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Toward black-box-type full- and reduced-dimensional variational (ro)vibrational computations

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A black-box-type algorithm is presented for the variational computation of energy levels and wave functions using a (ro)vibrational Hamiltonian expressed in an arbitrarily chosen body-fixed frame and in any set of internal coordinates of full or reduced vibrational dimensionality. To make the required numerical work feasible, matrix representation of the operators is constructed using a discrete variable representation (DVR). The favorable properties of DVR are exploited in the straightforward and numerically exact inclusion of any representation of the potential and the kinetic energy including the **G** matrix and the extrapotential term. In this algorithm there is no need for an *a priori* analytic derivation of the kinetic energy operator, as all of its matrix elements at each grid point are computed numerically either in a full- or a reduced-dimensional model. Due to the simple and straightforward definition of reduced-dimensional models within this approach, a fully anharmonic variational treatment of large, otherwise intractable molecular systems becomes available. In the computer code based on the above algorithm, there is no inherent limitation for the maximally coupled number of vibrational degrees of freedom. However, in practice current personal computers allow the treatment of about nine fully coupled vibrational dimensions. Computation of vibrational band origins of full and reduced dimensions showing the advantages and limitations of the algorithm and the related computer code are presented for the water, ammonia, and methane molecules. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3076742]

I. INTRODUCTION

The Born–Oppenheimer (BO) approximation[1,2] defines two fields of research for computational quantum chemistry, namely, electronic structure and nuclear motion theories. Although the approximate approaches and related algorithms employed in solving the time-independent Schrödinger equations in the two areas have a lot of common features, from the perspective of the present investigation on variational rovibrational spectroscopy it is more important to point out the differences in these algorithms than to emphasize their similarities. Note that (low-order) perturbational algorithms, used with considerable success in both fields,[3–6] are outside of the scope of this paper.

Nonrelativistic electronic structure theory almost always utilizes a universal Hamiltonian expressed in Cartesian coordinates, whereby not only the kinetic but also the potential energy operator is known exactly in a simple analytic form. One is usually interested in the lowest or the few lowest electronic states and wave functions and it has also become common to use standard basis sets for these computations. Consequently, single codes could be written irrespective of the size of the system to be treated and the arrangement of its constituent atoms. Apart from relatively minor though very important technical differences in the algorithms utilized in the different electronic structure codes, it is the different approximations introduced to treat the electron correlation problem which lead to codes applicable to drastically different molecular sizes and result in varying accuracy in the electronic energies and related properties.[5,7]

In contrast to electronic structure computations, most of the algorithms used to solve the nuclear motion Schrödinger equation variationally and the codes based on them are specialized in more than one respect.[8–12] Most importantly, the potential energy operator is never known in an exact form; only approximations to the potential energy surfaces (PES)[7,13] can be developed. The first class of approaches, based on tailor-made analytic kinetic energy operators[14–16] and codes utilizing them, proved to be especially useful for tri-, tetra-, and pentatomic species.[17–25] Within this class, almost without exception, separate codes had to be developed for molecules of different size and bonding arrangements. Obviously, there have been initiatives to develop universal variational nuclear motion codes. The traditional type of such universal codes uses the Eckart–Watson (EW) Hamiltonian(s)[26,27] expressed in the Eckart frame and built upon rectilinear normal coordinates. We are aware of several computer codes based on the EW Hamiltonians capable of yielding variationally computed vibrational spectra for polyatomic systems.[8,10,11,28–39] The principal advantage of these codes is their universality while their most important shortcoming is connected with the rectilinear nature of normal

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coordinates and the use of the Eckart frame. As a result, floppy molecular systems and those having PESs with multiple minima cannot be treated straightforwardly within this approach. There have also been attempts to use arbitrarily chosen body-fixed frames and curvilinear internal coordinates,[40,41] for example by Luckhaus and co-workers,[42–45] Lauvergnat *et al.*,[46,47] Yurchenko *et al.*,[48] and Makarewicz.[49] This third class of approaches seems to be the only one which offers the possibility of a true black-box-type algorithm to compute rovibrational spectra of complex and floppy molecules, similar to the widely appreciated black-box approaches of electronic structure theory. Nevertheless, as it is also shown here, practical realization of such a universal algorithm for nuclear motion computations is far from being straightforward.

In nuclear motion computations rotation-vibration (rv) energy levels and wave functions (and properties based on them) are computed. Often, however, only the rotationless vibrational levels (and transition wavenumbers) are required, which are obtained by the solution of a Hamiltonian constrained to zero total angular momentum ($J=0$, where J is the quantum number of the overall molecular rotation). Furthermore, adding the capability of the computation of rotational-vibrational states to an existing vibrations-only code is straightforward. Thus, it is deemed to be sufficient to concentrate here on the constrained, $J=0$ problem.

In order to obtain quantum dynamical results on large(r) molecular systems variationally, approximations in the quantum treatment must be introduced. The much needed savings on the computational effort can be achieved along two routes. First, reduced-dimensional models can be introduced by means of stopping or constraining the motions of the subsystem considered to be irrelevant. These techniques involve approximations in the physical model. Second, mathematical approximations (e.g., truncated n-mode representation, grid reduction) can be introduced in the solution of a given physical model, constrained or not, in order to reduce the numerical effort.

In this paper we present (a) the theory behind an approach leading toward a black-box-type procedure to compute rovibrational spectra, with special emphasis on the numerical evaluation of the kinetic energy matrix, (b) our carefully tested implementation of this procedure in a computer code, built upon the use of discrete variable representation (DVR)[50,51] and a direct-product basis, especially useful when a large number of eigenstates is to be computed from the resulting sparse Hamiltonian matrix of special structure, and (c) numerical results on simple model-type molecular systems, water, ammonia, and methane in order to demonstrate the flexibility and utility of our code. The code developed during this work is called GENIUSH, in reference to its main characteristics: general (GE) (ro)vibrational code with numerical (N), internal-coordinate (I), user-specified (US) Hamiltonians (H). Indeed, GENIUSH is able to compute eigenpairs of a (ro)vibrational operator corresponding to any body-fixed frame and internal coordinates defined by the user. Furthermore, inclusion of the user-defined representation of the PES is numerically exact.

