Vibrational energy levels with arbitrary potentials using the Eckart-Watson Hamiltonians and the discrete variable representation

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An effective and general algorithm is suggested for variational vibrational calculations of N-atomic molecules using orthogonal, rectilinear internal coordinates. The protocol has three essential parts. First, it advocates the use of the Eckart-Watson Hamiltonians of nonlinear or linear reference configuration. Second, with the help of an exact expression of curvilinear internal coordinates (e.g., valence coordinates) in terms of orthogonal, rectilinear internal coordinates (e.g., normal coordinates), any high-accuracy potential or force field expressed in curvilinear internal coordinates can be used in the calculations. Third, the matrix representation of the appropriate Eckart-Watson Hamiltonian is constructed in a discrete variable representation, in which the matrix of the potential energy operator is always diagonal, whatever complicated form the potential function assumes, and the matrix of the kinetic energy operator is a sparse matrix of special structure. Details of the suggested algorithm as well as results obtained for linear and nonlinear test cases including H_2O, H_3^+, CO_2, HCN/HNC, and CH_4 are presented. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2756518]

I. INTRODUCTION

Breaking away from the traditional treatment of molecular rotational-vibrational spectra using perturbational approaches, variational computation of rovibrational levels was introduced by Handy and co-workers[1,2] in the 1970s, following the introduction of simple and exact Hamiltonians by Watson for nonlinear[3] and linear[4] molecules, based on the use of regular rectilinear normal coordinates.

Many important developments in theoretical molecular spectroscopy came after these groundbreaking studies which used exact kinetic energy operators in (nearly) variational computations. These investigations[5–22] were aimed at determining a large number of accurate rotational-vibrational energy levels of polyatomic species of increasing size and complexity. This goal has been more or less achieved for triatomic species,[23] for which exceedingly accurate potential energy surfaces (PESs) can be developed. Nevertheless, for larger systems even the best direction to pursue in nuclear motion computations has not been completely clear, especially when the aim is the determination of spectra up to the dissociation limits.

Two directions have been followed. One is based on Hamiltonians expressed in curvilinear internal coordinates,[7] e.g., valence coordinates, offering the advantage that such Hamiltonians, with appropriately chosen basis sets, matrix element computations, and diagonalization techniques, can approximate the complete eigenspectrum of molecules. Due to obvious dimensionality problems, this technique could only be pursued for small species, most importantly for tri- and tetratomics. Based on the most simple arguments, the other direction prefers to have a single Hamiltonian which would be the same for almost all molecular systems. This is offered by the Hamiltonians of Watson,[3,4] expressed in a set of rectilinear normal coordinates. While the Eckart-Watson Hamiltonians are general, and thus make the introduction and programming of tailor-made Hamiltonians for each new system exhibiting particular bonding arrangements unnecessary, the use of this Hamiltonian has been limited by two difficulties. First, these Hamiltonians, by design, do not efficiently describe all large amplitude motions due to the rectilinear nature of the coordinates they are built on. Second, due to the numerical integration schemes employed, in general it has proved to be impossible to use PESs expressed in arbitrary coordinates with these Hamiltonians without resorting to some kind of an expansion of the PES in normal coordinates, thus separating, to a certain extent, the otherwise nonseparable functions. The best solution within the finite basis representation (FBR) developed so far for the separability of the potential is due to Jung and Gerber[9] and Carter *et al.*[10–12] and is called the *n*-mode representation. In its most sophisticated form it allows exact treatment of up to five modes. This shortcoming of the method excludes the possibility of exact vibrational computations for systems having more than four atoms even if related highly accurate PESs were available. While the first shortcoming originates from the coordinate choice of the Eckart-Watson Hamilto-

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nians, the second problem, related to the PES, can be eliminated if one (a) represents the Hamiltonian using the discrete variable representation (DVR) technique,[24–26] employed successfully in variational approaches based on internal coordinate Hamiltonians, and (b) applies a formalism allowing the exact expression of arbitrary internal coordinates in terms of rectilinear internal (e.g., normal) coordinates. The DVR representation of the Eckart-Watson Hamiltonians is not without precedent in the literature, and such (ro)vibrational calculations have already appeared.[13–21] Seideman and Miller[13] developed DVRs for both the linear and nonlinear Eckart-Watson Hamiltonians and applied them for the H_2+H reaction system. Later, Yonehara *et al.*[15] worked out an efficient DVR Eckart-Watson algorithm based on a partial summation technique,[16] and applied it for formaldehyde. A similar approach that applies generalized vibrational coordinates was developed in a series of papers by Luckhaus and co-workers and a set of four-atomic molecules, H_2CO, HONO, H_2O_2, and NH_3, was studied.[18–21] In all these methods the DVR is based on an equidistant grid and Chebyshev polynomials.

We suggest here an algorithm, referred to as DEWE in what follows, standing for discrete variable representation (D) of the Eckart-Watson (EW) Hamiltonian with exact inclusion of an arbitrary potential energy function (E), for high-accuracy nuclear motion calculations of a general polyatomic molecule. The three essential elements of the suggested DEWE algorithm are as follows. First, apply the general form of the Eckart-Watson Hamiltonians, cited later in Eqs. (10) and (22) for the nonlinear and linear reference geometries, respectively, that work in rectilinear normal coordinates. Second, apply a (semi)global PES or a high-accuracy force field expressed in any set of curvilinear internal coordinates (e.g., valence coordinates) that can be exactly matched to any given values of rectilinear internal (e.g., normal) coordinates following the transformation given later in Eq. (32). Third, represent the kinetic and the potential energy operators in DVR. In this representation the potential energy matrix, within Gaussian quadrature accuracy, is always diagonal, no matter how complicated the actual potential function is. The form of the kinetic energy operator is given irrespective of the actual system, and the higher the dimensionality of the problem, the sparser the matrix representation of the whole operator is. The required eigenpairs of the sparse matrix, with a special structure, of the Eckart-Watson Hamiltonian operators can be obtained efficiently with iterative algorithms, like the Lanczos method.[27] Based on this algorithm a computer code was written and tested, using available PESs and force fields for nonlinear [H_2O (Ref. 23) and H_3^+ (Ref. 28)] and linear [CO_2 (Ref. 29) and HCN/HNC (Ref. 30)] triatomic molecules and for methane.[31] In the second half of the paper results obtained for these test cases are presented and discussed briefly.

II. RECTILINEAR INTERNAL COORDINATES

A. Nonlinear reference configuration

Let us consider a nonlinear molecule with N nuclei whose instantaneous Cartesian coordinates fixed in the laboratory are denoted by $\mathbf{x}_i$ ($i=1,2,\ldots,N$). To describe internal motions of the molecule it is useful to separate the three translational and three orientational variables.[32]

First, a set of redundant body-fixed rectilinear Cartesian coordinates is chosen ($\mathbf{z}_i$),

$$\mathbf{x}_i - \mathbf{X} = \mathbf{C}\mathbf{z}_i, \tag{1}$$

$i=1,\ldots,N$, where $\mathbf{X}$ stands for the coordinate of the center of nuclear mass, and matrix $\mathbf{C}$ is an orthogonal matrix that gives the spatial orientation of the body-fixed frame compared to the laboratory frame. Thus, the first Eckart condition,[33] that separates the motion of the center of nuclear mass (m_i denotes the mass of the ith nucleus) is written as

$$\sum_{i=1}^{N} m_i\mathbf{z}_i = 0. \tag{2}$$

Next, we introduce displacement coordinates from a reference geometry $\mathbf{c}_i$, in practice usually (but not necessarily) chosen to be the minimum of the PES, as

$$\boldsymbol{\rho}_i = \mathbf{z}_i - \mathbf{c}_i. \tag{3}$$

Furthermore, to settle the spatial orientation of the body frame, the second Eckart condition requires that

$$\sum_{i=1}^{N} m_i\mathbf{c}_i \times \boldsymbol{\rho}_i = \mathbf{0}. \tag{4}$$

In general, a set of $3N-6$ nonredundant, rectilinear internal coordinates are defined in terms of the displacement coordinates as

$$Q_k = \sum_{i=1}^{N}\sum_{\alpha} b_{\alpha ik}\rho_{\alpha i} = \sum_{i=1}^{N} \mathbf{b}_{ik}^T\boldsymbol{\rho}_i,$$

$$Q_k \in (-\infty, +\infty), \quad k=1,2,\ldots,3N-6, \quad \alpha=x,y,z. \tag{5}$$

With Watson's particular choice of internal coordinates[3] orthogonality is required and $\mathbf{l}_{ik}$ coefficients are introduced as

$$\mathbf{b}_{ik} = \sqrt{m_i}\mathbf{l}_{ik}, \tag{6}$$

$$Q_k = \sum_{i=1}^{N} \sqrt{m_i}\mathbf{l}_{ik}^T\boldsymbol{\rho}_i,$$

$$i=1,2,\ldots,N \quad \text{and} \quad k=1,2,\ldots,3N-6. \tag{7}$$

The elements of $\mathbf{l} \in \mathbb{R}^{3 \times N \times (3N-6)}$, when the orthogonality and the Eckart conditions (2) and (4) are taken into account, satisfy

$$\sum_{i=1}^{N} \mathbf{l}_{ij}^T\mathbf{l}_{ik} = \delta_{jk}, \quad \sum_{i=1}^{N} \sqrt{m_i}\mathbf{l}_{ik} = \mathbf{0}, \quad \text{and} \quad \sum_{i=1}^{N} \sqrt{m_i}\mathbf{c}_i \times \mathbf{l}_{ik} = \mathbf{0}$$

$$j,k=1,2,\ldots,3N-6. \tag{8}$$

A few comments are in order. Equations (8) form an underdetermined system of equations for the elements of $\mathbf{l}$. The well-known rectilinear normal coordinates can be regarded as a special case of the coordinates introduced in Eq. (5), requiring that the set of Q_k's diagonalizes both the kinetic

and harmonic potential energy matrices, as well as that Eqs. (8) are fulfilled. In the general case, however, one can build a set of orthogonal, rectilinear coordinates describing the internal motion of a molecule satisfying Eqs. (8) that is independent of the actual model potential.

B. Linear reference configuration

In the case of a linear reference structure, the three degrees of freedom of translational motion can be similarly separated as in the nonlinear case. To separate the rotational coordinates, however, the rotational Eckart condition, Eq. (4), reduces so that the orientation of only that axis can be determined along which the reference configuration of the molecule lies. So, out of the three Euler angles, ϕ, θ, and χ, only two can be considered to be independent. Let us choose the pair ϕ and θ, while χ can be set to a constant (e.g., zero), or for the sake of generality it can be considered as an arbitrarily chosen function of ϕ and θ. As a result of this, there will be only 2 rotational and $3N-5$ vibrational degrees of freedom.

