(\Gamma_i)} \right)^{p_{i\beta_i}} \quad (20)$$

where β_i is the component of the irrep Γ_i and the set of powers $\{p_{i\beta}\}$ must satisfy $\sum_{\beta_i} p_{i\beta_i} = \Omega_i$.

Step 2: The irreducible tensor operators $T_\sigma^{\{\Omega\alpha\Theta\}(\Gamma)}$ (17) are expanded in terms of individual components using CG coupling coefficients and are written as

$$\begin{aligned} T_\sigma^{\{\Omega\alpha\Theta\}(\Gamma)} &= ([\Theta_{12}][\Theta_{123}] \cdots [\Theta_{12 \dots M-1}][\Gamma])^{1/2} \\ &\times \sum_{\text{all } \sigma_i} F \begin{pmatrix} \Theta_1 & \Theta_2 & \Theta_{12} \\ \sigma_1 & \sigma_2 & \sigma_{12} \end{pmatrix} F \begin{pmatrix} \Theta_{12} & \Theta_3 & \Theta_{123} \\ \sigma_{12} & \sigma_3 & \sigma_{123} \end{pmatrix} \\ &\times \cdots F \begin{pmatrix} \Theta_{12 \dots M-1} & \Theta_M & \Gamma \\ \sigma_{12 \dots M-1} & \sigma_M & \sigma \end{pmatrix} \\ &\times \mathcal{S}_{1\sigma_1}^{\Omega_1(\alpha_1 \Theta_1)} \mathcal{S}_{2\sigma_2}^{\Omega_2(\alpha_2 \Theta_2)} \cdots \mathcal{S}_{M\sigma_M}^{\Omega_M(\alpha_M \Theta_M)}, \end{aligned} \quad (21)$$

where the F 's are covariant CG coefficients (sometimes referred to as 3-C Wigner symbols). Now by making the two successive substitutions Eq. (12) \rightarrow Eq. (18) \rightarrow Eq. (21), we finally arrive at the final expression for the covariant tensors

$$T_\sigma^{\{\Omega\alpha\Theta\}(\Gamma)} = \mathcal{U}_{\{\Omega_q \alpha_q \Theta_q\}}^{\{\Omega\alpha\Theta\}} \mathcal{Q}_\sigma^{\{\Omega_q \alpha_q \Theta_q\}(\Gamma)}, \quad (22)$$

where \mathcal{Q} is a vector whose the elements are the Γ -covariant polynomials up to a degree Ω_q in q . The matrix \mathcal{U} of the transformation is numerical and is formed by the coupling and orientation coefficients F and \mathcal{G} . This matrix is invertible only if the polynomials in S and q are of the same degrees, that is $\Omega = \Omega_q$. Note that Eq. (22) generalizes Eq. (12) or (13) which is recovered when $\Omega = 1$. Conversely, the $3N - 6$ linear terms in q are obtained when $\Omega_q = 1$ so that by inverting Eq. (22) and selecting the row p in the matrix \mathcal{U}^{-1} corresponding to $\sum_i \Omega_{iq} = 1$, we obtain the desired relation $\mathbf{q} = \mathbf{q}(\mathbf{S})$ as

$$q_{i\sigma}^{(\Gamma)} \equiv [\mathcal{Q}_{\sigma}^{\{\Omega_q=1\}(\Gamma)}]_p = \left(\mathcal{U}_{\{\Omega_q\alpha_q\Theta_q\}}^{\{\Omega_q\alpha\Theta\}} \right)_{pp'}^{-1} [T_{\sigma}^{\{\Omega_q\alpha\Theta\}(\Gamma)}]_{p'}. \quad (23)$$

More generally, any polynomial functions of the type $aq_i + bq_iq_j + \dots$ can easily be expressed in terms of S from $(\mathcal{U}^{-1})_{kl}$ by selecting the appropriate lines k . It is also worth mentioning that $\mathcal{U}_{\{\Omega_q=1\}}^{\{\Omega=1\}}$ is nothing but the usual L matrix defined in (13) while $\mathcal{U}_{\{\Omega_q \neq 1\}}^{\{\Omega=1\}}$ equals the nonlinear part \mathcal{L} . By analogy with Eq. (13), we thus write

$$\mathbf{q} = \mathbf{L}^{-1}\mathbf{S} + \mathcal{H}(\mathbf{S}), \quad (24)$$

and we have checked that the identity relations $S_i(q(S)) = S_i$ and $q_i(S(q)) = q_i$ hold. To summarize, the procedure described above allows to transform the initial, nonlinear problem (12) to a simple linear problem as $T_i = \mathcal{U}_{ij}\mathcal{Q}_j \leftrightarrow \mathcal{Q}_i = (\mathcal{U}^{-1})_{ij}T_j$. To our opinion, this “linearization” method goes beyond the present spectroscopic work and could be adapted to other problems.

2. Choice of a relevant subspace

Equation (22) remains valid whatever the symmetry group but the dimension D of the matrix \mathcal{U} for all $\{\Gamma_1, \dots, \Gamma_m\}$ -covariant polynomials may be huge when increasing simultaneously the number of vibrational modes and the orders Ω and Ω' (for example, $D > 100,000$ for tetrahedral T_d molecules at order 10). Again, group theory will allow dimensionality reduction. From the knowledge of the multiplication tables, the irrep matrices as well as the non-vanishing CG coefficients for a given group G , we can choose an appropriate subspace spanned by a relevant set of Γ_i -covariant basis polynomials $\{S_i\}$ to build and invert the linear system of equations (see Eqs. (22), (23)). The different rules for cyclic, dihedral and cubic point groups that may possess more than one E representation are summarized:

– For asymmetric top molecules (Abelian groups) having M vibrational representations Γ_i such that $\text{Dim}(\Gamma_i) = 1$, M linear systems of equations have to be solved separately for each Γ_i , $i = 1, \dots, M$. For example, water (C_{2v}) requires to build only A_1 and B_1 tensors to express the three normal coordinates in terms of S . Ethylene calculations (D_{2h}) will require to build the A_g -, A_u -, B_{1u} -, B_{2g} -, B_{2u} -, B_{3g} - and B_{3u} -covariant polynomials. Construction of B_{1g} polynomials is not necessary because the linear term $q^{(B_{1g})}$ is not allowed for ethylene.

– For C_{2n+1v} , two subsets have to be considered, namely $(A_1, E_{1a}, E_{2a}, \dots, E_{na})$ and $(A_2, E_{1b}, E_{2b}, \dots, E_{nb})$. The same rules hold for D_n groups because of the isomorphism $D_n \sim C_{nv}$. Note that the C_{nv} are formed by semi-direct products $C_n \rtimes C_s$ ⁷⁰. For example, the two sub-systems (A_1, E_a) and (A_2, E_b) are used to determine $(q_1, q_2, q_{3a}, q_{4a})$ and (q_{3b}, q_{4b}) for tetraatomic C_{3v} pyramidal molecules.