II. KINETIC ENERGY OPERATORS

A. The classical Hamiltonian in internal coordinates

Let us consider a molecule with N nuclei, whose positions are specified by $3N$ rectilinear Cartesian coordinates, $X_{i\alpha}$, $i=1,\ldots,N$ ($\alpha=X,Y,Z$), in the laboratory-fixed frame. The corresponding Lagrangian is

$$L=\frac{1}{2}\sum_{i=1}^{N} m_i \dot{\mathbf{X}}_i^{\mathrm{T}}\dot{\mathbf{X}}_i - V, \tag{1}$$

where dots denote time derivatives, m_i denotes the mass associated with the ith nucleus, and V is the potential energy depending only on the coordinates of the nuclei. In anticipation of a computationally more efficient representation, the $3N$ rectilinear Cartesian coordinates are replaced[52] by coordinates of the center of mass of the nuclei (NCM), $(X_X^{\mathrm{NCM}},X_Y^{\mathrm{NCM}},X_Z^{\mathrm{NCM}})$, which describe the translational motion of the system, the Euler angles, (ϕ,θ,χ), which specify the instantaneous orientation of a body-fixed frame with respect to the laboratory-fixed frame, and coordinates describing the internal motion of the system, $(q_1,q_2,\ldots,q_D)$, where $D \le 3N-6$. In this new set of coordinates the Lagrangian has the form, using the compact notation $\mathbf{q}=(q_1,q_2,\ldots,q_{D+6})$ and $q_{D+1}=\phi$, $q_{D+2}=\theta$, $q_{D+3}=\chi$, $q_{D+4}=X_X^{\mathrm{NCM}}$, $q_{D+5}=X_Y^{\mathrm{NCM}}$, and $q_{D+6}=X_Z^{\mathrm{NCM}}$,

$$L=\frac{1}{2}\sum_{kl=1}^{D+6}\left(\sum_{i=1}^{N} m_i \frac{\partial \mathbf{X}_i^{\mathrm{T}}}{\partial q_k}\frac{\partial \mathbf{X}_i}{\partial q_l}\right)\dot{q}_k\dot{q}_l - V = \frac{1}{2}\sum_{kl=1}^{D+6}\dot{q}_k g_{kl}\dot{q}_l - V, \tag{2}$$

where

$$g_{kl}=\sum_{i=1}^{N} m_i \frac{\partial \mathbf{X}_i^{\mathrm{T}}}{\partial q_k}\frac{\partial \mathbf{X}_i}{\partial q_l}, \quad k,l=1,2,\ldots,D+6, \tag{3}$$

was introduced. The momentum p_k, conjugate to q_k, is

$$p_k=\frac{\partial L}{\partial \dot{q}_k}=\sum_{l=1}^{D+6} g_{kl}\dot{q}_l, \tag{4}$$

and hence for nonsingular $\mathbf{g}$'s, $\dot{\mathbf{q}}=\mathbf{g}^{-1}\mathbf{p}$. After appropriate rearrangements the Hamiltonian is written as

$$H=\frac{1}{2}\sum_{kl=1}^{D+6} p_k(\mathbf{g}^{-1})_{kl}p_l + V = \frac{1}{2}\sum_{kl=1}^{D+6} p_k G_{kl} p_l + V, \tag{5}$$

where the notation $\mathbf{G}=\mathbf{g}^{-1}$ was introduced.

B. Formulation of the g and G matrices

1. t-*vector formalism*

The relationship between Cartesian coordinates in the laboratory-fixed frame, $X_{i\alpha}$, and those in the body-fixed frame, x_{ia}, is given by

$$X_{i\alpha}=X_\alpha^{\mathrm{NCM}}+\sum_a C_{\alpha a}x_{ia}, \tag{6}$$

where $x_{ia}(q_1,q_2,\ldots,q_D)$ denotes the Cartesian coordinates of the ith nucleus in the body-fixed frame with the axis $a=x,y,z$, while $\mathbf{C}(\phi,\theta,\chi)$ denotes the (orthogonal) direction cosine matrix between the laboratory-fixed and the body-fixed frames. The so-called **t** vectors[9,53] are now introduced as

$$t'_{i\alpha k}=\frac{\partial X_{i\alpha}}{\partial q_k} \quad \text{and} \quad t_{iak}=\sum_{\alpha} C_{\alpha a}t'_{i\alpha k}, \; k=1,2,\ldots,D+6. \tag{7}$$

It can be demonstrated[41] that the translational and rotational **t** vectors are

$$t_{iak+D+3}=\delta_{ak}, \quad t_{iak+D}=(\vec{e}_k\times\vec{x}_i)_a, \quad k=1(x),2(y),3(z), \tag{8}$$

where δ_{ak} is the Kronecker delta symbol, and $\vec{e}_k$ denotes the unit vector pointing along the kth axis of the body-fixed frame; the vibrational **t** vectors can be expressed as

$$t_{iak}=\frac{\partial x_{ia}}{\partial q_k}, \quad k=1,2,\ldots,D. \tag{9}$$

Elements of the **g** matrix can now be given in terms of the **t** vectors as

$$g_{kl}=\sum_{i=1}^{N} m_i \sum_a t_{iak}t_{ial}=\sum_{i=1}^{N} m_i \mathbf{t}_{ik}^{\mathrm{T}}\mathbf{t}_{il}. \tag{10}$$