Taking these facts into consideration, orthogonal, rectilinear internal coordinates can be defined, similarly to the case of the nonlinear reference configuration[4] as

$$Q_k = \sum_{i=1}^{N} \sqrt{m_i} \mathbf{l}_{ik}^T \boldsymbol{\rho}_i,$$

$$Q_k \in (-\infty, +\infty), \quad k = 1, 2, \ldots, 3N-5. \tag{9}$$

The elements of $\mathbf{l} \in \mathbb{R}^{3 \times N \times (3N-5)}$ satisfy similar conditions to those given in Eqs. (8), out of which the last one simplifies due to the linear nature of the reference configuration.

III. THE ECKART-WATSON HAMILTONIANS

A. Nonlinear reference configuration

The vibration-rotation Hamiltonians for a nonlinear reference configuration[34] was rearranged by Watson in 1968,[3] who worked in the set of orthogonal, rectilinear internal coordinates defined by Eq. (7). This rearranged Hamiltonian is referred to as Eckart-Watson Hamiltonian (of a nonlinear reference configuration) and has the following simple form:[3]

$$\hat{H} = \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} (\hat{J}_\alpha - \hat{\pi}_\alpha)(\hat{J}_\beta - \hat{\pi}_\beta) - \frac{\hbar^2}{8} \sum_\alpha \mu_{\alpha\alpha} + \frac{1}{2} \sum_{k=1}^{3N-6} \hat{P}_k^2 + \hat{V}. \tag{10}$$

The vibration-only part is

$$\hat{H}^{\text{vib}} = \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} \hat{\pi}_\alpha \hat{\pi}_\beta - \frac{\hbar^2}{8} \sum_\alpha \mu_{\alpha\alpha} + \frac{1}{2} \sum_{k=1}^{3N-6} \hat{P}_k^2 + \hat{V}, \tag{11}$$

or with the introduction of a useful notation,

$$\hat{W}_{nm} = n \cdot \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} \hat{\pi}_\alpha \hat{\pi}_\beta - m \cdot \frac{\hbar^2}{8} \sum_\alpha \mu_{\alpha\alpha} + \frac{1}{2} \sum_{k=1}^{3N-6} \hat{P}_k^2 + \hat{V}, \tag{12}$$

with n, $m = 0, 1$. In the above formulas $\hat{P}_k$ is the momentum conjugate to Q_k ($k = 1, 2, \ldots, 3N-6$), $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ are the components of the total angular momentum, and

$$\hat{\pi}_\alpha = \sum_{kl=1}^{3N-6} \zeta_{kl}^\alpha Q_k \hat{P}_l \text{ (Coriolis coupling operator)}, \tag{13}$$

$$\mu_{\alpha\beta} = (\mathbf{I}'^{-1})_{\alpha\beta} \text{ (generalized inverse inertia tensor)}, \tag{14}$$

$$I'_{\alpha\beta} = I_{\alpha\beta} - \sum_{klm=1}^{3N-6} \zeta_{km}^\alpha \zeta_{lm}^\beta Q_k Q_l, \tag{15}$$

and

$$\zeta_{kl}^\alpha = \sum_{\beta\gamma} e_{\alpha\beta\gamma} \sum_{i=1}^{N} l_{\beta ik} l_{\gamma il}, \tag{16}$$

where $e_{\alpha\beta\gamma}$ denotes the Levi-Civita symbol. The generalized inverse inertia tensor $\boldsymbol{\mu}$ in Eq. (14) can be factorized as

$$\mu_{\alpha\beta} = \sum_{\gamma\delta} (\mathbf{I}''^{-1})_{\alpha\gamma} I_{\gamma\delta}^0 (\mathbf{I}''^{-1})_{\delta\beta}, \tag{17}$$

where

$$I''_{\alpha\beta} = I_{\alpha\beta}^0 + \frac{1}{2} \sum_{k=1}^{3N-6} a_k^{\alpha\beta} Q_k, \tag{18}$$

$$a_k^{\alpha\beta} = 2 \sum_{\gamma\delta\varepsilon} e_{\alpha\gamma\varepsilon} e_{\beta\delta\varepsilon} \sum_{i=1}^{N} \sqrt{m_i} c_{\gamma i} l_{\delta ik}, \tag{19}$$

and $\mathbf{I}^0$ is the inertia tensor at the reference structure. The Jacobian[35] of the coordinate transformation from Cartesian to internal coordinates given in Eq. (7) and the Euler angles is

$$J \sim (\det \boldsymbol{\mu})^{-1/2} \sin\theta = (\det \mathbf{I}')^{1/2} \sin\theta, \tag{20}$$

and J^{-1} is involved in the operator (10), where $\det \mathbf{I}'$ stands for the determinant of the $\mathbf{I}'$ generalized inertia tensor. The volume element of the integration is

$$dV = d\phi \sin\theta d\theta d\chi dQ_1 dQ_2 \cdots dQ_{3N-6},$$

where ϕ, θ and χ are Eulerian angles with $\theta \in [0, \pi)$ and Q_k's are the vibrational coordinates. Whenever $\det \mathbf{I}'$ equals zero [or equivalently $\det \mathbf{I}'' = 0$ from the factorization given in Eq. (17)], the operator (10) [and of course (11) as well] becomes singular. In numerical studies the singularity of the operators can be remedied if it is assured that the wave function vanishes at the singular points. This can be done, for instance, by multiplying it by the square root of the Jacobian.[36]

B. Linear reference configuration

In 1970 Watson simplified Hougen's isomorphic rotation-vibration Hamilton operator[37] of molecules with lin-

ear reference configuration applying orthogonal, rectilinear internal coordinates. Let the molecule's reference configuration lie along the z axis, then

$$c_{\alpha i} = \delta_{\alpha z} c_{zi}, \quad \alpha = x, y, z, \tag{21}$$

and the form of the simplified Hamiltonian that is called the (linear) Eckart-Watson Hamiltonian[4] is

$$\hat{H}^{\mathrm{lin}} = \frac{\mu}{2}((\hat{J}_x' - \hat{\pi}_x)^2 + (\hat{J}_y' - \hat{\pi}_y)^2) + \frac{1}{2}\sum_{k=1}^{3N-5} \hat{P}_k^2 + \hat{V}. \tag{22}$$

The vibration-only part has the form

$$\hat{H}^{\mathrm{vib,lin}} = \frac{\mu}{2}(\hat{\pi}_x^2 + \hat{\pi}_y^2) + \frac{1}{2}\sum_{k=1}^{3N-5} \hat{P}_k^2 + \hat{V}, \tag{23}$$

or with the introduction of a practical notation,

$$\hat{W}_n = n \cdot \frac{\mu}{2}(\hat{\pi}_x^2 + \hat{\pi}_y^2) + \frac{1}{2}\sum_{k=1}^{3N-5} \hat{P}_k^2 + \hat{V}, \tag{24}$$

where $n = 0, 1$. In the above formulas $\hat{P}_k$ is the momentum conjugate to Q_k, $\hat{J}_x'$, and $\hat{J}_y'$ are the components of the total angular momentum, and

$$\hat{\pi}_\alpha = \sum_{kl=1}^{3N-5} \zeta_{kl}^\alpha Q_k \hat{P}_l, \quad \alpha = x, y, \tag{25}$$

$$\mu = I^0/(I'')^2, \tag{26}$$

$$I'' = I^0 + \frac{1}{2}\sum_{k=1}^{3N-5} a_k Q_k, \tag{27}$$

and

$$I^0 = \sum_{i=1}^N m_i c_{zi}^2, \quad a_k = 2\sum_{i=1}^N \sqrt{m_i} c_{zi} l_{zik}. \tag{28}$$

The Jacobian[35] of the transformation from Cartesian to orthogonal, rectilinear internal coordinates [Eq. (9)] and Euler angles is

$$J \sim 2(I'')^2 (I^0)^{-1} \sin \theta, \tag{29}$$

and

$$dV = d\phi \sin \theta d\chi dQ_1 dQ_2 \cdots dQ_{3N-5}.$$

Again, like in the case of a nonlinear reference structure, J^{-1} is involved in the operator (22), thus the Eckart-Watson Hamiltonian becomes singular whenever $I'' = 0$. This singularity can be treated if the wave function vanishes in the singular points, as was discussed in the case of a nonlinear reference geometry.

C. The potential

The kinetic energy parts of both Eckart-Watson Hamiltonians, Eqs. (10) and (22), are thus completely specified. As to the potential energy term, nowadays it is usually obtained from electronic structure computations and its accuracy is crucial from the point of view of the accuracy of the calculated (ro)vibrational energy levels. In the following, some technical aspects are considered concerning the numerical calculation of the potential energy operator's matrix elements.

The potential can be approximated by a Taylor series of normal coordinates expanded about the minimum of the PES.[8,38] The higher the order of this expansion, the higher the accuracy of the PES in the proximity of the minimum. Nevertheless, the most accurate potentials are (semi)global potentials given in a suitable set of curvilinear internal coordinates. Until now combination of the general Eckart-Watson Hamiltonians of an N-atomic molecule and such a highly accurate PES seemed to be unfeasible. The main problem was that generic PESs are unsuitable for the numerical integration schemes that have been used for determining the potential energy matrix. Here we show that arbitrary nonseparable potentials can be efficiently used with the Eckart-Watson Hamiltonians. First, one has to construct an expression for the curvilinear internal coordinates (e.g., valence coordinates) in terms of the orthogonal, rectilinear internal (e.g., normal) coordinates [Eq. (7) or (9)]. Second, the DVR of the Hamiltonian should be constructed that is clearly the most suitable choice in the present case.