– For C_{2nv} ($n \geq 2$), two sub-cases appear depending upon whether $2n = 4k + 4$ or $2n = 4k + 6$. For the first case ($2n = 4k + 4$), we have to consider four subspaces spanned by $(A_1, B_1, E_{2a}, E_{4a}, \dots, E_{(n-2)a})$, $(A_2, B_2, E_{2b}, E_{4b}, \dots, E_{(n-2)b})$, $(E_{1a}, E_{3a}, \dots, E_{(n-1)a})$ and $(E_{1b}, E_{3b}, \dots, E_{(n-1)b})$. For the case $2n = 4k + 6$, we have $(A_1, E_{2a}, E_{4a}, \dots, E_{(n-1)a})$, $(A_2, E_{2b}, E_{4b}, \dots, E_{(n-1)b})$, $(B_1, E_{1a}, E_{3a}, \dots, E_{(n-2)a})$ and $(B_2, E_{1b}, E_{3b}, \dots, E_{(n-2)b})$. Again, the same rules hold for D_n groups.

– Similarly, extension to D_{nh} ($n \geq 3$) only requires to add the parity labels (g, u) and $(', '')$ to the C_{nv} rules, respectively for odd and even values of n .

– D_{nd} (n even) point groups have the same rules as C_{2nv} while for D_{nd} (n odd) they are deduced from those of D_n by adding the parity g or u .

– For the T_d cubic group, the linear system (22) will be divided into four sub-systems generated by (A_1, A_2, E_a, E_b) -, (F_{1x}, F_{2x}) -, (F_{1y}, F_{2y}) - and (F_{1z}, F_{2z}) -covariant tensors to obtain the polynomial expansions in terms of S for (q_1, q_{2a}, q_{2b}) , (q_{3x}, q_{4x}) , (q_{3y}, q_{4y}) and (q_{3z}, q_{4z}) , respectively. Extension to O_h only requires adding parity indices g or u .

As an illustration, let us consider the PH_3 (C_{3v}) molecule which possesses 4 vibrational modes (two non-degenerate ones of symmetry A_1 and two degenerate ones of symmetry E). By focusing only on one coordinate, here $S_{3a}^{(E)}$, the nonlinear expansion (12) can be inverted

to give for example $q_{3a}^{(E)}$ as follows:

$$\begin{aligned}
S_{3a}^{(E)} &= 0.2268q_{3a}^{(E)} + 0.0044q_{4a}^{(E)} \\
&\quad - 0.0296q_1^{(A1)}q_{3a}^{(E)} + 0.0105(q_{3a}^{(E)})^2 + \dots \\
&\quad - 0.0027q_{3a}^{(E)}(q_{4b}^{(E)})^2 + 0.0020q_1^{(A1)}q_2^{(A1)}q_{4a}^{(E)} + \dots \\
&\quad + \dots \\
&\quad \downarrow \text{Eqs. (17)-(23)} \\
q_{3a}^{(E)} &= 4.4099S_{3a}^{(E)} - 0.1095S_{4a}^{(E)} \\
&\quad + 2.5460S_1^{(A1)}S_{3a}^{(E)} + 1.5898S_1^{(A1)}S_{4a}^{(E)} + \dots \\
&\quad + 1.4699(S_1^{(A1)})^2S_{3a}^{(E)} + 0.7348(S_{3a}^{(E)})^3 + \dots \\
&\quad + \dots,
\end{aligned} \tag{25}$$

where the number of digits has been voluntarily limited for clarity. For example, at order 6, the two matrices \mathcal{U} to be inverted in Eq. (22) are of dimension 501 and 422 for the subspaces $\{A_1, E_a\}$ and $\{A_2, E_b\}$, respectively. For the 7th order polynomial expansion of T_d molecules, four matrices of dimension 2943, 2832, 2832 and 2832 have to be inverted.

IV. CONSTRUCTION OF A CURVILINEAR IRREDUCIBLE TENSOR MODEL

A. Reduced ro-vibrational Hamiltonian

In Section III, an approach for computing a curvilinear Eckart-frame KEO based on the extensive use of symmetry properties has been proposed. From Eqs. (2), (10), and (11), we are now able to define a complete nuclear curvilinear Hamiltonian $H(S, d/dS, J_\alpha) = T(S, d/dS, J_\alpha) + V(S)$. As stated in the introduction part, the originality of the present approach is the possibility of considering the same harmonic oscillator Weyl-Heisenberg algebra as for the normal coordinates. We can thus introduce creation-annihilation operators A_i^+ and A_i from the coordinates S_i and momenta P_i with the usual commutation rules $[A_i, A_j^+] = \delta_{ij}$. Following the general method for writing the vibrational operators in second-quantized form (see for example Refs.^{56,71}), a *reduced* KEO can be defined to lower the total vibrational degree, from Ω_v to Ω_v^{red} , permitting a drastic reduction of the total number of terms with a minimal loss of accuracy. To this end, the normally-ordered form

: $T(A^+, A, J_\alpha)$: of the KEO has been employed. Contrary to the normal-mode approach, there is no need to apply our reduction-compression technique to the potential part $V(S)$.

At this stage, either the second-quantized KEO is back transformed to normally-ordered (S, P) operators or the (A^+, A) representation is kept. Though the number of operators rapidly grows with Ω_v , the advantage of using creation-annihilation operators is twofold: first, compact expressions for the matrix elements are derived and second, all vibrational selection rules are easily deduced. Conversely, the number of terms using the (S, P) representation is lower because the degree in P does not exceed 2 but computation of matrix elements is a bit more involved. In both cases, the reduced Hamiltonian reads

$$H_{red} = \sum_{\text{all indices}} h_{n_\alpha, n_\beta}^{\Omega_v^{red}(\mathbf{m}, \mathbf{n})} \prod_{i\sigma} (X_{i\sigma}^{(\Gamma_i)})^{m_{i\sigma}} (Y_{i\sigma}^{(\Gamma_i)})^{n_{i\sigma}} \times (J_\alpha)^{n_\alpha} (J_\beta)^{n_\beta}, \quad (26)$$

where $n_\alpha + n_\beta \leq 2$ and $\{\mathbf{m}, \mathbf{n}\} = \{m_1, n_1; m_2, n_2, \dots\}$ is a set of $2(3N - 6)$ vibrational indices and $\Omega_v^{red} = \mathbf{m} + \mathbf{n}$ the vibrational degree. We have either $(X, Y) = (S, P)$ with the supplementary condition $\sum_i n_i \leq 2$ or $(X, Y) = (A^+, A)$. The h parameters are composed of *ab initio* force constants, Coriolis parameters, etc. Following Ref.⁴⁸, Eq. (26) can be cast in a more compact form as $H_{red} = \tilde{\mathbf{h}}\mathbf{T}$ where $\tilde{\mathbf{h}}$ is the transpose of the vector containing the parameters and \mathbf{T} is the vector which contains all the operators.