It follows from Eq. (10) that **g** (and also $\mathbf{G}=\mathbf{g}^{-1}$) is specified entirely by the actual values of the internal coordinates and the definition of the body-fixed frame. Furthermore, it can be demonstrated that the translational motion of the NCM can be separated exactly from the rest of the coordinates, which allows introduction of the rv Hamiltonian as

$$H^{\mathrm{rv}}=\frac{1}{2}\sum_{kl=1}^{D+3} p_k G_{kl} p_l + V. \tag{11}$$

*2. **s**-vector formalism*

A possible construction of the **G** matrix is offered by its definition introduced below Eq. (5) using the **t** vectors. An alternative formulation, based on the chain rule, is often used,

$$G_{kl}=\sum_{i=1}^{N}\frac{1}{m_i}\sum_{\alpha}\frac{\partial q_k}{\partial X_{i\alpha}}\frac{\partial q_l}{\partial X_{i\alpha}}, \tag{12}$$

which is the well-known El'yashevich–Wilson[54,55] **G** matrix. Similarly to the **t** vectors [Eq. (7)], the so-called **s** vectors[54] are defined as

$$s'_{i\alpha k}:=\frac{\partial q_k}{\partial X_{i\alpha}} \quad \text{and} \quad s_{iak}:=\sum_{\alpha} C_{\alpha a}s'_{i\alpha k}, \quad k=1,2,\ldots,3N. \tag{13}$$

It can be shown that the vibrational **s** vectors assume the form

$$s_{iak}=\frac{\partial q_k}{\partial x_{ia}}. \tag{14}$$

A detailed procedure for the evaluation of translational and rotational **s** vectors can be found in Ref. 41, which relies only on the translational and rotational **t** vectors and the vibrational **s** vectors but does not assume the knowledge of the vibrational **t** vectors. Finally, the **G** matrix can also be written in terms of the **s** vectors as

$$G_{kl}=\sum_{i=1}^{N}\frac{1}{m_i}\sum_a s_{iak}s_{ial}=\sum_{i=1}^{N}\frac{1}{m_i}\mathbf{s}_{ik}^{\mathrm{T}}\mathbf{s}_{il}. \tag{15}$$

From a theoretical point of view, the **t**- and **s**-vector formalisms are equivalent, but numerically the computation of either the $\partial x_{ia}/\partial q_k$- or $\partial q_k/\partial x_{ia}$-type derivatives can be more favorable.

C. Reduced-dimensional models in classical mechanics

In nuclear motion computation of larger systems approximations based on physical considerations must often be introduced, yielding effective Hamiltonians. As inspired by the given application, certain types of internal coordinates may be decoupled from the rest.

Let us consider $3N-6$ internal coordinates, out of which there are only $D<3N-6$ active variables $(q_1,q_2,\ldots,q_D)$ in our model, and the rest of the coordinates $(\rho_1,\rho_2,\ldots,\rho_{3N-6-D})$ are fixed at a given value (or are prescribed functions of the active coordinates). In classical mechanics, constraining coordinates ρ_i is equivalent to choosing $\dot{\rho}_i=0$ $(i=1,2,\ldots,3N-6-D)$. The Lagrangian of such a constrained model is already derived in Eq. (2) with $D<3N-6$. This is equivalent to deleting rows and columns corresponding to the constrained coordinates in the full $\mathbf{g}\in\mathcal{R}^{(3N-3)\times(3N-3)}$.

Another possible approximation can be introduced if those rows and columns of the full-dimensional $\mathbf{G}\in\mathcal{R}^{(3N-3)\times(3N-3)}$ matrix are deleted which correspond to the constrained coordinates.

D. Quantum mechanical formulation

In order to rewrite Eq. (11) to its quantum mechanical counterpart, a method advocated by Podolsky[56] can be applied, whereby

$$\hat{H}^{\mathrm{rv}}=\frac{1}{2}\sum_{kl=1}^{D+3}\tilde{g}^{-1/4}\hat{p}_k^{\dagger}G_{kl}\tilde{g}^{1/2}\hat{p}_l\tilde{g}^{-1/4}+V, \tag{16}$$

where $\tilde{g}=\det\mathbf{g}$, and $\hat{p}_k$ has the form

$$\hat{p}_k=-i\hbar\frac{\partial}{\partial q_k}, \quad k=1,2,\ldots,D, \tag{17}$$

and

$$\hat{p}_{D+1}=\hat{J}_x, \quad \hat{p}_{D+2}=\hat{J}_y, \quad \hat{p}_{D+3}=\hat{J}_z, \tag{18}$$

if the volume element is (using Wilson's normalization) $dq_1dq_2\cdots dq_D \sin\theta d\theta d\phi d\chi$. Elements of **G** and $\tilde{g}$ are expressed in terms of the internal coordinates and they are not functions of the Euler angles (see Sec. II B). Thus an effective vibrational operator can be introduced,

$$\hat{H}^{\mathrm{vP}} = \frac{1}{2}\sum_{kl=1}^{D} \tilde{g}^{-1/4}\hat{p}_k^{\dagger} G_{kl}\tilde{g}^{1/2}\hat{p}_l\tilde{g}^{-1/4} + V. \tag{19}$$

From now on this form will be referred to as the Podolsky form, $\hat{H}^{\mathrm{vP}}$, in order to distinguish it from a "rearranged" form, $\hat{H}^{\mathrm{vR}}$, that can be obtained after trivial manipulations as

$$\hat{H}^{\mathrm{vR}} = \frac{1}{2}\sum_{kl=1}^{D} \hat{p}_k^{\dagger} G_{kl}\hat{p}_l + U + V, \tag{20}$$

where

$$U = \frac{\hbar^2}{32}\sum_{kl=1}^{D}\left[\frac{G_{kl}}{\tilde{g}^2}\frac{\partial\tilde{g}}{\partial q_k}\frac{\partial\tilde{g}}{\partial q_l} + 4\frac{\partial}{\partial q_k}\left(\frac{G_{kl}}{\tilde{g}}\frac{\partial\tilde{g}}{\partial q_l}\right)\right] \tag{21}$$

or after a useful rearrangement

$$U = \frac{\hbar^2}{32}\sum_{kl=1}^{D}\left[\frac{G_{kl}}{\tilde{G}^2}\frac{\partial\tilde{G}}{\partial q_k}\frac{\partial\tilde{G}}{\partial q_l} - 4\frac{\partial}{\partial q_k}\left(\frac{G_{kl}}{\tilde{G}}\frac{\partial\tilde{G}}{\partial q_l}\right)\right]. \tag{22}$$