IV. CURVILINEAR INTERNAL COORDINATES EXPRESSED IN TERMS OF ORTHOGONAL, RECTILINEAR INTERNAL COORDINATES

Let the bond vectors $\mathbf{r}_{pi}$ $(i, p = 1, 2, \ldots, N$ and $i \neq p)$ in a molecule with N nuclei be defined as

$$\mathbf{r}_{pi} = \mathbf{x}_i - \mathbf{x}_p. \tag{30}$$

From Eqs. (1) and (3),

$$\mathbf{r}_{pi} = (\mathbf{x}_i - \mathbf{X}) - (\mathbf{x}_p - \mathbf{X}) = \mathbf{C}(\mathbf{z}_i - \mathbf{z}_p), \tag{31}$$

and using Eqs. (7) or (9) taking into account the orthogonality conditions on $\mathbf{l}_{ik}$,[39]

$$\mathbf{r}_{pi} = \mathbf{C}\left[\mathbf{c}_i - \mathbf{c}_p + \sum_{k=1}^D \left(\frac{1}{\sqrt{m_i}}\mathbf{l}_{ik} - \frac{1}{\sqrt{m_p}}\mathbf{l}_{pk}\right)Q_k\right]. \tag{32}$$

Eq. (32) gives the bond vectors in terms of Q_k $(k = 1, 2, \ldots, D)$. In the case of nonlinear (linear) reference configuration D equals $3N-6$ $(3N-5)$ and there are three (two) independent orientational variables involved in the direction cosine matrix $\mathbf{C}$ describing the spatial orientation. Thus, curvilinear internal coordinates can easily be expressed entirely as a function of Q_k's for an arbitrary nonlinear N-atomic molecule. Note that curvilinear internal coordinates (e.g., bond lengths and angles) depend only on scalar products of bond vectors and $\mathbf{C}$ is an orthogonal matrix.

As a simple example, for the case of a triatomic molecule with 3 as the apex atom, one can write

$$r_i = \sqrt{\sum_\alpha \left[c_{\alpha i} - c_{\alpha 3} + \sum_{k=1}^D \left(\frac{1}{\sqrt{m_i}}l_{\alpha i k} - \frac{1}{\sqrt{m_3}}l_{\alpha 3 k}\right)Q_k\right]^2},$$

$$i = 1, 2, \tag{33}$$

and

$$\cos\alpha = \frac{1}{r_1 \cdot r_2}$$

$$\times \sum_\alpha \left(c_{\alpha 1} - c_{\alpha 3} + \sum_{k=1}^{D} \left(\frac{1}{\sqrt{m_1}} l_{\alpha 1k} - \frac{1}{\sqrt{m_3}} l_{\alpha 3k} \right) Q_k \right)$$

$$\times \left(c_{\alpha 2} - c_{\alpha 3} + \sum_{k=1}^{D} \left(\frac{1}{\sqrt{m_2}} l_{\alpha 2k} - \frac{1}{\sqrt{m_3}} l_{\alpha 3k} \right) Q_k \right),$$

$$\tag{34}$$

where r_1, r_2, and α denotes the two bond lengths and the bond angle, respectively, and $D=3(4)$ if the reference configuration is nonlinear (linear).

V. DISCRETE VARIABLE REPRESENTATION

As the eigenfunctions of the one-dimensional harmonic oscillator contain the normalized Hermite polynomials, $H_j(Q)$, it is a natural choice to construct the basis set from these functions in the present algorithm. Instead of the spectral functions, the Hermite-DVR basis was applied due to considerations concerning the computational efficiency pointed out later in this section.

To build the DVR representation, the coordinate matrix of dimension $N_k \times N_k$ was constructed with the elements $(\mathbf{Q}_k)_{ij} = \langle H_i(Q_k) | Q_k | H_j(Q_k) \rangle$ for each vibrational degree of freedom, $k=1,2,\ldots,D$. For the kth vibrational degree of freedom the quadrature points, q_{k,n_k}, are the eigenvalues of the kth coordinate matrix, and the Hermite-DVR basis is defined as $\mathcal{H}_{n_k}(Q_k) = \sum_{j=0}^{N_k-1} (\mathbf{T}_k)_{n_k j} H_j(Q_k)$, where columns of $\mathbf{T}_k$ are the eigenvectors of $\mathbf{Q}_k$. The Hermite-DVR direct product basis was constructed as $\{ \prod_{k=1}^{D} \mathcal{H}_{n_k}(Q_k) \}_{n_1=1,n_2=1,\ldots,n_D=1}^{N_1,N_2,\ldots,N_D}$.

As a result of this construction, the matrix of the coordinate operator is diagonal. Furthermore, applying the Gaussian quadrature approximation, the matrix representation of an operator that depends only on the coordinate operators is always diagonal and thus the matrix representation of the potential energy operator is simply

$$\langle \mathcal{H}_n | \hat{V}(\mathbf{Q}) | \mathcal{H}_m \rangle = V(q_{1,n_1}, q_{2,n_2}, \ldots, q_{D,n_D})$$

$$\times \delta_{n_1,m_1} \delta_{n_2,m_2} \cdot \ldots \cdot \delta_{n_D,m_D}, \tag{35}$$

where $\mathcal{H}_n = \mathcal{H}_{n_1}(Q_1)\mathcal{H}_{n_2}(Q_2) \cdot \ldots \cdot \mathcal{H}_{n_D}(Q_D)$ and n, the index of the product function, is unambiguously expressed in terms of the $n_1, n_2, \ldots, n_D$ indices (see Appendix for details). Similarly, the matrix elements of the generalized inverse inertia tensor are obtained as

$$\langle \mathcal{H}_n | \mu_{\alpha\beta}(\mathbf{Q}) | \mathcal{H}_m \rangle = \mu_{\alpha\beta}(q_{1,n_1}, q_{2,n_2}, \ldots, q_{D,n_D})$$

$$\times \delta_{n_1,m_1} \delta_{n_2,m_2} \cdot \ldots \cdot \delta_{n_D,m_D}, \tag{36}$$

where $\mu_{\alpha\beta}(q_{1,n_1}, q_{2,n_2}, \ldots, q_{D,n_D})$ is constructed using Eq. (17) with the analytical inversion of the $\mathbf{I}''(q_{1,n_1}, q_{2,n_2}, \ldots, q_{D,n_D}) \in \mathbb{R}^{3\times 3}$ matrix introduced in Eq. (18). Thus, the extrapotential term, in the case of a nonlinear reference geometry, can be simply calculated from Eq. (36) and its determination has only a negligible computational cost.

The differential operator needed in the term $(1/2)\Sigma_k \hat{P}_k^2$ can straightforwardly be computed using exact analytical formulae.[40]

Computationally, the most demanding parts of the vibrational Eckart-Watson Hamiltonians, Eqs. (11) and (23), are the terms containing the Coriolis coupling operators. The matrix representation of these terms can be constructed in at least two ways. According to the first route, the commutation relations,[3] for the case of a nonlinear reference structure $\Sigma_\alpha [\mu_{\alpha\beta}, \hat{\pi}_\alpha] = 0$ ($\alpha=x,y,z$), are applied, resulting in

$$\frac{1}{2}\sum_{\alpha\beta} \hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta = \frac{1}{4}\sum_{\alpha\beta} (\mu_{\alpha\beta}\hat{\pi}_\alpha\hat{\pi}_\beta + \hat{\pi}_\alpha\hat{\pi}_\beta\mu_{\alpha\beta}). \tag{37}$$

Then, the truncated resolution of identity in the applied basis is inserted between $\mu_{\alpha\beta}$ and $\hat{\pi}_\alpha$ in the first term, and between $\hat{\pi}_\beta$ and $\mu_{\alpha\beta}$ in the second term on the right hand side of Eq. (37). Applying the diagonal matrix representation of $\mu_{\alpha\beta}$, a matrix element in the nth row and mth column can be calculated as

$$\left\langle \mathcal{H}_n \left| \frac{1}{2}\sum_{\alpha\beta} \hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta \right| \mathcal{H}_m \right\rangle$$

$$= \sum_{\alpha\beta} \frac{(\boldsymbol{\mu}_{\alpha\beta})_{nn} + (\boldsymbol{\mu}_{\alpha\beta})_{mm}}{4} (\boldsymbol{\pi}_\alpha\boldsymbol{\pi}_\beta)_{nm}, \tag{38}$$

where in the $\hat{\pi}_\alpha\hat{\pi}_\beta$ product Q_k-, $\partial/\partial Q_k$-, Q_k^2-, $Q_k\partial/\partial Q_k$-, and $\partial^2/\partial Q_k^2$-type operators are present, whose matrix representations are calculated analytically based on Ref. 40, and the use of the commutation relations ensures that the constructed matrix is symmetric.

The second route uses the form given on the left hand side of Eq. (37) and inserts the truncated resolution of identity twice, both from the left and the right of $\mu_{\alpha\beta}$. Again, applying the fact that the matrix representation of $\mu_{\alpha\beta}$ is diagonal, the matrix element in the nth row and mth column is

$$\left\langle \mathcal{H}_n \left| \frac{1}{2}\sum_{\alpha\beta} \hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta \right| \mathcal{H}_m \right\rangle$$

$$= \frac{1}{2}\sum_{\alpha\beta} \sum_{p=1}^{\mathcal{N}} (\boldsymbol{\pi}_\alpha)_{np} (\boldsymbol{\mu}_{\alpha\beta})_{pp} (\boldsymbol{\pi}_\beta)_{pm}, \tag{39}$$

where $\mathcal{N} = N_1 \cdot N_2 \cdots N_D$. Considering the special structure of the matrix of $\hat{\pi}_\alpha$, the matrix elements given in Eq. (39) can be calculated without explicitly carrying out the summation over all the grid points in the computer code. The matrix representation of the terms Q_k and $\partial/\partial Q_k$ appearing in the $\hat{\pi}_\alpha$ Coriolis coupling operator can again be calculated analytically.[40] Explicit DVR formulae for an efficient calculation of $\hat{\pi}_\alpha\mu_{\alpha\beta}\hat{\pi}_\beta$ are given in the Appendix.

Similar considerations about the structure of the matrix representations stand for the case of a linear reference geometry. In this case, however, the generalized inertia tensor is a scalar and commutes with the Coriolis coupling operator, $[\hat{\pi}_\alpha, I''] = 0$.[4] Thus, according to the first approach the elements are calculated as

$$\left\langle \mathcal{H}_n \left| \frac{\mu}{2}(\hat{\pi}_x^2 + \hat{\pi}_y^2) \right| \mathcal{H}_m \right\rangle = \frac{\boldsymbol{\mu}_{nn} + \boldsymbol{\mu}_{mm}}{2}((\boldsymbol{\pi}_x^2)_{nm} + (\boldsymbol{\pi}_y^2)_{nm}),$$

(40)

where the use of the commutation relations guarantees the symmetry of the constructed matrix. In contrast to this, if the second strategy is followed than the corresponding element can be calculated as

$$\left\langle \mathcal{H}_n \left| \frac{\mu}{2}(\hat{\pi}_x^2 + \hat{\pi}_y^2) \right| \mathcal{H}_m \right\rangle = \frac{1}{2}\sum_{p=1}^{\mathcal{N}} \boldsymbol{\mu}_{pp}((\boldsymbol{\pi}_x)_{np}(\boldsymbol{\pi}_x)_{pm}$$

$$+ (\boldsymbol{\pi}_y)_{np}(\boldsymbol{\pi}_y)_{pm}),$$ (41)

where, again, $\mathcal{N} = N_1 \cdot N_2 \ldots N_D$, and the special structure of the matrix of $\hat{\pi}_\alpha$ can be used to efficiently execute the summation.