For a full account of symmetry properties, the tensor formalism employed in Section III can be also considered to avoid linearly-dependent combinations of operators caused by degenerate vibrations. The basic idea is to assume that the reduced curvilinear Hamiltonian (26), which is an invariant polynomial, can be written as

$$H_{red}^{tens} = \sum_{\text{all indices}} t_{\{\Omega_v^{red}\alpha\Theta\}}^{\Omega_r(K_r, \alpha_r\Gamma)} \left(\varepsilon V^{\{\Omega_v^{red}\alpha\Theta\}(\Gamma)} \otimes R^{\Omega_r(K_r, \alpha_r\Gamma)} \right)^{(\Gamma_0)}, \quad (27)$$

where V stands for the vibrational tensors, defined in terms of (A^+, A) or (S, P) operators, and R for the rotational tensors of degree Ω_r in J_x , J_y and J_z . Here ε is the parity in the conjugate momenta such that $\varepsilon = (-1)^{\Omega_r}$ due to the time reversal invariance. From Eqs. (2), (10), and (11), the KEO part simply writes $\sum_{\{i\}} K_{\{i\}} (\varepsilon V^{\{i\}(\Gamma)} \otimes R^{(\Gamma)})^{(\Gamma_0)}$ while the potential and extra-potential parts are obtained by setting $R = I_d$ in (27), that is $V + \tilde{W} \sim \sum_{\{i\}} v_{\{i\}}^+ V^{\{i\}(\Gamma_0)} + w_{\{i\}}^+ V^{\{i\}(\Gamma_0)}$. The non-empirical tensor parameters $t = \{K, v, w\}$ are determined numerically without using any fitting procedure. In few words, the Hamiltonian (27) is first expanded using CG coefficients like Eq. (21) and, after some rearrangements,

takes the compact form $H_{red}^{tens} = \tilde{\mathbf{t}}\mathbf{Z}\mathbf{T}$ where \mathbf{Z} is a group symmetry transformation matrix of dimension $dim(t) \times dim(h)$ where

$$\begin{aligned} dim(t) &= dim(h) \text{ for Abelian point groups,} \\ dim(t) &< dim(h) \text{ for non-Abelian point groups.} \end{aligned}$$

As a general rule, the higher the number of degenerate vibrations is, the less the number of tensor parameters t compared to h will be. The case $dim(t) = dim(h)$ simply means that the use of irreducible tensor operators for asymmetric top molecules do not allow dimensionality reduction, that is $(q_1^{(\Gamma_1)} \otimes q_2^{(\Gamma_2)})^{(\Gamma)}$ reads $q_1^{(\Gamma_1)} q_2^{(\Gamma_2)}$ up to a phase. In other words, though elegant and allowing a unified formulation, tensor operators are not mandatory to accelerate calculations when only one-dimensional irreps are involved. Finally, by equating (26) and (27), the t 's are related to the h 's and are obtained by solving the overdetermined (when $dim(t) < dim(h)$) system of equations

$$\tilde{\mathbf{Z}}\mathbf{t} = \mathbf{h}, \quad (28)$$

using standard MKL libraries for the minimization procedure. Concerning line intensity calculations, the construction of the Γ_{dip} -covariant dipole moment tensor is quite similar. It simply consists in changing the irrep Γ_0 in Eq. (27) by Γ_{dip} defined in such a way that the x , y and z components of the molecule-fixed frame dipole moment transform as Γ_{dip} .

B. Basis-set and matrix elements

The choice of a primitive basis set is of primary importance in variational calculations. These basis functions are usually chosen to be eigenfunctions of a zero-order model, exactly solvable or not. **Generally, the use of a harmonic basis functions is a not a good choice when employing internal R coordinates. However, the situation is somewhat different when working directly in the symmetry coordinates S . Indeed, it can be shown that the 1D cuts of $V(S)$ along each coordinate S_i have a quite harmonic behaviour (see *e.g.* Fig. 1 of Ref.⁴⁸ for CF_4), making the use of harmonic functions as a primitive basis natural.** From Eqs. (10) and (14), the following zero-order Hamiltonian $H_0 = \sum_i \frac{\omega_i L_{ii}^2}{2} P_i^2 + k_i S_i^2$ is considered, where the k_i 's are the quadratic *ab initio* force constants contained in $V(S)$. The associated eigenfunctions $\phi_i(S_i) = \mathcal{N}_v H_v(\kappa_i^2 S_i) \exp(-\kappa_i^2 S_i^2/2)$ allow to compute all matrix elements

analytically. Within the associated Fock space, these states are the so-called squeezed Fock states

$$|v_i; \kappa_i\rangle = S_{qi}(\kappa_i)|v_i\rangle, \quad \kappa_i = \left(\frac{2k_i}{L_{ii}^2 \omega_i} \right)^{1/4}, \quad (29)$$

where $S_{qi}(\kappa)$ is a squeeze operator having the $SU(1, 1)$ group structure which is the most elementary non-compact Lie group widely used in quantum optics and defined as⁷²⁻⁷⁴

$$S_{qi}(\kappa) = \exp \left[-\frac{\beta_i}{2} (A_i^{+2} - A_i^2) \right], \quad (30)$$

with the squeezing parameter $\beta_i = \ln \kappa_i$. In order to compute matrix elements, we prefer using the standard Fock states $|v_i\rangle$, for which the proposed tensorial formalism is already implemented, and transforming the Hamiltonian as⁷¹

$$\tilde{H}(X, Y, J_\alpha) = S_q^\dagger H(X, Y, J_\alpha) S_q = H(\tilde{X}, \tilde{Y}, J_\alpha), \quad (31)$$

with $\tilde{X} = \tilde{S} = \kappa S$, $\tilde{Y} = \tilde{P} = \kappa^{-1} P$ or $\tilde{X} = \tilde{A}^+ = -A \sinh \beta + A^+ \cosh \beta$, $\tilde{Y} = \tilde{A} = A \cosh \beta - A^+ \sinh \beta$. We give these two options because we may choose either the route $(S, P) \rightarrow (\tilde{S}, \tilde{P}) \rightarrow (\tilde{A}^+, \tilde{A})$ or $(S, P) \rightarrow (A^+, A) \rightarrow (\tilde{A}^+, \tilde{A})$. For computational convenience, the first option is generally preferred. Note the κ_i parameters could be optimized variationally and if required, some shift parameters λ_i could be also introduced resulting in displaced squeezed Fock states $|v_i; \lambda_i, \kappa_i\rangle$ of primary importance in quantum optics⁷⁵⁻⁷⁷. In the space spanned by $\{\tilde{S}_i\}$, the functions $\langle \tilde{S}|v_i\rangle = \mathcal{N}_v H_v(\tilde{S}_i) \exp(-\tilde{S}_i^2/2)$ are eigenfunctions of the zero-order Hamiltonian $\tilde{H}_0 = \sum_i \frac{\tilde{\omega}_i}{2} (\tilde{P}_i^2 + \tilde{S}_i^2)$ with $\tilde{\omega}_i = L_{ii} \sqrt{2\omega_i k_i}$ and standard formula may be used.