U, often called the extrapotential term, is an inherently quantum mechanical term in the Hamiltonian. Both the vibration-only Podolsky form, Eq. (19), and the rearranged form, Eq. (20), contain the determinant of the rotational-vibrational $\mathbf{g} \in \mathcal{R}^{(D+3)\times(D+3)}$ matrix (or that of the $\mathbf{G}$ matrix) irrespective of whether the full rovibrational or only the effective vibrational problem is solved. Consequently, even if only the vibrations are studied, the choice of the body-fixed frame might affect the convergence rate of the computed vibrational levels and also, for instance, the singular regions ($\tilde{g}=0$) of the Hamiltonian.

From a theoretical point of view the Podolsky and the rearranged forms of the (ro)vibrational Hamiltonian are equivalent; however, their numerical behavior is different.

E. Reduced-dimensional models in quantum mechanics

Approximations inspired by physical considerations discussed in Sec. II C in a classical mechanical context remain valid also in the quantum mechanical treatment. Constrained models constructed by reducing the $\mathbf{g}$ and also $\mathbf{G}$ matrices will be presented later. It is perhaps worth pointing out that the two reduction strategies in general provide different models of the system, and thus numerically different results.

III. MATRIX REPRESENTATION OF THE HAMILTONIAN AND THE ITERATIVE EIGENSOLVER

Traditionally, the Hamiltonians given in Eqs. (19) and (20) are further rearranged to a simpler symbolic form considering the actually chosen body-fixed frame and internal coordinates. The matrix representation of this system-adapted symbolic form is then implemented to compute (ro)vibrational eigenpairs. In the algorithm and computer code presented here and called GENIUSH the problem is solved in a reversed manner. The Hamiltonians given in Eq. (19) or Eq. (20) are not rearranged further but connected directly to an eigensolver dealing explicitly only with the universal G_{kl}, $\tilde{g}$, and U quantities. This allows one to write a universal computer code. In each application the G_{kl}, $\tilde{g}$, and U quantities, specific for the chosen body-fixed frame and internal coordinates, are determined numerically.

In what follows the essential parts of GENIUSH are presented in detail. First, the DVR[50,51] is considered which is used to construct the matrix representation of the operators. Second, technical difficulties of the numerical construction of the kinetic energy are discussed. Due to the usage of a DVR coupled with a direct-product grid the resulting Hamiltonian matrix is very sparse but is often of extreme size. To avoid the explicit construction of this large Hamiltonian matrix or even of its nonzero elements, a Lanczos iterative eigensolver[57] is used, which requires only an efficient multiplication of the Hamiltonian matrix with a vector. Finally, an efficient matrix-vector multiplication scheme parallelized with OPENMP and issues related to the eigensolver part are presented.

A. Discrete variable representation

Normalized, standard orthogonal polynomials (such as Hermite, Laguerre, Legendre, and Chebyshev), $H_j(q)$, can be employed to construct a basis. Instead of using spectral functions, the corresponding DVR basis[58] is employed in GENIUSH. So far, the Hermite and the Legendre DVR bases have been implemented. Other DVR bases can trivially be added and they may prove useful for certain applications.

In order to build a DVR, the coordinate matrix of dimension $N_k^0 \times N_k^0$ is constructed having the elements $(\mathfrak{q}_k)_{ij} = \langle H_i(q_k)|q_k|H_j(q_k)\rangle$ for each active vibrational degree of freedom, $k=1,2,\ldots,D$. For the kth vibrational degree of freedom the quadrature points, ξ_{k,n_k}, are the eigenvalues of the kth coordinate matrix, and the DVR basis is defined as $\mathcal{H}_{n_k}(q_k)=\sum_{j=0}^{N_k^0-1}(\mathbf{T}_k)_{n_k,j}H_j(q_k)$, where columns of $\mathbf{T}_k$ are the eigenvectors of $\mathfrak{q}_k$. The DVR direct-product basis is constructed as $\{\prod_{k=1}^{D}\mathcal{H}_{n_k}(q_k)\}_{n_1=1,\ n_2=1,\ldots,n_D=1}^{N_1^0,N_2^0,\ldots,N_D^0}$. As a result, the matrix of the coordinate operator is diagonal. Furthermore, due to the Gaussian quadrature approximation and the special properties of the DVR basis functions, the matrix representation of an operator that depends only on the coordinates is also always diagonal.

It is desirable to employ as compact of a representation of the Hamiltonian as possible. The first step toward this goal is to optimize the primitive DVR grid points employing a suitable one-dimensional (1D) model Hamiltonian. In the present work the potential-optimized (PO) DVR approach[59] was utilized. In the PO-DVR approach the operator

$$\hat{h}_k^{\mathrm{1D}} = \tfrac{1}{2}\hat{p}_k^{\dagger}G_{kk}(q_k;\mathbf{q}_{\mathrm{e}}')\hat{p}_k + V(q_k;\mathbf{q}_{\mathrm{e}}'), \quad k=1,2,\ldots,D, \tag{23}$$

provides an excellent choice for simplifying the full operator given in Eq. (20), where all the coordinates, except the kth active mode, are fixed at their equilibrium values. The extrapotential term is left out from this 1D operator. Eigenvalues and eigenvectors corresponding to Eq. (23) are then evaluated using a large number of primitive grid points, N_k^0, distributed on a wide interval of the kth coordinate.