In spite of the fact that the first approach calculates the matrix elements of the $\hat{\pi}_\alpha \hat{\pi}_\beta$ operator exactly, it is the second route that should be favored as it results in a sparser matrix. If the number of basis functions is N for all of the D dimensions, then $\mathcal{N} = N^D$, and the number of the nonzero elements in the matrix is at maximum $\mathcal{N}\Sigma_{k=0}^3 \binom{D}{k}(N-1)^k \sim \mathcal{O}(\mathcal{N}^{1+3/D})$ according to the first approach, whereas it reduces to $\mathcal{N}\Sigma_{k=0}^2 \binom{D}{k}(N-1)^k \sim \mathcal{O}(\mathcal{N}^{1+2/D})$ in the second case. The slower convergence of the second method due to the insertion of two truncated resolutions of identity instead of one might need to be considered only if the first few eigenvalues are to be calculated applying a small basis set. This situation will be encountered in practice, for instance, when larger molecular systems are treated.

Next, it is worth mentioning that if the terms containing the Coriolis coupling operators are left out from the Eckart-Watson Hamiltonian, see $\hat{W}_{00}$, $\hat{W}_{01}$, and $\hat{W}_0$ defined in Eqs. (12) and (24), respectively, then the number of the nonzero elements is only $\mathcal{N}\Sigma_{k=0}^1 \binom{D}{k}(N-1)^k \sim \mathcal{O}(\mathcal{N}^{1+1/D})$. When the dimensionality of the problem is low (e.g., $D=3$ for a triatomic molecule with a nonlinear reference configuration), the number of nonzero elements in the matrix representation of the operator missing the Coriolis terms is drastically lower then that of the complete Eckart-Watson Hamiltonian. In contrast to this, as the dimension of the problem increases, the difference between the number of nonzero elements in the two cases, $\mathcal{O}(\mathcal{N}^{1+1/D})$ as compared to $\mathcal{O}(\mathcal{N}^{1+2/D})$ or $\mathcal{O}(\mathcal{N}^{1+3/D})$, becomes less significant.

In DVR the matrix of the potential energy operator is always diagonal, and the kinetic energy matrix has a highly special structure. The special structure of the matrix of the full Eckart-Watson Hamiltonian, $\hat{W}_{11}$, and that of the incomplete operators, $\hat{W}_{00}$, $\hat{W}_{01}$, and $\hat{W}_{10}$ introduced in Eq. (12), obtained when the second strategy was applied is presented in Fig. 1 for the case of three vibrational degrees of freedom. The Eckart-Watson Hamiltonian matrices get sparser as the number of vibrational degrees of freedom increases. The required eigenvalues and eigenfunctions of the matrix of the Eckart-Watson Hamiltonian constructed can be efficiently determined with an iterative algorithm, such as the Lanczos technique.[27] In contrast to this, in FBR the structure of the matrix of the potential energy operator would depend on the
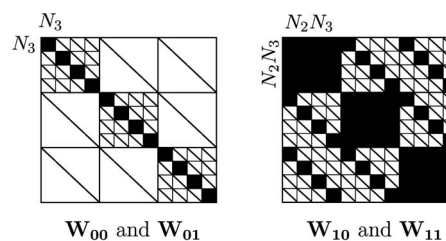

FIG. 1. Pictorial representation of the nonzero elements of the matrices of the $\hat{W}_{00}$, $\hat{W}_{01}$, $\hat{W}_{10}$, and $\hat{W}_{11}$ operators in the case of three vibrational degrees of freedom with the number of basis functions $N_1=3$ and $N_2=4$ while N_3 is the dimension of the small black blocks.

actual potential and, for instance, in the case of a global PES it would result in a full matrix, that obviously would make the diagonalization part of the algorithm prohibitively expensive.

VI. TEST MOLECULES WITH NONLINEAR REFERENCE CONFIGURATIONS

The vibrational part of the Eckart-Watson Hamiltonian corresponding to a nonlinear reference structure, Eq. (11), was applied for the case of $H_2^{16}O$ with the so-called CVRQD PES,[23] for H_3^+ with the PES published in Ref. 28, and for $^{12}CH_4$ with the T8 force field[31] within the present DEWE algorithm. The H_3^+ system is not a typical molecule fitting in the traditional normal coordinate picture; nevertheless, a convenient set of Q_k's defined in Eq. (7) can be built. Elements of l_{ik} introduced in Eq. (6) were generated with INTDER2000.[41] As a matter of fact, a normal coordinate analysis was carried out with some reliable, user supplied force constants (not necessarily those of the actual potential), as a result of which l_{ik} coefficients were obtained meeting the orthogonality and Eckart conditions formulated in Eq. (8) with the actual masses and the chosen reference configuration. The reference configuration is not necessarily the equilibrium one. As to its actual choice significant tolerance was observed in the convergence rate of the eigenvalues, given that the reference structure is reasonable. These coefficients were applied in the DEWE calculations and their actual values affected only the rate of convergence.

As the potential expressed in curvilinear internal coordinates is exactly included in the DEWE nuclear motion treatment, the resulting eigenvalues can be directly compared with the results obtained from traditional treatments, like the DOPI [DVR (D)–Hamiltonian in orthogonal (O) coordinates–direct product (P) basis–iterative (I) diagonalization,[22] where the Sutcliffe-Tennyson curvilinear internal coordinate Hamiltonian[7] of triatomic species is applied] scheme. The results obtained are given in Tables I–III for $H_2^{16}O$, H_3^+, and $^{12}CH_4$, respectively.

The influence of each term in the kinetic energy part of the Eckart-Watson Hamiltonian, Eq. (12), on the calculated energy levels was also studied in detail. Results obtained with the three incomplete $\hat{W}_{00}$, $\hat{W}_{01}$, and $\hat{W}_{10}$ operators, as well as with the complete Eckart-Watson Hamiltonian, $\hat{W}_{11} = \hat{H}^{vib}$, are presented and discussed.

TABLE I. Zero-point energy and vibrational band origins of $H_2{}^{16}O$, in cm^{-1}, obtained with the CVRQD PES of Ref. 23.

$(v_1 v_2 v_3)$	$\hat{W}_{00}$[a]	$\hat{W}_{01}$[a]	$\hat{W}_{10}$[a]	$\hat{W}_{11}$[a]	DOPI[b]
(0 0 0)	4649.22 (−10.92)	4636.30 (2.01)	4651.23 (−12.92)	4638.31 (0.00)	4638.31
(0 1 0)	1582.46 (12.61)	1581.58 (13.49)	1595.94 (−0.87)	1595.08 (0.00)	1595.08
(0 2 0)	3126.70 (25.49)	3124.64 (27.56)	3154.22 (−2.02)	3152.20 (0.00)	3152.20
(1 0 0)	3656.95 (0.10)	3657.23 (−0.18)	3656.77 (0.28)	3657.05 (0.00)	3657.05
(0 0 1)	3742.57 (13.16)	3742.98 (12.75)	3755.32 (0.41)	3755.73 (0.00)	3755.73
(0 3 0)	4628.80 (38.77)	4625.02 (42.56)	4671.26 (−3.68)	4667.57 (0.00)	4667.57
(1 1 0)	5223.39 (12.11)	5222.82 (12.67)	5236.05 (−0.55)	5235.49 (0.00)	5235.49
(0 1 1)	5281.31 (50.20)	5280.90 (50.61)	5331.88 (−0.37)	5331.51 (0.00)	5331.51
(0 4 0)	6082.54 (52.54)	6075.94[c] (59.14)	6141.44 (−6.36)	6135.10[c] (−0.02)	6135.08
(1 2 0)	6751.56 (24.41)	6749.85 (26.11)	6777.63 (−1.66)	6775.97 (0.00)	6775.96
(0 2 1)	6783.89 (88.26)	6782.41 (89.74)	6873.53 (−1.38)	6872.15 (0.00)	6872.15
(2 0 0)	7198.09 (3.10)	7198.68 (2.52)	7200.62 (0.57)	7201.19 (0.00)	7201.19
(1 0 1)	7236.32 (12.90)	7236.99 (12.23)	7248.55 (0.67)	7249.22 (0.00)	7249.22
(0 0 2)	7421.10 (23.78)	7421.86 (23.02)	7444.12 (0.76)	7444.88 (0.00)	7444.88
(0 5 0)	7477.38[d] (66.48)	7465.40[c] (78.46)	7555.48[d] (−11.62)	7544.19[c] (−0.33)	7543.86
(1 3 0)	8237.86 (37.22)	8234.43[c] (40.65)	8278.39 (−3.31)	8275.10[c] (−0.01)	8275.08
(0 3 1)	8246.69 (128.08)	8243.69 (131.08)	8377.55 (−2.78)	8374.77 (0.00)	8374.77
(2 1 0)	8739.73 (22.19)	8739.45 (22.47)	8762.14 (−0.22)	8761.92 (0.00)	8761.92
(1 1 1)	8758.87 (48.16)	8758.77 (48.26)	8807.10 (−0.07)	8807.03 (0.00)	8807.03
(0 6 0)	8792.77[d] (79.40)	8771.13[c] (101.04)	8896.06[d] (−23.89)	8875.62[c] (−3.45)	8872.17
(0 1 2)	8925.07 (75.32)	8925.06 (75.33)	9000.34 (0.05)	9000.40 (0.00)	9000.39

[a]Results obtained with the DEWE algorithm applying the operator $\hat{W}_{nm} = n \cdot (1/2)\Sigma_{\alpha\beta}\mu_{\alpha\beta}\hat{\pi}_\alpha\hat{\pi}_\beta - m \cdot (\hbar^2/8)\Sigma_\alpha\mu_{\alpha\alpha} + (1/2)\Sigma_{k=1}^{3N-6}\hat{P}_k^2 + V^{CVRQD}$. Deviations from the DOPI results ($DOPI - \hat{W}_{nm}$) are given in parentheses. The reference geometry chosen was $r_{OH} = 1.810\,081\,2$ bohr and $\alpha(HOH) = 104.500\,00°$, and nuclear masses $m_H = 1.007\,276\,5$ u and $m_O = 15.990\,526$ u were used throughout the calculations. The number of basis functions applied for the vibrational degrees of freedom was (20,20,20).