Vibrational basis functions may be properly symmetrized in G using irreducible tensor operators as

$$\Phi_{v\sigma_v}^{(C_v)} \equiv | (v_1 v_2 \cdots v_M) C_v \sigma_v \rangle = \mathcal{N}_v T_v^{\{\Omega \alpha \Theta\}^{(C_v)}} | 0 \rangle, \quad (32)$$

where the tensors T_v are the same as (17) except that the S_i coordinates are now replaced by the creation operators \tilde{A}_i^+ . \mathcal{N}_v is a factor ensuring normalized functions. Eq. (32) is nothing but successive applications of creation operators on the vacuum state that can be thus seen as a generalization of the usual 1D harmonic oscillator formula. As usual, a “pruned basis” is defined by selecting only a limited set of relevant primitive vibrational functions and denoted as^{44,47,48}

$$F_\kappa(n) = \sum_{i=1}^M \kappa_i v_i \leq n, \quad (33)$$

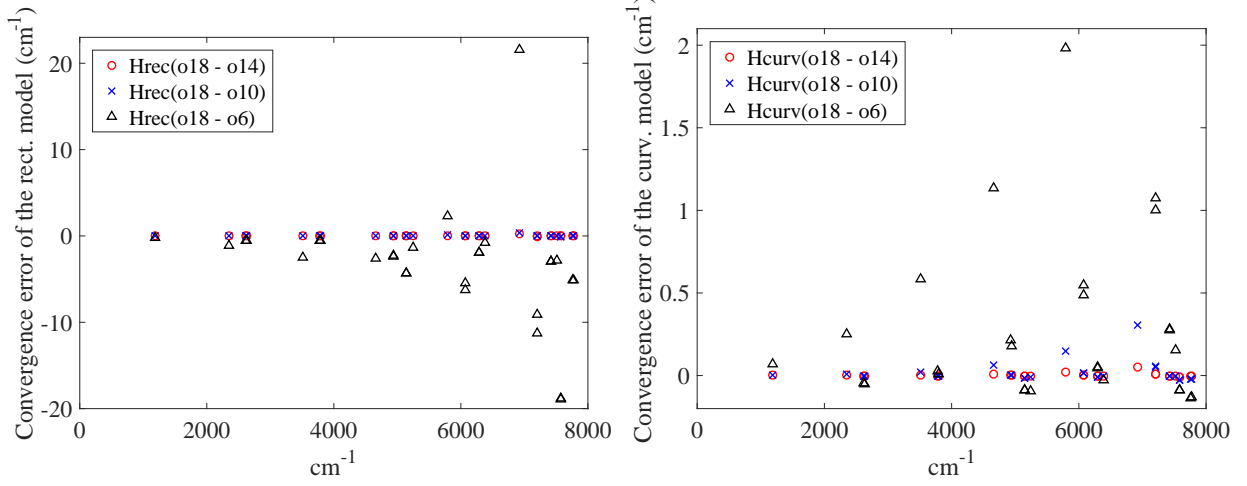


FIG. 1. Convergence of the curvilinear and normal-mode (rectilinear) Hamiltonians and impact on the vibrational energy levels of H_2S . Both models have been expanded at order 6, 10, 14 and 18 where $H(o(18))$ was taken as the reference calculation.

with $v_i = 0, \dots, n$ and where κ_i are some weight coefficients chosen to select an appropriate number of stretching, bending or torsional basis functions for each mode.

Concerning rotation, an appropriate method has been used to build symmetry-adapted functions for cubic point groups (T_d, O_h)⁷⁸, for both integer and half-integer angular momenta J . For asymmetric and symmetric tops, the rotational functions are symmetrized in the chain $O(3) \supset G$ ($G = C_{nh}, C_{nv}, D_{nh}, D_{nd}$) and obtained from

$$\Phi_{M \sigma_r}^{(J, nC_r)} \equiv |J, nC_r \sigma_r; M\rangle = \mathcal{N}_r(k) T_r^{(J, k, C_r)} |J, 0, M\rangle, \quad (34)$$

where the tensors $T_r^{(J, k, C_r)}$ are built from the ladder operators J_+^k and J_-^k and $\mathcal{N}_r(k)$ is a normalization factor⁶⁹. The rovibrational matrix element of the Hamiltonian (KEO+potential) can be directly computed from the coupling of the vibrational (32) and rotational (34) functions and from (27). Using the Wigner-Eckart theorem, we write

$$\begin{aligned} \langle \Phi_{v' \sigma'}^{(J, C_{vr})} | H(\Gamma_0) | \Phi_v^{(J, C_{vr})} \rangle &= \frac{(-1)^{C_v + C'_r + C_{vr} + \Gamma_v}}{[C_{vr}]^{1/2}} \\ &\times \left\{ \begin{array}{ccc} C_r & C_{vr} & C_v \\ C'_v & \Gamma_v & C'_r \end{array} \right\} \delta_{\sigma \sigma'} \\ &\times (r.m.e)_{vib} (r.m.e)_{rot}, \end{aligned} \quad (35)$$

where Γ_v is the symmetry of the vibrational operators and C_{vr} the total rovibrational symmetry of the basis functions. All the necessary ingredients, namely the 6C coupling coefficients