Next, the first few eigenvectors, $N_k^{\mathrm{PO}} \le N_k^0$, of the 1D problem ordered in a matrix, $\mathbf{u}_k \in \mathcal{R}^{N_k^0 \times N_k^{\mathrm{PO}}}$, are used to construct the kth "optimized" coordinate matrix, $(\mathfrak{q}_k^{\mathrm{PO}})_{ij} = \sum_{l=1}^{N_k^0} (\mathbf{u}_k)_{li} \xi_{k,l} (\mathbf{u}_k)_{lj}$ $(i,j=1,2,\ldots,N_k^{\mathrm{PO}})$. The eigenvalues of $\mathfrak{q}_k^{\mathrm{PO}}$ are the PO-DVR quadrature points, $\xi_{k,n_k}^{\mathrm{PO}}$ $(n_k=1,2,\ldots,N_k^{\mathrm{PO}})$. The eigenvectors of $\mathfrak{q}_k^{\mathrm{PO}}$ ordered in a matrix, $\mathbf{T}_k^{\mathrm{PO}}$, are used to set up the PO-DVR of the differential operators via the so-called transformation method.[50]

There are several advantages of the use of this optimization method. First, it offers an inexpensive and valuable test of the actual coordinate definition, as it also provides the "energy levels" of a 1D but already meaningful model of the system. Second, it automatically provides an optimized interval for the quadrature points corresponding to each internal coordinate. Third, and this is the main advantage of PO-DVR, due to the optimization a reduced number of grid points is sufficient to obtain eigenpairs with the desired accuracy.

In what follows N_k denotes the number of grid points corresponding to the kth degree of freedom. If PO-DVR is used $N_k = N_k^{\mathrm{PO}}$; otherwise $N_k = N_k^0$ $(k=1,2,\ldots,D)$. The direct-product grid constructed from these points has the size $\mathcal{N} = \Pi_{k=1}^{D} N_k$. In computations a direct-product grid can be used directly or truncated based on geometrical or energetic requirements, thus resulting in a nondirect-product grid. Due to a simple indexing scheme used in the implementation of GENIUSH the matrix-vector multiplication and eigensolver algorithms developed for the direct-product case can be employed also for a reduced (nondirect-product) case.

B. Numerical construction of the kinetic energy

In order to construct the matrix of a kinetic energy operator corresponding to an arbitrarily chosen body-fixed frame and internal coordinates, only the numerical values of $\mathbf{G}$, $\tilde{g}$, and U are required at the quadrature points. These quantities are constructed point by point on the DVR grid using directly the (ro)vibrational Hamiltonian operators in the Podolsky form, Eq. (19), or in the rearranged form, Eq. (20). The fact that in DVR any quantity depending only on the coordinates can be represented as a diagonal matrix makes the present approach efficient without the need of introducing any approximations in the kinetic energy terms.

1. t-vector formalism

The rotational and vibrational $\mathbf{t}$ vectors introduced in Eqs. (8) and (9) are used to construct $\mathbf{g}$, the central quantity in the present treatment. It is inverted to obtain $\mathbf{G} = \mathbf{g}^{-1} \in \mathcal{R}^{(D+3)\times(D+3)}$. If the vibration-only operator is used, it is sufficient to evaluate the vibrational sub-block of the $\mathbf{G}$ matrix.

If the Podolsky form of the Hamiltonian, Eq. (19), is employed, $\tilde{g} = \det \mathbf{g}$ is left to be computed, which is numerically straightforward. Within this formalism only the first derivatives of the body-fixed Cartesian coordinates in terms of the internal coordinates, $\partial \mathbf{x}_i / \partial q_k$, are required. These derivatives can be evaluated either by numerical (using standard double precision arithmetic) or analytic differentiation.

If the rearranged form of the Hamiltonian, Eq. (20), is used, the extrapotential term, U, must also be computed. In full-dimensional models or reduced-dimensional models constructed by reduction in $\mathbf{g}$, it is better to use Eq. (21) for U. In reduced-dimensional models constructed by reduction in $\mathbf{G}$, it is more straightforward to use the formulation of Eq. (22). Our numerical tests show that brute-force numerical differentiation of the formulas in Eqs. (21) and (22) can introduce numerical instabilities in the treatment. In order to avoid such numerical instabilities each term in Eqs. (21) and (22) are expressed numerically (not necessarily in a symbolic form) in terms of the first, second, and third derivatives of the body-fixed Cartesian coordinates in terms of the internal coordinates, $\partial \mathbf{x}_i / \partial q_k$, $\partial^2 \mathbf{x}_i / \partial q_k \partial q_l$, and $\partial^3 \mathbf{x}_i / \partial q_k \partial q_l \partial q_m$, which are evaluated in an accurate procedure. An accuracy of < 0.01 cm^{-1} in the eigenvalues can be firmly achieved only if the higher-order derivatives of the body-fixed Cartesian coordinates in terms of internal coordinates are evaluated by analytic differentiation using standard double precision arithmetic (64 bit reals) or by numerical differentiation using increased numerical precision (128 bit reals). Details of the approach are discussed in the Appendix. In the current version of GENIUSH analytic derivatives are available for an arbitrary set of internal coordinates defined with a Z-matrix and an xxy (scattering)[41] body-fixed frame. Any other coordinate definition can be treated by (quadruple precision) numerical derivatives.

2. s-vector formalism

The $\mathbf{s}$-vector formalism offers an alternative to the $\mathbf{t}$-vector formalism toward the numerical use of kinetic energy operators. The extrapotential term, U, can be formulated entirely also in terms of $\mathbf{s}$ vectors, as it was given in Ref. 9. In this expression of U first derivatives of the rotational $\mathbf{s}$ vectors and first and second derivatives of the vibrational $\mathbf{s}$ vectors in terms of internal coordinates appear.