[b]Converged results obtained with the DOPI algorithm (Ref. 22). Exactly the same CVRQD PES and nuclear masses were applied as in the DEWE calculations.

[c]Digits underlined did not converge upon the increase of the basis size due to the singularity present in the operators $\hat{W}_{01}$ and $\hat{W}_{11}$.

[d]Eigenvalues with low convergence rate. The digits underlined did not converge tightly with the applied (20,20,20) basis set. The convergence was tested with larger basis sets. Applying $\hat{W}_{00}$ with (25,25,25) and (30,30,30) basis sets the eigenvalues are 7477.37 and 7477.35 cm^{-1} for the (0 5 0) level and 8791.98 and 8792.27 cm^{-1} for the (0 6 0) level, respectively. Applying $\hat{W}_{10}$, the eigenvalues for the (25,25,25) and (30,30,30) basis sets are 7555.47 and 7555.47 cm^{-1} for the (0 5 0) level, and 8895.73 and 8896.01 cm^{-1} for the (0 6 0) level, respectively.

TABLE II. Zero-point energy and vibrational band origins of H_3^+, in cm^{-1}, obtained with the PES of Ref. 28.

Symmetry	$\hat{W}_{00}$[a]	$\hat{W}_{01}$[a]	$\hat{W}_{10}$[a]	$\hat{W}_{11}$[a]	DOPI[b]
A_1	4388.84 (−26.54)	4361.91 (0.39)	4389.23 (−26.93)	4362.30 (0.00)	4362.30
E	2498.82 (22.37)	2498.72 (22.47)	2521.27 (−0.08)	2521.19 (0.00)	2521.19
E	2498.82 (22.37)	2498.72 (22.47)	2521.27 (−0.08)	2521.19 (0.00)	2521.19
A_1	3178.31 (0.89)	3178.97 (0.23)	3178.53 (0.67)	3179.20 (0.00)	3179.20
A_1	4753.85 (23.78)	4752.89 (24.74)	4778.50 (−0.87)	4777.63 (0.00)	4777.63
E	4923.08 (74.52)	4922.81 (74.79)	4997.83 (−0.23)	4997.60 (0.00)	4997.60
E	4923.08 (74.52)	4922.81 (74.79)	4997.83 (−0.23)	4997.60 (0.00)	4997.60
E	5530.34 (24.48)	5530.86 (23.96)	5554.27 (0.55)	5554.82 (0.00)	5554.82
E	5530.34 (24.48)	5530.86 (23.96)	5554.27 (0.55)	5554.82 (0.00)	5554.82
A_1	6261.82 (2.03)	6263.11 (0.74)	6262.56 (1.29)	6263.85 (0.00)	6263.85
E	6939.94 (65.06)	6937.77 (67.23)	7006.96 (−1.96)	7005.00 (0.00)	7005.00
E	6939.97[c] (65.03)	6937.80[c] (67.20)	7006.98[c] (−1.98)	7005.02[c] (−0.02)	7005.00
A_1	7181.50[c] (103.10)	7179.96[c] (104.64)	7286.19[c] (−1.59)	7284.62[c] (−0.02)	7284.60
A_2	7319.43 (173.10)	7319.43 (173.10)	7492.42 (0.11)	7492.53 (0.00)	7492.53

[a]Results obtained with the DEWE algorithm applying the operator $\hat{W}_{nm} = n \cdot (1/2)\Sigma_{\alpha\beta}\mu_{\alpha\beta}\hat{\pi}_\alpha\hat{\pi}_\beta - m \cdot (\hbar^2/8)\Sigma_\alpha\mu_{\alpha\alpha} + (1/2)\Sigma_{k=1}^{3N-6}\hat{P}_k^2 + \hat{V}$. Deviations from the DOPI results ($DOPI - \hat{W}_{nm}$) are given in parentheses. The reference configuration chosen was $r_{HH} = 1.649\,990\,0$ bohr with the hydrogens on the apices of an equilateral triangle, and $m_H = 1.007\,537\,2$ u. The number of basis functions applied was (19,19,19).

[b]Converged results obtained with the DOPI algorithm (Ref. 22). Exactly the same PES and nuclear masses were applied as in the DEWE calculations.

[c]The digits underlined did not converge to 0.01 cm^{-1} with the present basis due to the singularity present in the operator(s). Except for $\hat{W}_{00}$, the results became divergent with increase in basis size, for $\hat{W}_{00}$ the converged values of the two levels in question are 6939.94 and 7181.48, respectively.

TABLE III. Zero-point energy and vibrational band origins of $^{12}CH_4$, in cm^{-1}, referenced to the zero-point energy, obtained with the T8 force field of Ref. [31].

$(n_1n_3)(n_2n_4)$sym	$\hat{W}_{00}$[a,b]	$\hat{W}_{01}$[a,b]	$\hat{W}_{10}$[a,b]	$\hat{W}_{11}$[a,c]	Ref. [43]
(00)(00)A1	9690.9 (0.6)	9686.9 (4.6)	9695.4 (−3.9)	9691.5 (0.0)	9691.5
(00)(01)F2	1299.9 (11.6)	1299.9 (11.6)	1311.6 (−0.1)	1311.5 (0.2)	1311.7
	1300.0 (11.7)	1300.0 (11.7)	1311.7 (0.0)	1311.7 (0.0)	1311.7
	1300.1 (11.6)	1300.1 (11.6)	1311.7 (0.0)	1311.7 (0.0)	1311.7
(00)(10)E	1524.2 (9.0)	1524.2 (9.0)	1533.2 (0.0)	1533.2 (0.1)	1533.3
	1524.2 (9.1)	1524.2 (9.1)	1533.3 (0.0)	1533.3 (0.0)	1533.3

[a]Results obtained with the DEWE algorithm applying the operator $\hat{W}_{nm} = n \cdot (1/2)\Sigma_{\alpha\beta}\mu_{\alpha\beta}\hat{\pi}_\alpha\hat{\pi}_\beta - m \cdot (\hbar^2/8)\Sigma_\alpha\mu_{\alpha\alpha} + (1/2)\Sigma_{k=1}^{3N-6}\hat{P}_k^2 + V^{T8}$. The reference geometry was a regular tetrahedron with the hydrogens on the apices and the carbon in the middle with $r_{CH}=2.057\,910$ bohr, and nuclear masses $m_H=1.007\,276$ u and $m_C=11.996\,709$ u were used throughout the calculations. $\mathbf{l}_{ik}$ coefficients were obtained with INTDER2000 applying the diagonal, second order force constants from Ref. [46]. For each of the nine vibrational degrees of freedom five basis functions were applied.
[b]Deviations from the results obtained with the complete $\hat{W}_{11}$ operator ($\hat{W}_{11} - \hat{W}_{nm}$) are given in parentheses.
[c]Deviations from the results presented in Ref. [43] [(Ref. [43]) $-\hat{W}_{11}$] are given in parentheses. Note that using six basis functions for each vibrational degrees of freedom results in 0.0 deviations.

A. H₂O

The case of the $H_2^{16}O$ isotopologue was studied with the full high-accuracy semiglobal CVRQD PES.[23] The CVRQD PES expressed in bond lengths and angles was involved in DEWE via Eq. (33) and (34). Energy levels obtained with the DEWE and DOPI approaches are in full agreement except for the higher bending levels. On one hand, it is difficult to converge large amplitude vibrational motions within the applied set of coordinates, and on the other hand in the large-amplitude bending motion the singular region of the operator is sampled. If the instantaneous configuration is linear, det $\mathbf{I}''$ and thus the Jacobian becomes zero [see Eq. (20)], and the Eckart-Watson Hamiltonian becomes singular. Consequently, levels that significantly sample linear configurations cannot be converged within the present approach; however, the singularity of the Eckart-Watson Hamiltonian could in principle be treated.[36]

When $\hat{W}_{01}$ or $\hat{W}_{11}$ were applied, "ghost levels" appeared amongst the obtained eigenvalues. They appear irregularly upon the increase of the basis size, but do not affect the numerical values of the "true" levels, at least up to the applied basis size. Such ghost levels do not converge and originate from the singularities of the $\hat{W}_{01}$, and $\hat{W}_{11}$, operators that is carried by the second (often called extrapotential) term in Eq. (12).[36] It is worth emphasizing that $\hat{W}_{00}$ and in this case $\hat{W}_{10}$ are free of singularities.

As to the utility of results obtained with incomplete operators, $\hat{W}_{00}$ provides a relatively inaccurate approximation to the exact vibrational band origins (VBOs). The $\hat{W}_{01}$ operator approximates well the zero-point energy (ZPE), whereas all the higher levels fail significantly. $\hat{W}_{10}$ gives relatively good values referenced to the ZPE, but the ZPE itself has a significant error. As a rule of thumb, it is expected that the effect of the first and the second terms in Eq. (12) scale with the rotational constants (that can be approximated by the equilibrium ones if a reference configuration close to the equilibrium is applied). Indeed, the large rotational constants characterizing the equilibrium structure of $H_2^{16}O$ are in line with the poor agreement between the exact vibrational energy levels and those obtained with the incomplete operators.

B. H₃⁺

The molecular ion H_3^+ was studied with the global PES published in Ref. [28]. This PES expressed in Jacobi coordinates was involved in DEWE by an exact expression of the Jacobi coordinates in terms of rectilinear internal (e.g., normal) coordinates, via the scalar products of the bond vectors, Eq. (32).

For the VBOs presented in Table II there is nice agreement between the DEWE and DOPI results; however, this case is not trouble-free either. Ghost levels appear amongst the true energy levels when the $\hat{W}_{01}$, $\hat{W}_{10}$, and $\hat{W}_{11}$ operators are applied. The ghost levels do not converge and they do not affect the values of the true levels up to an optimal basis size. This behavior can be explained by the singularity of these operators. It is important to note that the ghost levels do not converge, thus they can easily be filtered out.

As to the incomplete operators, $\hat{W}_{00}$ is expected to yield unreliable results for this system. Indeed, its use results in really bad approximations to the energy levels of H_3^+. Inclusion of the extrapotential term in $\hat{W}_{01}$ results in an excellent ZPE, but to obtain reliable energies referenced to the ZPE the use of $\hat{W}_{10}$ is required. Similarly to the case of $H_2^{16}O$, $\hat{W}_{10}$ fails for the ZPE itself.