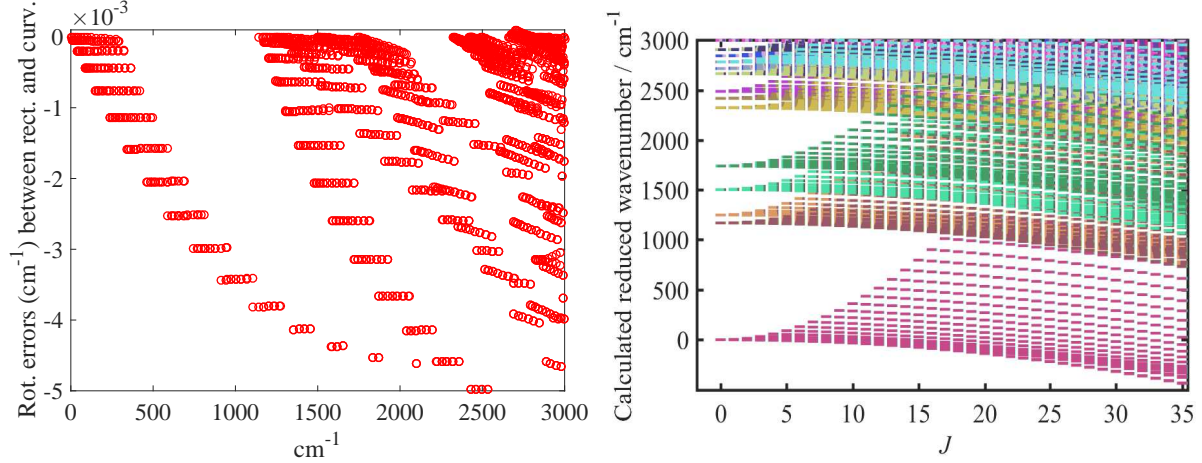


FIG. 2. (Left figure) Rotational errors between the curvilinear and rectilinear models up to $J = 15$ for H_2CO . The energy levels have been computed variationally using the reduced $\Psi_v(18 \rightarrow 8)$ functions. (Right figure) Variationally-computed reduced energy levels $E_{v,J} - 1.5J(J+1) - 4K_a^2$ up to $J = 35$ for H_2CO using the curvilinear model. Each color represents a mixing coefficient in the eigenfunction decomposition.

as well as the vibrational and rotational matrix elements $(r.m.e)_{vib}$ and $(r.m.e)_{rot}$, can be found elsewhere^{65,67,69}. Once constructed, the Hamiltonian matrix is diagonalized for each symmetry block (J, C_{vr}) .

To conclude with the basis functions, it is worth mentioning that all our tools initially developed for normal-mode calculations (*pruned* basis, reduced vibrational eigenfunctions $\Psi_v(m \rightarrow n)$, *vibrational subspace* (VSS) procedure^{44,47,48}) also apply for this work. In other words, our normal-mode and curvilinear models will share the same computer codes, without any modifications.

C. Applications to H_2S , H_2CO , PH_3 and SiH_4

The final step of this work is the validation of the curvilinear EF KEO developed in Section III and implemented in the tensor model of Section IV. As illustrative examples, we focus here on four molecular systems, namely H_2S (C_{2v}) and H_2CO (C_{2v}) for the case of Abelian point groups and PH_3 (C_{3v}) and SiH_4 (T_d) for the non-Abelian case. As a starting point, we have used the potential energy surfaces published in Refs.^{79–82} as well as the phosphine dipole moment surface of Ref.⁸³. Since our previous normal-mode (rectilinear) model

TABLE I. Selected vibrational energy levels for H₂S and comparison between Polyansky *et al.*⁷⁹, the rectilinear (Rect.) model and our curvilinear (Curv.) model (this work). The $F(20)$ basis (32) was employed for the variational calculations.

$v_1 v_2 v_3 C_v$	Calc. Ref. ⁷⁹	Curv. (this work)	Rect.	Rect. - Curv.	Ref. ⁷⁹ -Curv.
0 1 0 A_1	1182.90	1182.893	1182.893	0.0000	0.01
0 2 0 A_1	2354.15	2354.126	2354.126	0.0001	0.02
1 0 0 A_1	2614.39	2614.359	2614.359	-0.0003	0.03
0 0 1 B_1	2628.79	2628.765	2628.765	-0.0003	0.02
0 3 0 A_1	3513.84	3513.801	3513.800	0.0003	0.04
1 1 0 A_1	3779.04	3778.999	3778.999	-0.0002	0.04
0 1 1 B_1	3789.18	3789.137	3789.138	-0.0002	0.04
0 4 0 A_1	4661.57	4661.522	4661.520	0.0011	0.05
1 2 0 A_1	4932.45	4932.395	4932.395	-0.0001	0.05
0 2 1 B_1	4938.66	4938.604	4938.604	-0.0002	0.06
1 0 1 B_1	5147.27	5147.214	5147.216	-0.0017	0.05
0 0 2 A_1	5243.53	5243.477	5243.478	-0.0006	0.05
0 5 0 A_1	5796.63	5796.559	5796.556	0.0033	0.07
1 3 0 A_1	6074.69	6074.626	6074.625	0.0002	0.06
0 3 1 B_1	6077.26	6077.197	6077.197	0.0000	0.06
2 1 0 A_1	6288.70	6288.627	6288.629	-0.0021	0.07
1 0 2 A_1	7576.42	7576.338	7576.348	-0.0100	0.07
2 0 1 B_1	7576.48	7576.397	7576.407	-0.0100	0.07
1 1 2 A_1	8696.71	8696.661	8696.672	-0.0111	0.04
2 1 2 A_1	11008.86	11008.900	11008.893	0.0064	-0.03
3 1 1 B_1	11008.85	11008.888	11008.881	0.0065	-0.03

has been already validated on 4-6 atomic systems^{46,84,85}, we have compared calculations using rectilinear and curvilinear (this work) coordinates. Note this section does not intend to make in-depth studies but aims at validating our $H(S, P, J)$ model.

Hydrogen sulfide: For H_2S , the PES of Polyansky *et al.*⁷⁹, initially expanded in the Morse-cosine variables and converted in symmetry S coordinates for this work, was employed. In order to study the convergence of the polynomial expansions (13) and (24), the KEO part of our curvilinear model (26) was expanded at order 6, 10, 14 and 18 in S . To be consistent, the normal-mode model was also expanded at the same orders but in q . For the variational calculations, the $F(20)$ basis (32) composed of 911 vibrational functions of symmetry A_1 and 791 of symmetry B_1 was employed. Fig. 1 shows the convergence of the curvilinear and normal-mode Hamiltonians and its impact on the vibrational levels. Here the $H(o(18))$ model was taken as the benchmark calculation. The first information is that the $H(o(12))$ or $H(o(14))$ models are almost converged. The second and most important point is that $H(S, P)$ (right panel) converges more rapidly than $H(q, p)$ (left panel). This is partly explained by the PES part which is not transformed for the curvilinear case while it has to be Taylor-expanded in q for the rectilinear case. Typically, our initial PES $V(S)$ contains only 17 terms against ~ 700 once transformed in q at order 18. Tab. I shows comparisons of some vibrational band centers between Polyansky *et al.*⁷⁹, our rectilinear and curvilinear models. The results between $H(S, P)$ and $H(q, p)$ are in good agreement.