After having studied the numerical behavior of the different possible formalisms in detail, we prefer to use the $\mathbf{t}$-vector formalism over the $\mathbf{s}$-vector formalism. In theory, the two representations are equivalent; however, technically the first requires the computation of $\partial x_{ia} / \partial q_k$, $\partial^2 x_{ia} / \partial q_l \partial q_k$, and $\partial^3 x_{ia} / \partial q_m \partial q_l \partial q_k$, whereas the second assumes the knowledge of $\partial q_k / \partial x_{ia}$, $\partial^2 q_k / \partial q_l \partial x_{ia}$, and $\partial^3 q_k / \partial q_m \partial q_l \partial x_{ia}$. To explain our preference, we note that (a) in the $\mathbf{s}$-vector formalism, implementation of internal coordinates defined for ammonia in Sec. IV B using a dummy atom turned out to be numerically unstable and (b) introduction of reduced-dimensional models having approximations in the $\mathbf{g}$ matrix is more straightforward in the $\mathbf{t}$-vector formalism.

C. Numerical representation of the potential energy

Numerical inclusion of any representation of the PES is straightforward due to the favorable properties of DVR. There is no need to adapt a specific representation of the actual PES (Taylor expansion, n-mode representation, etc.). Inclusion of potentials with multiple minima separated by low-energy barriers is numerically exact, which is necessary for reliable description of a molecular system with large amplitude motions.

TABLE I. Algorithm of the matrix-vector multiplication in GENIUSH using the rearranged form of the vibrational Hamiltonian [Eq. (20)].

Numerical manipulations	Parallelization	Operation count[a]
$\mathbf{y}=(\mathbf{U}+\mathbf{V})\,\mathbf{x}$	←OpenMP	$\mathcal{N}$
do $l=1,\ldots,D$		$D\times($
$\quad\vert\quad \mathbf{y}_l^{(1)}=\mathbf{p}_l\mathbf{x}$	←OpenMP	$N_l\mathcal{N}$
end do		$)$
do $k=1,\ldots,D$		$D\times($
$\quad\vert\quad \mathbf{y}^{(2)}=\mathbf{0}$		
$\quad\vert\quad$ do $l=1,\ldots,D$		$D\times($
$\quad\vert\quad\quad\vert\quad \mathbf{y}^{(2)}=\mathbf{y}^{(2)}+\mathbf{G}_{kl}\mathbf{y}_l^{(1)}$	←OpenMP	$\mathcal{N}$
$\quad\vert\quad$ end do		$)$
$\quad\vert\quad \mathbf{y}=\mathbf{y}+\frac{1}{2}\mathbf{p}_k^\dagger\mathbf{y}^{(2)}$	←OpenMP	$N_k\mathcal{N}$
end do		$)$
Total		$(1+2DN+D^2)\mathcal{N}$

[a] $N=N_1=N_2=\cdots=N_D$ was assumed in the computation of the total operation count. $\mathcal{N}$ is the size of the direct product grid, in this case $\mathcal{N}=N^D$.

D. The vibrational Hamiltonian in DVR

Matrix representations of the vibrational Hamiltonians given in Eqs. (19) and (20) are constructed on the direct-product grid specified above. Matrices of the quantities depending only on the coordinates assume a simple diagonal form, e.g.,

$$(\mathbf{V})_{nm}=V(\xi_{1,n_1},\xi_{2,n_2},\ldots,\xi_{D,n_D})\prod_{i=1}^{D}\delta_{n_i,m_i}, \tag{24}$$

$n,\ m=1,2,\ldots,\mathcal{N}$. The matrices of $\tilde{g}$, U, and G_{kl} $(k,l=1,2,\ldots,3N-3)$ are similarly constructed. Note that an unambiguous correspondence can be established between the index n of the direct-product grid and the subindices $(n_1,n_2,\ldots,n_D)$ of the grid points of each vibrational degree of freedom, for instance, $n=(n_1-1)\Pi_{i=2}^{D}N_i+\cdots+(n_{D-1}-1)N_D+n_D$.

To make the computation of the matrix elements more feasible, insert the truncated resolution of identity four times in Eq. (19) and twice in Eq. (20), resulting in

$$\mathbf{H}^{\mathrm{vP}}=\frac{1}{2}\sum_{kl=1}^{D}\tilde{\mathbf{g}}^{-1/4}\mathbf{p}_k^\dagger\mathbf{G}_{kl}\tilde{\mathbf{g}}^{1/2}\mathbf{p}_l\tilde{\mathbf{g}}^{-1/4}+\mathbf{U}+\mathbf{V} \tag{25}$$

and

$$\mathbf{H}^{\mathrm{vR}}=\frac{1}{2}\sum_{kl=1}^{D}\mathbf{p}_k^\dagger\mathbf{G}_{kl}\mathbf{p}_l+\mathbf{U}+\mathbf{V}, \tag{26}$$

where

$$(\mathbf{p}_k)_{nm}=-i(\mathbf{D}_k^{[1]})_{n_k,m_k}(1-\delta_{n_k,m_k})\prod_{i=1,\ i\neq k}^{D}\delta_{n_i,m_i}, \tag{27}$$

and $\mathbf{D}_k^{[1]}\in\mathcal{R}^{N_k\times N_k}$ is the matrix of the differential operator $\partial/\partial q_k$ in DVR constructed by the transformation method.

E. Iterative eigensolver

In order to compute up to the lowest few hundred eigenpairs of the Hamiltonian matrix, a Lanczos iterative eigensolver is used in GENIUSH. The present implementation is based on a single-vector Lanczos algorithm.[57] The Hamiltonian matrix is transformed using either the conjugate gradient or a shift-power method[60,61] to obtain the eigenpairs corresponding to the lowest eigenvalues.