C. CH₄

The first few vibrational band origins of $^{12}CH_4$ were calculated with DEWE applying the T8 eighth-order force field[31] approximation of the PES of the ground electronic state of CH_4 expressed in five-atomic Radau coordinates.[42] The T8 PES was used in DEWE by an exact expression of the five-atomic Radau coordinates in terms of rectilinear internal (e.g., normal) coordinates, via the scalar products of the bond vectors, see Eq. (32).

Results obtained with DEWE applying a DVR basis with 5 grid points on each vibrational degrees of freedom are presented in Table III. For purposes of comparison the converged results of Ref. [43] obtained with a (curvilinear) internal coordinate Hamiltonian are employed. The lowest six VBOs obtained with DEWE are converged within 0.06 cm^{-1} on average.

TABLE IV. Zero-point energy and (ro)vibrational band origins of $^{12}C^{16}O_2$, in cm^{-1}, obtained with Chédin's sextic force field. (Ref. 29). [In the potential an energy cutoff of $\varepsilon = 20\,000$ cm^{-1} had to be applied, as described in Ref. 22(a)].

$(v_1\ v_b^{|l|}\ v_3)$	$\hat{W}_0$ [a,b]	$\hat{W}_1$ [a,c]	DOPI [d]				
			$J=0$	$J=1$	$J=2$	$J=3$	$J=4$
$(0\ 0^0\ 0)$	2535.09(0.36)	2535.45(0.00)	2535.45	0.78	2.34	4.68	7.80
$(0\ 1^1\ 0)$	666.94(0.74)	667.68(0.39)		668.07	1.57	3.91	7.04
$(0\ 1^1\ 0)$	666.94(0.74)	667.68(0.39)		668.07	1.56	3.90	7.03
$(1\ 0^0\ 0)$	1284.17(0.81)	1284.98(0.00)	1284.98	0.78	2.34	4.69	7.81
$(0\ 2^2\ 0)$	1335.01(1.48)	1336.48(0.78)			1337.27	2.35	5.48
$(0\ 2^2\ 0)$	1335.01(1.48)	1336.48(0.78)			1337.27	2.35	5.48
$(0\ 2^0\ 0)$	1386.82(0.64)	1387.46(0.00)	1387.46	0.78	2.34	4.68	7.80
$(1\ 1^1\ 0)$	1930.82(1.55)	1932.37(0.39)		1932.76	1.57	3.92	7.05
$(1\ 1^1\ 0)$	1930.82(1.55)	1932.37(0.39)		1932.76	1.56	3.91	7.03
$(0\ 3^3\ 0)$	2004.23(2.20)	2006.43(1.17)				2007.61	3.14
$(0\ 3^3\ 0)$	2004.23(2.20)	2006.43(1.17)				2007.61	3.14
$(0\ 3^1\ 0)$	2074.91(1.35)	2076.27(0.39)		2076.66	1.57	3.91	7.05
$(0\ 3^1\ 0)$	2074.91(1.35)	2076.27(0.39)		2076.66	1.56	3.90	7.03
$(0\ 0^0\ 1)$	2345.83(1.49)	2347.32(0.00)	2347.32	0.77	2.32	4.64	7.74
$(2\ 0^0\ 0)$	2545.80(1.81)	2547.62(0.00)	2547.62	0.78	2.35	4.69	7.82
$(1\ 2^2\ 0)$	2583.74(2.28)	2586.02(0.78)			2586.81	2.35	5.49
$(1\ 2^2\ 0)$	2583.74(2.28)	2586.02(0.78)			2586.81	2.35	5.49
$(1\ 2^0\ 0)$	2668.48(0.95)	2669.43(0.00)	2669.43	0.78	2.34	4.67	7.79
$(0\ 4^4\ 0)$	2674.60(2.93)	2677.53(1.57)					2679.10
$(0\ 4^4\ 0)$	2674.60(2.93)	2677.53(1.57)					2679.10
$(0\ 4^2\ 0)$	2758.96(2.06)	2761.02(0.78)			2761.80	2.35	5.48
$(0\ 4^2\ 0)$	2758.96(2.06)	2761.02(0.78)			2761.80	2.35	5.48
$(0\ 4^0\ 0)$	2793.76(1.53)	2795.30(0.00)	2795.30	0.78	2.34	4.69	7.81

[a]Results obtained with the DEWE algorithm applying the operator $\hat{W}_n = n \cdot (\mu/2)(\hat{\pi}_x^2 + \hat{\pi}_y^2) + (1/2)\Sigma_{k=1}^{3N-5}\hat{P}_k^2 + \hat{V}^{\text{Chédin6}}$. The reference geometry was linear with an $r_{CO} = 2.192\,080\,0$ bohr bond length. Atomic masses $m_C = 12.000\,000$ u, and $m_O = 15.994\,910$ u were used throughout the calculations. The number of basis functions applied for the vibrational degrees of freedom was (16,16,16,16).

[b]Deviations from the results obtained with the complete $\hat{W}_1$ operator ($\hat{W}_1 - \hat{W}_0$) are given in parentheses.

[c]Deviations from the DOPI results with the lowest possible J value of that level [$\text{DOPI}(J_{\min}) - \hat{W}_1$] are given in parentheses.

[d]Converged results obtained with the DOPI algorithm (Ref. 22). Exactly the same potential and atomic masses were applied as in the calculations with DEWE. Rovibrational energy levels are referenced to the corresponding rovibrational level with the lowest possible J.

As to the applicability of the incomplete $\hat{W}_{00}$, $\hat{W}_{01}$, and $\hat{W}_{10}$ operators, with the $\hat{W}_{00}$ and $\hat{W}_{01}$ operators the VBOs referenced to the ZPE fail significantly, in line with the relatively large rotational constant of methane. $\hat{W}_{10}$ approximates well the first few eigenvalues referenced to the ZPE, which means that the extrapotential term, $-(\hbar^2/2)\Sigma_\alpha \mu_{\alpha\alpha}$, has a nearly constant contribution to the eigenenergies. However, there is not much merit to approximate the "exact" eigenenergies with those of $\hat{W}_{10}$, as it contains the most expensive part, $(1/2)\Sigma_{\alpha\beta}\hat{\pi}_\alpha \mu_{\alpha\beta}\hat{\pi}_\beta$, of the complete $\hat{W}_{11}$ operator.

At this point it is appropriate to make some technical remarks concerning the calculations applying the complete $\hat{W}_{11}$ operator. In the five-atomic case ($D=9$) it is necessary to calculate the Hamiltonian matrix-vector multiplications needed in the Lanczos iterative eigensolver without explicitly storing the (nonzero) elements of the Hamiltonian matrix in the main memory. This on-the-fly matrix-vector multiplication was parallelized in an elementary way (with OpenMP), and the longest calculation employing a Hamiltonian of size $1.95 \cdot 10^6 \times 1.95 \cdot 10^6$ with $1.20 \cdot 10^9$ nonzero elements terminated in less than one day. An even more efficient programming of the matrix-vector multiplication part

of the code DEWE must be found in order to apply it for even larger systems while keep working on an ordinary personal computer.

VII. TEST MOLECULES WITH LINEAR REFERENCE CONFIGURATIONS

The vibrational part of the linear Eckart-Watson Hamiltonian, Eq. (23), was applied for the case of CO_2 with Chédin's sextic force field[29] and for the HCN/HNC system with the semiglobal so-called VQZANO+ PES.[30] The l_{ik} coefficients were generated with INTDER2000 (Ref. 41) in a normal coordinate analysis to obtain coefficients that fulfill the requirements, analogous to those formulated in Eq. (8) for the nonlinear case, with the actual set of masses and the chosen linear reference configuration. Similar to the nonlinear case, the user supplied force constants in the normal coordinate analysis do not necessarily have to be those of the actual potential, and the reference configuration can be a reasonable linear structure different from the equilibrium structure.

The effects of kinetic energy terms in the Eckart-Watson Hamiltonian of linear configuration were studied on the obtained energy levels, and the notation introduced in Eq. (24) was applied.

A. CO$_2$

For the case of CO$_2$ all the energy levels obtained with Chédin's sextic force field[29] are given in Table IV up to the fourth bending level. Results of the present DEWE algorithm are compared with those obtained using DOPI.[22] Again, a direct comparison can be made as in both cases the same potential is involved.

VBOs corresponding to $l=0$ (where l is the quantum number of the total vibrational angular momentum about the linear axis, $l=-v_b, -v_b+2,\ldots, v_b-2, v_b$, and v_b is the number of quanta of the linear bending[44]) obtained with the DEWE and DOPI approaches are the same within numerical accuracy. Besides these energy levels further ones can be obtained in a DEWE vibrational calculation which are "missing" from a DOPI calculation for $J=0$ (where J stands for the quantum number of the total angular momentum). These new levels do not correspond, however, to physically existing ones as the Sayvetz condition[45] requires $(\hat{J}_z - \hat{\pi}_z)\Psi = 0$. In spite of this, they can be paired with existing (ro)vibrational levels with $l \neq 0$, and these "nonphysical" VBOs could be interpreted as the vibration-only part of the whole rovibrational energy of a level with v_b bending quanta ($l \neq 0$). The true rovibrational levels can be obtained with DOPI-type rovibrational calculations for $J=|l|$, as presented in Table IV.

Vibrational perturbation theory yields compact formulae for the rovibrational energy,

$$E_{rotvib} = E_{vib}(v_1, v_b, v_3) + E_{rot}, \tag{42}$$

$$E_{rot} = B_v[J(J+1) - l^2] - D_J[J(J+1) - l^2]^2 + H_J[J(J+1) - l^2]^3 + \cdots, \tag{43}$$

$$J = |l|, |l|+1, |l|+2, \ldots,$$

and if $J = |l|$,

$$E_{rot} \approx B_e|l|, \tag{44}$$

where $B_v, D_J, H_J, \ldots$ are, in order, the rotational constant, the quartic centrifugal distortion constant, the sextic centrifugal distortion constant, etc., discussed in detail in, for example, Ref. 47, and B_e denotes the rotational constant in the equilibrium geometry. Equation (44) gives an approximation of the "rotational contribution" to the lowest rovibrational level with a given (v_1, v_b, v_3) set of vibrational quanta (stretching, linear bending, and stretching quantum numbers, respectively).

On the basis of Eq. (43), levels with $l=0$ have zero rotational contribution and these are the only ones that are obtained exactly with the vibration-only Eckart-Watson Hamiltonian, Eq. (23). If $l \neq 0$, the vibration-only DEWE approach delivers nonphysical vibration-only energies that differ from the corresponding physically correct rovibrational values by approximately $B_e|l|$ (for $^{12}C^{16}O_2$, $B_e \approx 0.39$ cm^{-1}), given that the reference configuration applied in the DEWE calculation is close to the equilibrium structure.