Formaldehyde: Like H_2S , H_2CO also belongs to C_{2v} but possesses 6 nondegenerate vibrational modes. Here the Jacobian (14) has been developed at order 9 and the full Hamiltonian $H(S, P, J)$ at order 14 before applying the reduction procedure described in Section IV to finally obtain the reduced $H_{Curv}^{red}(14 \rightarrow 9)$ model. In order to properly converge the normal mode model, the reduced $H_{Rect}^{red}(18 \rightarrow 9)$ Hamiltonian was used. All variational calculations have been performed using the $F(18)$ basis composed of 38962 functions A_1 , 28446 A_2 , 29436 B_1 and 37752 B_2 . Selected vibrational levels are given in Tab. II and compared to those of Yachmenev *et al.*⁸⁰. Once again, the agreement between the levels of Ref.⁸⁰ and those obtained from rectilinear and curvilinear coordinates is good. For $J > 0$ calculations, the vibrational reduced eigenfunctions $\Psi_v(18 \rightarrow 8)$, involving only 643 A_1 , 310 A_2 , 370 B_1 and 558 B_2 functions, were used to solve the rovibrational problem. Fig. 2 (left panel) shows the rotational errors between the curvilinear and rectilinear models up to $J = 15$ and we can see that agreement is quite good. By increasing the polynomial orders of the Jacobians or reciprocal μ tensor, these results could probably be slightly improved. Fig. 2 (right panel) displays the reduced energy levels $E_{vJ} - 1.5J(J + 1) - 4.2K_a^2$ up to $J = 35$. To better illustrate the complex eigenvector redistribution when increasing J , each colour in this figure

TABLE II. Selected vibrational energy levels for H₂CO and comparison between Yachmenev *et al.*⁸⁰, the rectilinear $H_{Rect}(18 \rightarrow 9)$ model (=Rect.) and our curvilinear $H_{Curv}(14 \rightarrow 8)$ model (=Curv, this work).

$v_1v_2v_3v_4v_5v_6C_v$	Calc. Ref. ⁸⁰	Curv. (this work)	Rect.	Rect. - Curv.	Ref. ⁸⁰ -Curv.
0 0 0 1 0 0 B_1	1166.10	1166.092	1166.093	0.0003	0.01
0 0 0 0 0 1 B_2	1245.60	1245.591	1245.591	0.0004	0.01
0 0 1 0 0 0 A_1	1499.10	1499.104	1499.105	0.0003	0.00
0 1 0 0 0 0 A_1	1744.61	1744.680	1744.680	0.0001	-0.07
0 0 0 2 0 0 A_1	2325.18	2325.153	2325.150	-0.0031	0.03
0 0 0 1 0 1 A_2	2418.43	2418.410	2418.409	-0.0006	0.02
0 0 0 0 0 2 A_1	2487.73	2487.646	2487.646	-0.0002	0.08
0 0 1 1 0 0 B_1	2664.64	2664.609	2664.608	-0.0005	0.03
1 0 0 0 0 0 A_1	2781.74	2781.719	2781.721	0.0014	0.01
0 0 0 0 1 0 B_2	2842.37	2842.414	2842.415	0.0010	-0.05
0 1 0 1 0 0 B_1	2903.35	2903.402	2903.402	0.0002	-0.05
0 1 0 0 0 1 B_2	2995.91	2995.947	2995.947	-0.0001	-0.04
0 0 2 0 0 0 A_1	2997.24	2997.230	2997.229	-0.0005	0.01
0 1 1 0 0 0 A_1	3236.11	3236.140	3236.140	-0.0001	-0.03

represents a mixing coefficient $(c_i^j)^2$ of the wavefunction decomposition $\Psi^j = c_1^j\phi_1 + c_1^j\phi_1 + \dots$ with $\sum_k (c_k^j)^2 = 1$.

Phosphine: This molecule belongs to the non-Abelian point group C_{3v} which exhibits two doubly degenerate irreps of type E . We have started from the PES $V(S)$ calculated by Nikitin *et al.*⁸¹ and used recently to compute spectra of the two deuterated isotopologues⁸⁴. Here we aim at computing the infrared phosphine spectra to validate all the coordinate transformations described in Section III. To this end, the $H_{Curv}(16 \rightarrow 7)$ reduction was considered and the normal mode DMS of Ref.⁸³ transformed in the S coordinates from Eq. (24). Using the VSS procedure of Refs.^{44,47,48} and the reduced functions $\Psi_v(15 \rightarrow 7)$, we have computed the rovibrational energy levels and all transition intensities up to $J = 18$ with an intensity cutoff of $10^{-25} \text{ cm}^{-1}/(\text{cm}^{-2} \cdot \text{molecule}^{-1})$. Fig. 3 shows the very good agreement