1. Matrix-vector multiplication and efficiency considerations

In the Lanczos iterative eigensolver the most time-consuming step is the computation of the product of the Hamiltonian matrix with a vector, $\mathbf{y}=\mathbf{H}\mathbf{x}$. Thus, the efficient evaluation of $\mathbf{y}$ is crucial for the efficient computation of eigenpairs. Storage of the whole Hamiltonian matrix or even its nonzero elements in the main memory (or even on the hard disk) is unfeasible already for a four-atomic application.

An efficient algorithm that avoids the storage of the Hamiltonian matrix and which can be parallelized with OPENMP (Ref. 62) is based on the following considerations. The matrix-vector multiplication using $\mathbf{H}^{\mathrm{vP}}$ is computed as

$$\mathbf{y}=\mathbf{H}^{\mathrm{vP}}\mathbf{x}=\frac{1}{2}\tilde{\mathbf{g}}^{-1/4}\sum_{k=1}^{D}\left(\mathbf{p}_k^\dagger\sum_{l=1}^{D}(\mathbf{G}'_{kl}(\mathbf{p}_l\mathbf{x}'))\right)+\mathbf{V}\mathbf{x}, \tag{28}$$

where

$$\mathbf{G}'_{kl}=\mathbf{G}_{kl}\tilde{\mathbf{g}}^{1/2}\quad\text{and}\quad\mathbf{x}'=\tilde{\mathbf{g}}^{-1/4}\mathbf{x}. \tag{29}$$

Using $\mathbf{H}^{\mathrm{vR}}$ the multiplication is done as

$$\mathbf{y}=\mathbf{H}^{\mathrm{vR}}\mathbf{x}=\frac{1}{2}\sum_{k=1}^{D}\left(\mathbf{p}_k^\dagger\sum_{l=1}^{D}(\mathbf{G}_{kl}(\mathbf{p}_l\mathbf{x}))\right)+(\mathbf{U}+\mathbf{V})\mathbf{x}, \tag{30}$$

where $\mathbf{G}_{kl}$ $(k,l=1,2,\ldots,D)$, $\tilde{\mathbf{g}}^{-1/4}$, $\tilde{\mathbf{g}}^{1/2}$, $\mathbf{U}$, and $\mathbf{V}$ are diagonal matrices. Furthermore, the special structure of $\mathbf{p}_k$, Eq. (27), due to the direct-product basis and grid can be exploited in the matrix-vector multiplication, $\mathbf{y}_k=\mathbf{p}_k\mathbf{x}$, as

$$\mathbf{y}_k[n+p\mathfrak{N}_k]=\sum_{j=1}^{N_k}\mathbf{D}_k^{[1]}[n_k+p,j]\cdot\mathbf{x}[\,n+(j-n_k)\mathfrak{N}_k)], \tag{31}$$

where $p=-(n_k-1),\ldots,0,\ldots,N_k-(n_k-1)$, and $n=\Sigma_{k=1}^{D}(n_k-1)\mathfrak{N}_k+1$, where $\mathfrak{N}_k=\Pi_{j=k+1}^{D}N_j$. Apart from the $\mathbf{x}$ and the product $\mathbf{y}_k$ vectors only the small $\mathbf{D}_k^{[1]}$ matrices are stored. It is important to point out that using this multiplication scheme the elements of the product vector $\mathbf{y}_k$ are directly (not iteratively) computed, which is required for the parallelization of this time-consuming step (see Table I).

The total memory requirement of the algorithm using $\mathbf{H}^{\mathrm{vR}}$ corresponds to the storage of $(D(D+1)/2+D+5)\mathcal{N}$ number of 64 bit reals, which corresponds to the storage of $\mathbf{G}_{kl}=\mathbf{G}_{lk}$ $(k,l=1,2,\ldots,D)$, $(\mathbf{U}+\mathbf{V})$, the $\mathbf{y}_l$ $(l=1,2,\ldots,D)$ scratch vector, and further four working vectors of the size $\mathcal{N}$. If the Podolsky form, $\mathbf{H}^{\mathrm{vP}}$, is used, an additional vector of size $\mathcal{N}$ must be stored in the main memory containing the elements of the $\tilde{\mathbf{g}}^{-1/4}$ (diagonal) matrix.

Besides the matrix-vector multiplication, there is another important issue to consider. In principle, the Lanczos vectors spanning the Krylov subspace are orthogonal to each other by construction. However, due to the finite numerical precision of the calculation, this orthogonality is lost during the

TABLE II. ZPVE and the first 20 VBOs of $H_2{}^{16}O$, in cm^{-1}, obtained with GENIUSH using three different full, 3D models (V: valence coordinates, J: Jacobi coordinates, I: interatomic coordinates) and the CVRQD PES of Ref. 21.