Concerning the incomplete operator, the use of $\hat{W}_0$ results in good approximations, the $\hat{W}_0$ eigenvalues are within 1–2 cm^{-1} of the exact VBOs, at least for the lower (ro)vibrational levels. This is in line with the relatively small rotational constant of $^{12}C^{16}O_2$ at its equilibrium structure.

B. HCN and HNC

Rearrangement of two chemically stable isomers built up from the [H,C,N] set of atoms, HCN and HNC, corresponds to a large amplitude molecular motion. Conveniently chosen internal coordinates, most importantly the orthogonal Jacobi coordinates, describe efficiently this motion and VBOs can be obtained within a single calculation for both the HCN and HNC forms.[30]

The present normal coordinate treatment seems to be unable to efficiently account for this large amplitude motion and give the vibrational levels of HCN and HNC within a single calculation. However, with the adequate choice of the reference configuration, VBOs corresponding to the chosen configuration can be obtained. In Table V the first few vibrational energy levels ($l=0$) are listed obtained with the VQZANO+ PES.[30] The upper part of the table lists results corresponding to a linear reference geometry close to the HCN minimum, whereas the lower part of the table lists results obtained when the reference configuration was a linear HNC structure in the DEWE approach. DOPI results are presented for comparison, where both columns were obtained within a single calculation.

For the HCN part, the DEWE and the DOPI approaches give again the same numerical values for the VBOs. However, for HNC the VBOs showed poor convergence when either the $\hat{W}_1$ or the $\hat{W}_0$ operators were applied. This numerical problem can originate from the influence of the energetically lower-lying HCN valley. As to the singularity, the singular region of the operator $\hat{W}_1$, where $I'' = 0$, lies far from the equilibrium configuration, and thus it does not affect the presented levels. It is worth mentioning that $\hat{W}_0$ is free of singularities.

Concerning the effect of the Coriolis terms on the energy levels, $\hat{W}_0$ results in reasonable values of the VBOs; however, the agreement is not as good as it was for the case of CO$_2$, in accord with the somewhat larger rotational constant.

VIII. SUMMARY

An efficient algorithm and a general N-atomic computer code are presented using a Hamiltonian built upon rectilinear normal coordinates for nuclear motion calculations. The algorithm is called DEWE, standing for discrete variable representation (D) of the Eckart-Watson (EW) Hamiltonian with exact inclusion of the potential (E). DEWE has several distinguishing characteristics.

First, it is based on the Eckart-Watson Hamiltonian operators for nonlinear and linear reference structures. These operators have general forms and they work in rectilinear normal coordinates which can be automatically constructed for a molecule. Second, highly accurate global PESs or force fields expressed in curvilinear internal coordinates can be involved in the nuclear motion computations *exactly*, due to the analytical transformation from rectilinear normal coordi-

TABLE V. Zero-point energy and vibrational band origins ($l=0$) of [H,C,N], in cm^{-1}, obtained with the VQZANO+ PES of Ref. 30.

$(v_1\, v_b^{|l|}\, v_3)$	HCN		
	$\hat{W}_0$ [a,b]	$\hat{W}_1$ [a,b]	DOPI [c]
$(0\ 0^0\ 0)$	3479.37(2.09)	3481.46(0.00)	3481.46
$(0\ 2^0\ 0)$	1407.96(6.95)	1414.92(0.00)	1414.92
$(0\ 0^0\ 1)$	2100.45(0.13)	2100.59(0.00)	2100.58
$(0\ 4^0\ 0)$	2787.65(13.81)	2801.46(0.00)	2801.46
$(1\ 0^0\ 0)$	3301.04(6.71)	3307.74(0.00)	3307.74
$(0\ 2^0\ 1)$	3503.66(7.33)	3510.99(0.00)	3510.99
$(0\ 6^0\ 0)$	4155.46(20.79)	4176.25(0.00)	4176.24
	HNC		
	$\hat{W}_0$ [a,d]	$\hat{W}_1$ [a,d]	DOPI [c]
$(0\ 0^0\ 0)$	8662.69(4.40)	8667.09(0.00)	8667.09
$(0\ 2^0\ 0)$	931.7$\underline{7}$ [e](10.15)	941.9$\underline{4}$ [e](−0.02)	941.92
$(0\ 4^0\ 0)$	1883.$\underline{76}$ [e](19.34)	1903.$\underline{89}$ [e](−0.79)	1903.10
$(0\ 0^0\ 1)$	2024.53(0.41)	2024.94(0.00)	2024.94
$(0\ 6^0\ 0)$	28$\underline{13.39}$ [e](21.42)	28$\underline{54.56}$ [e](−19.75)	2834.80
$(0\ 2^0\ 1)$	2943.7$\underline{8}$ [e](11.27)	2955.0$\underline{6}$ [e](−0.01)	2955.04
$(1\ 0^0\ 0)$	3653.96(11.14)	3665.1$\underline{4}$ [e](−0.04)	3665.10

[a]Results obtained with the DEWE algorithm applying the operator $\hat{W}_n = n \cdot (\mu/2)(\hat{\pi}_x^2 + \hat{\pi}_y^2) + (1/2)\Sigma_{k=1}^{3N-5}\hat{P}_k^2 + V^{\mathrm{VQZANO+}}$. Atomic masses $m_\mathrm{H} = 1.007\ 825\ 0$ u, $m_\mathrm{C} = 12.000\ 000$ u, and $m_\mathrm{N} = 14.003\ 074$ u were used throughout the calculations.

[b]The reference geometry was linear with $r_\mathrm{HC} = 2.014\ 000\ 2$ bohrs and $r_\mathrm{CN} = 2.179\ 203\ 2$ bohrs bond lengths. The number of basis functions applied for the vibrational degrees of freedom was (16,16,16,16).

[c]Results obtained with the DOPI algorithm (Ref. 22). Exactly the same PES and nuclear masses were applied as in the calculations with DEWE.

[d]The reference geometry was linear with $r_\mathrm{HN} = 1.878\ 000\ 2$ bohr and $r_\mathrm{NC} = 2.209\ 000\ 2$ bohrs bond lengths. The number of basis functions applied for the vibrational degrees of freedom was (16,16,16,16).

[e]Levels that cannot be converged within the accuracy of the underlined digits with the applied basis set. This convergence problem can originate from the proximity of the lower HCN valley of the PES.

nates to curvilinear internal coordinates. Third, the kinetic and the potential energy operators are represented in DVR, in which the matrix representation of the potential energy is always diagonal, no matter how complicated the potential function is in the actual coordinates, and the matrix of the kinetic energy operator is a sparse matrix with a highly special structure. Consequently, the required eigenpairs of the matrix of the Eckart-Watson Hamiltonian(s) can be efficiently obtained with an iterative Lanczos algorithm.

The above approach was tested and compared with converged VBOs obtained by variational approaches centered on curvilinear internal coordinate Hamiltonians for H_2O, H_3^+, and HCN/HNC applying high-accuracy global PESs, for CO_2 with an empirical sextic force field, and for CH_4 with an eight-order force field. Exactly the same vibrational energy levels were obtained with the curvilinear internal and the rectilinear internal (e.g., normal) coordinate computations for all but a few levels of the triatomic systems. Without treatment of the singularity in the Eckart-Watson Hamiltonian[36] for nonlinear reference structures, certain highly excited levels that sample a linear geometry will fail to converge. Furthermore, the description of large-amplitude vibrational motions might not be efficient in the applied rectilinear set of coordinates.

Though DEWE can be applied for triatomics, we think that for triatomic molecules there exist considerably more efficient methods for nuclear motion computations, such as DOPI, applying tailor-made Hamiltonians. The goal of the present work was not to develop even more efficient codes for a given set of triatomic molecules with a unique bonding arrangement, but to suggest an approach that is generally applicable to any polyatomic molecule irrespective of its bonding structure. Singularity causes problems in only a small number of molecules which can easily take a linear form along their large amplitude internal motions. For larger, non quasilinear species this problem will not occur. Besides generality, the DEWE algorithm retains the important capability of approaches built upon internal coordinate Hamiltonians to make use of recently developed high-accuracy PESs or efficient force fields expressed in curvilinear internal coordinates. This ability is considered to be of great importance as the accuracy of the potential involved in a (ro)vibrational calculation is crucial from the point of view of the accuracy of the energy levels obtained. As to the future, our goals include the further improvement of the efficiency of our present code and apply it to "exact" (ro)vibrational studies of molecular systems having five to seven atoms.

ACKNOWLEDGMENTS

APPENDIX: EFFICIENT CALCULATION OF THE HERMITE-DVR MATRIX ELEMENTS OF THE $\hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta$ OPERATOR

Extract a matrix element from Eq. (39),

$$\langle \mathcal{H}_n | \hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta | \mathcal{H}_m \rangle = \sum_{p=1}^{\mathcal{N}} (\boldsymbol{\pi}_\alpha)_{np} (\boldsymbol{\mu}_{\alpha\beta})_{pp} (\boldsymbol{\pi}_\beta)_{pm}, \tag{A1}$$

where $\mathcal{N} = \Pi_{i=1}^{D} N_i$. It is worth noting that between the index of the direct product matrix, n, and the subindices, $(n_1, n_2, \ldots, n_D)$, the following unambiguous relation can be established: $n = (n_1 - 1)N_2 \cdot \ldots \cdot N_D + (n_2 - 1)N_3 \cdot \ldots \cdot N_D + \ldots + n_D$. Consequently, a row or a column of the matrix can be referenced by either n or $(n_1, n_2, \ldots, n_D)$.

In the summation (A1) only those members have a nonzero contribution for which the conditions formulated below are satisfied.