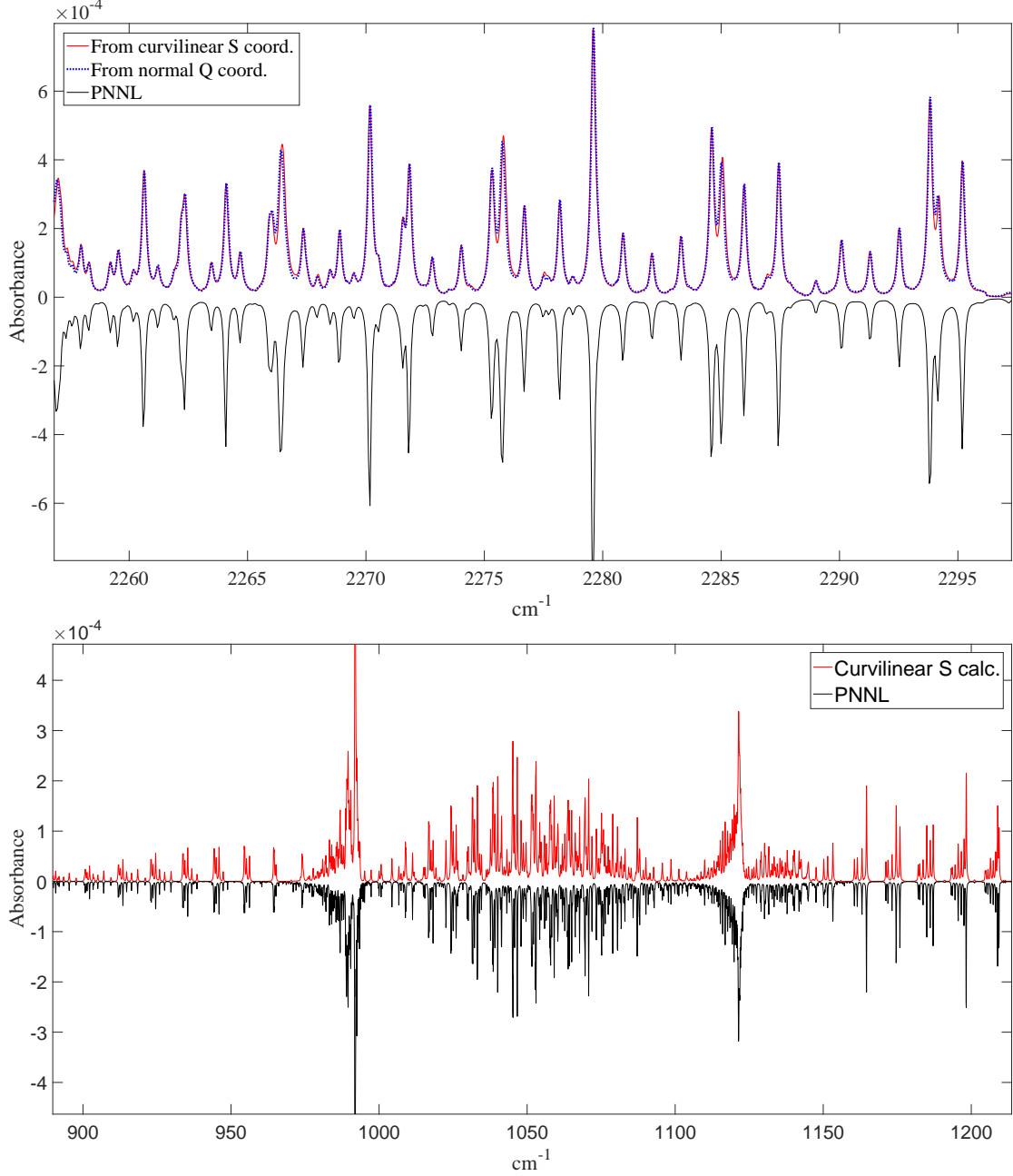


FIG. 3. Example comparison of theoretical absorption spectra of PH_3 using rectilinear (normal coordinates) and curvilinear models with PNNL records⁸⁶ at 296 K.

between the PNNL⁸⁶ and calculated spectra using curvilinear and rectilinear coordinates.

Silane: As a final test, we consider the silane molecule of symmetry T_d and the PES derived by Owens *et al.*⁸² that is transformed in S using Eq. (6) of Ref.⁴⁴. Here we focus on the convergence of the Jacobian J_k^l (14) and on its impact on the calculated vibrational energy levels. Starting from $\mu(q)$ of order 8, the final KEO of Eq. (9) is expanded to order

TABLE III. Convergence of the vibrational energy levels of SiH₄ with respect to the order $o(n)$ of the Jacobian expansion (14) and comparison with Owens *et al.*⁸².

$v_1v_2v_3v_4C_v$	Calc. Ref. ⁸²	$J_k^l(o(4))$	$J_k^l(o(6))$	$J_k^l(o(8))$	Ref. ⁸² - $o(4)$	Ref. ⁸² - $o(6)$	Ref. ⁸² - $o(8)$
0 0 0 1 F_2	912.85	912.68	912.82	912.85	0.17	0.03	0.00
0 1 0 0 E	970.14	970.09	970.13	970.14	0.05	0.01	0.00
0 0 0 2 A_1	1810.90	1810.35	1810.82	1810.92	0.55	0.08	-0.02
0 0 0 2 F_2	1823.15	1822.58	1823.07	1823.18	0.57	0.08	-0.03
0 0 0 2 E	1827.00	1826.69	1826.96	1827.01	0.31	0.04	-0.01
0 1 0 1 F_2	1880.87	1880.59	1880.84	1880.87	0.28	0.03	0.00
0 1 0 1 F_1	1885.36	1885.08	1885.34	1885.37	0.28	0.02	-0.01
0 2 0 0 A_1	1935.84	1935.72	1935.83	1935.83	0.12	0.01	0.01
0 2 0 0 E	1941.29	1941.18	1941.27	1941.28	0.11	0.02	0.01
0 0 0 3 F_2	2738.48	2737.79	2738.38	2738.52	0.69	0.10	-0.04
0 1 0 2 E	2779.32	2778.49	2779.26	2779.34	0.83	0.06	-0.02
0 1 0 2 F_1	2791.84	2791.00	2791.77	2791.88	0.84	0.07	-0.04
0 1 0 2 A_1	2793.94	2793.38	2793.90	2793.95	0.56	0.04	-0.01
0 1 0 2 F_2	2795.53	2794.73	2795.46	2795.58	0.80	0.07	-0.05
0 1 0 2 E	2798.25	2797.72	2798.21	2798.27	0.53	0.04	-0.02
0 1 0 2 A_2	2801.56	2801.06	2801.54	2801.60	0.50	0.02	-0.04
0 2 0 1 F_2	2846.60	2846.11	2846.56	2846.58	0.49	0.04	0.02
0 2 0 1 F_1	2854.36	2853.92	2854.33	2854.37	0.44	0.03	-0.01
0 2 0 1 F_2	2857.18	2856.75	2857.14	2857.19	0.43	0.04	-0.01
0 3 0 0 E	2902.60	2902.36	2902.57	2902.57	0.24	0.03	0.03
0 3 0 0 A_1	2913.34	2913.15	2913.32	2913.33	0.19	0.02	0.01

12 and reduced to order 7 while keeping the 6th order PES $V(S)$ unchanged. Note that all our previous normal mode calculations on XY₄ molecules employed the 14th order PES $V(q)$ composed of nearly 200,000 terms against only 670 for $V(S)$. Using the modified $F(14)$ basis (13 stretching functions and 14 bending functions) composed of 22381 A_1 , 19589 A_2 , 41935 E , 61046 F_1 , 63834 F_2 functions, we have calculated the vibrational energy levels of

SiH₄ when the Jacobian J_k^l is truncated at order 4, 6 and 8. To illustrate the convergence of the KEO, we compare in Tab. III selected vibrational energy levels with those obtained by Owens *et al.*⁸². We can see that order 4 is not sufficient to accurately reproduce the band centers. At order 6, the Jacobian is almost converged because the resulting energies are not so far from the $J_k^l(o(8))$ model which is in good agreement with Ref.⁸². **Similar results have been obtained for methane.**

V. CONCLUSION AND PERSPECTIVES

In the present paper, we have proposed a general method to build an Eckart-frame tensorial rotation-vibration kinetic energy operator expressed in curvilinear internal coordinates for N -atomic semirigid molecules and for arbitrary point groups. Starting from the usual normal-mode Watson KEO, we have described in detail all steps of transformations and shown how symmetry can be employed to compute all necessary terms for the coordinate changes. To make the link between the symmetry-adapted normal and curvilinear coordinates, we have established a group-theoretically based procedure to invert nonlinear polynomials that could be also useful in different contexts. Unlike normal coordinates, the potential energy surface is not transformed here and is taken directly from analytical functions that fit the *ab initio* points computed on a suitable grid. The use of irreducible tensor operators allowed to express the KEO and PES parts in a very compact, convenient and unified form, whatever the symmetry point group. Particularity of the present approach is the possibility of using the same compression-reduction tools as initially introduced for normal coordinates in previous works^{44,47,48} and most importantly the same variational computer code for spectra predictions. Our Eckart-frame ro-vibrational curvilinear model has been validated on four molecular systems, namely H₂S, H₂CO, PH₃ and SiH₄. More in-depth studies using this curvilinear model will be considered later.