1. Diagonal elements ($n = m \Leftrightarrow n_i = m_i$, $i = 1, 2, \ldots, D$)

If $\exists l \in \{1, 2, \ldots, D\}: p_l \neq n_l$ and $p_l \neq m_l$, but of course $n_l = m_l$, and $n_k = m_k = p_k$, $k = 1, 2, \ldots, l-1, l+1, \ldots, D$,

$$\sum_{p=1}^{\mathcal{N}} (\boldsymbol{\pi}_\alpha)_{np} (\boldsymbol{\mu}_{\alpha\beta})_{pp} (\boldsymbol{\pi}_\beta)_{pn} = -\sum_{l=1}^{D} \sum_{i \neq n_l}^{N_l} \left[\mu_{\alpha\beta}(q_{1,n_1}, \ldots, q_{l,i}, \ldots, q_{D,n_D}) \left(\sum_{k=1}^{D} Z_{kl}^\alpha \frac{q_{k,n_k}}{q_{l,n_l} - q_{l,i}} \right) \left(\sum_{k'=1}^{D} Z_{k'l}^\beta \frac{q_{k',n_{k'}}}{q_{l,i} - q_{l,n_l}} \right) \right]. \tag{A2}$$

2. Off-diagonal elements ($n \neq m$)

(A) If $\exists l \in \{1, 2, \ldots, D\}: n_l \neq m_l$, $n_l \neq p_l$ and $p_l \neq m_l$, but $n_k = p_k = m_k$, $k = 1, 2, \ldots, l-1, l+1, \ldots D$, then

$$\sum_{p=1}^{\mathcal{N}} (\boldsymbol{\pi}_\alpha)_{np} (\boldsymbol{\mu}_{\alpha\beta})_{pp} (\boldsymbol{\pi}_\beta)_{pm} = -\sum_{i \neq n_l}^{N_l} \left[\mu_{\alpha\beta}(q_{1,n_1}, \ldots, q_{l,i}, \ldots, q_{D,n_D}) \left(\sum_{k=1}^{D} Z_{kl}^\alpha \frac{q_{k,n_k}}{q_{l,n_l} - q_{l,i}} \right) \right.$$
$$\left. \times \left(\sum_{k'=1}^{D} Z_{k'l}^\beta \frac{q_{k',m_{k'}}}{q_{l,i} - q_{l,m_l}} \right) \right] \cdot \delta_{n_1 m_1} \delta_{n_2 m_2} \cdot \ldots \cdot (1 - \delta_{n_l m_l}) \cdot \ldots \cdot \delta_{n_D m_D}. \tag{A3}$$

(B) If $\exists j, l \in (1, 2, \ldots, D): n_j \neq p_j = m_j$ and $n_l = p_l \neq m_l$, but $n_k = p_k = m_k$, $k = 1, 2, \ldots, j-1, j+1, \ldots, l-1, l+1, \ldots D$, then

$$\sum_{p=1}^{\mathcal{N}} (\boldsymbol{\pi}_\alpha)_{np} (\boldsymbol{\mu}_{\alpha\beta})_{pp} (\boldsymbol{\pi}_\beta)_{pm} = -\left[\mu_{\alpha\beta}(q_{1,n_1}, \ldots, q_{j,n_j}, \ldots, q_{l,m_l}, \ldots, q_{D,n_D}) \left(\sum_{k=1}^{D} Z_{kl}^\alpha \frac{q_{k,n_k}}{q_{l,n_l} - q_{l,m_l}} \right) \left(\sum_{k'=1}^{D} Z_{k'j}^\beta \frac{q_{k',m_{k'}}}{q_{j,n_j} - q_{j,m_j}} \right) \right.$$

$$+ \mu_{\alpha\beta}(q_{1,n_1}, \ldots, q_{j,m_j}, \ldots, q_{l,n_l}, \ldots, q_{D,n_D}) \left(\sum_{k=1}^{D} Z_{kj}^\alpha \frac{q_{k,n_k}}{q_{j,n_j} - q_{j,m_j}} \right)$$

$$\left. \times \left(\sum_{k'=1}^{D} Z_{k'l}^\beta \frac{q_{k',m_{k'}}}{q_{l,n_l} - q_{l,m_l}} \right) \right] \cdot \delta_{n_1 m_1} \cdot \ldots \cdot (1 - \delta_{n_j m_j}) \cdot \ldots \cdot (1 - \delta_{n_l m_l}) \cdot \ldots \cdot \delta_{n_D m_D}. \tag{A4}$$

In the above formulas dimensionless normal coordinates were used and the notation $Z_{kl}^\alpha = \zeta_{kl}^\alpha \sqrt{(\omega_l/\omega_k)}$ was introduced, where ζ_{kl}^α was defined in Eq. (16), and ω_l and ω_k denote "harmonic frequencies" corresponding to the lth and kth degrees of vibrational freedom. In the present calculations general orthogonal, rectilinear internal coordinates were applied, not necessarily the normal coordinates that correspond to the actual potential, and the numerical value of the "harmonic frequencies" affected only (and only slightly) the rate of convergence upon the increase of the basis size.

[1] M. G. Bucknell, N. C. Handy, and S. F. Boys, Mol. Phys. **28**, 759 (1974).

[2] R. J. Whitehead and N. C. Handy, J. Mol. Spectrosc. **55**, 356 (1975).

[3] J. K. G. Watson, Mol. Phys. **15**, 479 (1968).

[4] J. K. G. Watson, Mol. Phys. **19**, 465 (1970).

[5] G. D. Carney, L. L. Sprandel, and C. W. Kern, Adv. Chem. Phys. **37**, 305 (1978).

[6] J. T. Hougen, P. R. Bunker, and J. W. C. Johns, J. Mol. Spectrosc. **34**, 136 (1970).

[7] B. T. Sutcliffe and J. Tennyson, Int. J. Quantum Chem. **39**, 183 (1991).

[8] K. M. Dunn, J. E. Boggs, and P. Pulay, J. Chem. Phys. **86**, 5088 (1987).

[9] J. O. Jung and R. B. Gerber, J. Chem. Phys. **105**, 10332 (1996).

[10] S. Carter, S. J. Culik, and J. M. Bowman, J. Chem. Phys. **107**, 10458 (1997).

[11] S. Carter and J. M. Bowman, J. Chem. Phys. **108**, 4397 (1998).

[12] J. M. Bowman, S. Carter, and X. Huang, Int. Rev. Phys. Chem. **22**, 533 (2003).

[13] T. Seideman and W. H. Miller, J. Chem. Phys. **97**, 2499 (1992).

[14] G. G. Balint-Kurti and P. Pulay, J. Mol. Struct.: THEOCHEM **341**, 1 (1995).

[15] T. Yonehara, T. Yamamoto, and S. Kato, Chem. Phys. Lett. **393**, 98 (2004).

[16] M. J. Bramley and T. Carrington, J. Chem. Phys. **99**, 8519 (1993).

[17] F. Wang, F. R. W. McCourt, and E. I. von Nagy-Felsobuki, J. Mol. Struct.: THEOCHEM **497**, 227 (2000).

[18] B. Fehrensen, D. Luckhaus, and M. Quack, Z. Phys. Chem. **209**, 1 (1999).

[19] B. Fehrensen, D. Luckhaus, and M. Quack, Chem. Phys. Lett. **300**, 312 (1999).

[20] D. Luckhaus, J. Chem. Phys. **113**, 1329 (2000).

[21] D. Luckhaus, J. Chem. Phys. **118**, 8797 (2003).

[22] G. Czakó, T. Furtenbacher, A. G. Császár, and V. Szalay, Mol. Phys. **102**, 2411 (2004); T. Furtenbacher, G. Czakó, B. T. Sutcliffe, A. G. Császár, and V. Szalay, J. Mol. Struct. **780–781**, 283 (2006).

[23] O. L. Polyansky, A. G. Császár, S. V. Shirin, N. F. Zobov, P. Barletta, J. Tennyson, D. W. Schwenke, and P. J. Knowles, Science **299**, 539 (2003); P. Barletta, S. V. Shirin, N. F. Zobov, O. L. Polyansky, J. Tennyson, E. F. Valeev, and A. G. Császár, J. Chem. Phys. **125**, 204307 (2006).

[24] D. O. Harris, G. G. Engerholm, and W. D. Gwinn, J. Chem. Phys. **43**, 1515 (1965).

[25] A. S. Dickinson and P. R. Certain, J. Chem. Phys. **49**, 4209 (1968).

[26] J. C. Light and T. Carrington, Jr., Adv. Chem. Phys. **114**, 263 (2000).

[27] C. Lanczos, J. Res. Natl. Bur. Stand. **45**, 255 (1950).

[28] O. L. Polyansky, R. Prosmiti, W. Klopper, and J. Tennyson, Mol. Phys. **98**, 261 (2000).

[29] A. Chédin, J. Mol. Spectrosc. **76**, 430 (1979).

[30] T. van Mourik, G. J. Harris, O. L. Polyansky, J. Tennyson, A. G. Császár, and P. J. Knowles, J. Chem. Phys. **115**, 3706 (2001).

[31] D. W. Schwenke and H. Partridge, Spectrochim. Acta, Part A **57**, 887 (2001).

[32] B. T. Sutcliffe, in *Handbook of Molecular Physics and Quantum Chemistry*, edited by S. Wilson (Wiley, Chichester, 2003), Vol. 1, P. 6, Chap. 32, pp. 501–525.

[33] C. Eckart, Phys. Rev. **47**, 552 (1935).

[34] B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).

[35] Yu. S. Makushkin and O. N. Ulenikov, J. Mol. Spectrosc. **68**, 1 (1977).

[36] R. Bartholomae, D. Martin, and B. T. Sutcliffe, J. Mol. Spectrosc. **87**, 367 (1981).

[37] J. T. Hougen, J. Chem. Phys. **36**, 519 (1962).

[38] A. G. Császár and I. M. Mills, Spectrochim. Acta, Part A **53**, 1101 (1997).

[39] R. W. Redding and F. O. Meyer III, J. Mol. Spectrosc. **74**, 486 (1979).

[40] V. Szalay, J. Chem. Phys. **99**, 1978 (1993).

[41] W. D. Allen, INTDER2000, a general program which performs various vibrational analysis and higher-order nonlinear transformations among force field representations; W. D. Allen, A. G. Császár, V. Szalay, and I. M. Mills, Mol. Phys. **89**, 1213 (1996); W. D. Allen and A. G. Császár, J. Chem. Phys. **98**, 2983 (1993).

[42] F. T. Smith, Phys. Rev. Lett. **45**, 1157 (1980).

[43] X.-G. Wang and T. Carrington, Jr., J. Chem. Phys. **119**, 101 (2003).

[44] P. R. Bunker and P. Jensen, *Molecular Symmetry and Spectroscopy* (NRC, Ottawa, 1998).

[45] A. Sayvetz, J. Chem. Phys. **7**, 383 (1939).

[46] T. J. Lee, J. M. L. Martin, and P. R. Taylor, J. Chem. Phys. **102**, 254 (1995).

[47] D. Papoušek and M. R. Aliev, *Molecular Vibrational-Rotational Spectra* (Academia, Prague, 1982).