In a near future, we plan to extend this work by following three directions. The first one will consist in the treatment of floppy molecules, starting for instance from the Hougen-Bunker-Johns formulation⁸⁷ while the second one will focus on the construction of non-empirical effective models by applying a series of contact transformations from the second-quantized operators A_i and A_i^+ defined in Section IV. For the very first time, a curvilinear spectroscopic model will be thus constructed for high resolution spectroscopy. Finally, fol-

lowing the strategy of Chubb *et al.*⁸⁸, the construction of tensor operators for linear molecules could be also considered since $D_{\infty h}$ can be formulated in terms of D_{nh} with $n=2, 3 \dots$.

ACKNOWLEDGMENTS

The author acknowledges support from the Romeo computer center of Reims-Champagne-Ardenne. This work was supported by the Programme National de Planétologie (PNP) of CNRS/INSU, co-funded by CNES. This work is dedicated to Professor Viktor Szalay.

Appendix A: Derivation of the KEO from tensor calculus

We show in this appendix how expression (7) can be reformulated using tensor calculus. Introducing the covariant and contravariant metric tensors defined respectively as $g_{ij} = \frac{\partial q_k}{\partial S_i} \frac{\partial q_k}{\partial S_j}$ and $g^{ij} = (g_{ij})^{-1}$, the Christoffel symbols of the first and second kind associated with quadratic differential forms are given by⁸⁹

$$\begin{aligned} [ij, k]_x &= \frac{1}{2} \left(\frac{\partial g_{ik}}{\partial x_j} + \frac{\partial g_{jk}}{\partial x_i} - \frac{\partial g_{ij}}{\partial x_k} \right) \quad (\text{First kind}), \\ \left\{ \begin{matrix} k \\ i \ j \end{matrix} \right\}_x &= g^{kl} [ij, l]_x \quad (\text{Second kind}). \end{aligned} \quad (\text{A1})$$

According to the law of transformation of Christoffel symbols of the second kind for $q \rightarrow S$, we can write

$$\frac{\partial^2 S_k}{\partial q_i \partial q_j} = \frac{\partial S_k}{\partial q_l} \left\{ \begin{matrix} l \\ i \ j \end{matrix} \right\}_q - \frac{\partial S_l}{\partial q_i} \frac{\partial S_r}{\partial q_j} \left\{ \begin{matrix} k \\ l \ r \end{matrix} \right\}_S, \quad (\text{A2})$$

and taking into account that $\{ : . \}_q = 0$, Eq. (7) becomes

$$p_i p_j = \sum_{kl} J_i^k J_j^l \left[P_k P_l - i \left\{ \begin{matrix} r \\ k \ l \end{matrix} \right\}_S P_r \right] \quad (\text{A3})$$

Note that despite of the use of co- and contravariant indices, Christoffel symbols of the second kind are not tensors *stricto sensu* because of the second derivative involved in the transformation law.

Though Eqs. (6) and (7) are generally preferred for practical calculations, Eq. (A3) may be seen as a generalization of the Podolsky expression. To this end, let us set $i = j$ in Eq.

(A3) and see how it simplifies. To be short, some steps have been voluntarily skipped. After rearrangement of all dummy indices, the Laplacian takes the following form

$$\nabla^2 \rightarrow g^{lr} \frac{\partial^2}{\partial S_l \partial S_r} - g^{lr} \left\{ \begin{matrix} k \\ l \ r \end{matrix} \right\}_S \frac{\partial}{\partial S_k} \quad (\text{A4})$$

where from (A1)

$$\begin{aligned} g^{lr} \left\{ \begin{matrix} k \\ l \ r \end{matrix} \right\}_S &= \frac{g^{lr} g^{kp}}{2} \left(\frac{\partial g_{lp}}{\partial S_r} + \frac{\partial g_{rp}}{\partial S_l} - \frac{\partial g_{lr}}{\partial S_p} \right) \\ &= (1) + (2) + (3) \end{aligned} \quad (\text{A5})$$

Calculation of the term (1)

From $g^{kp} g_{lp} = \delta_{lk}$, we write

$$g^{kp} \frac{\partial g_{lp}}{\partial S_r} = -g_{lp} \frac{\partial g^{kp}}{\partial S_r},$$

so that

$$\begin{aligned} \frac{g^{lr} g^{kp}}{2} \frac{\partial g_{lp}}{\partial S_r} &= -\frac{g^{lr} g_{lp}}{2} \frac{\partial g^{kp}}{\partial S_r} \\ &= -\frac{1}{2} \frac{\partial g^{kp}}{\partial S_p} \end{aligned} \quad (\text{A6})$$

Calculation of the term (2)

Similarly, we can write

$$\frac{g^{lr} g^{kp}}{2} \frac{\partial g_{rp}}{\partial S_l} = -\frac{1}{2} \frac{\partial g^{kp}}{\partial S_p} \quad (\text{A7})$$

Calculation of the term (3)

We have $g = g_{lr} G_{lr}$ with G the cofactor and g the determinant of the covariant metric tensor so that $\frac{\partial g}{\partial S_p} = G_{lr} \frac{\partial g_{lr}}{\partial S_p}$ and knowing that $G_{lr} = g g^{lr}$, we write

$$g^{-1} \frac{\partial g}{\partial S_p} = g^{lr} \frac{\partial g_{lr}}{\partial S_p},$$

and finally

$$\begin{aligned} \frac{g^{kp} g^{lr}}{2} \frac{\partial g_{lr}}{\partial S_p} &= \frac{g^{kp}}{2g} \frac{\partial g}{\partial S_p} \\ &= g^{kp} \frac{\partial \ln g^{1/2}}{\partial S_p} \equiv g^{kp} \left\{ \begin{matrix} i \\ p \ i \end{matrix} \right\}_S \end{aligned} \quad (\text{A8})$$

From Eqs. (A8), (A6) and (A7) and after rearrangements, Eq. (A4) finally becomes

$$\begin{aligned} \nabla^2 &= g^{kp} \frac{\partial^2}{\partial S_k \partial S_p} + \left[g^{kp} \frac{\partial \ln g^{1/2}}{\partial S_p} + \frac{\partial g^{kp}}{\partial S_p} \right] \frac{\partial}{\partial S_k} \\ &= g^{-1/2} \frac{\partial}{\partial S_p} g^{1/2} g^{kp} \frac{\partial}{\partial S_k} \\ &= \text{div} (\overrightarrow{\text{grad}}) \end{aligned} \quad (\text{A9})$$

which is nothing but the Podolsky expression usually used in the coordinates transformation from Cartesian to general coordinates. Though popularized by Podolsky²⁵ in 1928, this expression was already employed in vector analysis and relativity⁹⁰.

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