Label	DOPI[a]	$\tilde{\nu}$ (3D,V)[b,c]	$\tilde{\nu}$ (3D,J)[b,d]	$\tilde{\nu}$ (3D,I)[b,e]
(0 0 0)	4638.31	4638.31 (0.00)	4638.31 (0.00)	4638.31 (0.00)
(0 1 0)	1595.08	1595.08 (0.00)	1595.08 (0.00)	1595.07 (0.00)
(0 2 0)	3152.20	3152.20 (0.00)	3152.20 (0.00)	3152.19 (0.01)
(1 0 0)	3657.05	3657.05 (0.00)	3657.05 (0.00)	3657.05 (0.00)
(0 0 1)	3755.73	3755.73 (0.00)	3755.73 (0.00)	3755.73 (0.00)
(0 3 0)	4667.57	4667.57 (0.00)	4667.57 (0.00)	$4667.\underline{47}$ (0.11)
(1 1 0)	5235.49	5235.49 (0.00)	5235.49 (0.00)	5235.49 (0.00)
(0 1 1)	5331.51	5331.51 (0.00)	5331.51 (0.00)	5331.51 (0.00)
(0 4 0)	6135.08	6135.08 (0.00)	6135.08 (0.00)	$613\underline{6.19}$ (−1.11)
(1 2 0)	6775.96	6775.96 (0.00)	6775.96 (0.00)	$6775.9\underline{1}$ (0.06)
(0 2 1)	6872.15	6872.15 (0.00)	6872.15 (0.00)	$6872.1\underline{4}$ (0.01)
(2 0 0)	7201.19	7201.19 (0.00)	7201.19 (0.00)	7201.19 (0.00)
(1 0 1)	7249.22	7249.22 (0.00)	7249.22 (0.00)	7249.22 (0.00)
(0 0 2)	7444.88	7444.88 (0.00)	7444.88 (0.00)	7444.88 (0.00)
(0 5 0)	7543.86	7543.86 (0.00)	7543.86 (0.00)	$755\underline{0.89}$ (−7.04)
(1 3 0)	8275.08	8275.08 (0.00)	8275.08 (0.00)	$8275.\underline{39}$ (−0.31)
(0 3 1)	8374.77	8374.77 (0.00)	8374.77 (0.00)	8374.75 (0.02)
(2 1 0)	8761.92	8761.92 (0.00)	8761.92 (0.00)	$8761.9\underline{3}$ (−0.01)
(1 1 1)	8807.03	8807.03 (0.00)	8807.03 (0.00)	8807.03 (0.00)
(0 6 0)	8872.17	8872.17 (0.00)	8872.17 (0.00)	$89\underline{42.88}$ (−70.71)
(0 1 2)	9000.39	9000.39 (0.00)	9000.39 (0.00)	9000.40 (0.00)

[a] Converged 3D reference results were obtained with the DOPI algorithm (Ref. 17). Exactly the same CVRQD PES and nuclear masses were applied as in the GENIUSH calculations.

[b] Results obtained with GENIUSH. Nuclear masses $m_H = 1.007\,276\,5$ u and $m_O = 15.99\,052\,6$ u and an *xxy* body-fixed frame were used throughout the calculations. Underlined digits did not converge upon the increase in the basis size due to the singularity of the Hamiltonian. Deviations from results of DOPI are given in parentheses $(\tilde{\nu}(\text{DOPI}) - \tilde{\nu})$.

[c] The active internal coordinates, $r_{1\text{v}}$, $r_{2\text{v}}$, and $\cos\theta_\text{v}$ and the Podolsky-form of the vibrational Hamiltonian, given in Eq. (19), were used. (30,30) PO-DVR grid points, each optimized on a primitive grid of 80 points and the interval $[0.5, 2.5]$ Å were used for the $r_{1\text{v}}$ and $r_{2\text{v}}$ coordinates, and 30 primitive Legendre-DVR grid points were utilized for $\cos\theta_\text{v}$.

[d] The active internal coordinates, $r_{1\text{j}}$, $r_{2\text{j}}$, and $\cos\theta_\text{j}$, and the Podolsky-form of the vibrational Hamiltonian, given in Eq. (19), were used. (30,30) PO-DVR grid points, each optimized on a primitive grid of 80 points and the interval $[0.5, 2.5]$ Å were used for the $r_{1\text{j}}$ and $r_{2\text{j}}$ coordinates, and 30 primitive Legendre-DVR grid points were utilized for $\cos\theta_\text{j}$.

[e] The active internal coordinates were r_1, r_2, and r_3. A (40,40,40) primitive grid was used on $r_1, r_2 \in [0.6, 1.5]$ Å and $r_3 \in [1.0, 2.5]$ Å intervals.

course of the Lanczos iteration. If the original orthogonality is not maintained artificially, spurious eigenvalues and copies of real eigenvalues enter the computed spectrum. Consequently, maintaining the orthogonality is highly desirable. Orthogonality of Lanczos vectors can be maintained by a simple Schmidt reorthogonalization in each Lanczos step (complete reorthogonalization) or by other more sophisticated techniques.[63] It is common to each technique that they require the storage of all the previous Lanczos vectors. In GENIUSH the Lanczos vectors of size $\mathcal{N}$ are stored on the hard disk.

The number of iteration steps required to converge the Lanczos procedure is approximately proportional to the number of required eigenpairs. The scaling of the total central processing unit (CPU) time in terms of the size of the direct-product grid for $\mathbf{H}^{\text{vR}}$ is $t_{\text{CPU}} \sim$ (No. of required eigenpairs) $\times (1 + 2DN + D^2)\mathcal{N}$. If the Podolsky form is employed, two additional vector-vector multiplications are required in each matrix-vector multiplication step.

IV. NUMERICAL RESULTS

In order to demonstrate the robustness and flexibility of the program GENIUSH, three-, four-, and five-atomic examples both in full and reduced vibrational dimensionality and using different sets of internal coordinates are presented in the next sections. The actual choice of the internal coordinates affects the convergence properties of the eigenpairs.

In most of the following examples the rearranged form of the vibrational Hamiltonian, Eq. (20), is employed. Usage of the Podolsky form, Eq. (19) affects principally the convergence of the levels influenced by the singular region of the Hamiltonian.

Before giving details about the computations and their results, let us summarize how the vibrational model can be defined in the current version of the code GENIUSH.

First, Cartesian coordinates expressed in the chosen body-fixed frame must be specified in terms of the chosen set of internal coordinates. This work is helped by a Z-matrix reader implemented in GENIUSH based on the Z-matrix reader

TABLE III. ZPVE and VBOs of $H_2{}^{16}O$, in cm^{-1}, obtained with GENIUSH using 2D vibrational models (J: Jacobi coordinates, I: interatomic coordinates, **g**: reduction in the **g** matrix, **G**: reduction in the **G** matrix) and the CVRQD PES of Ref. 21.

Label	3D[a]	$\tilde{\nu}$ (2D,J,**g**)[b,c,e]	$\tilde{\nu}$ (2D,I,**g**)[b,d,e]	$\tilde{\nu}$ (2D,J,**G**)[b,c,f]	$\tilde{\nu}$ (2D,I,**G**)[b,d,f]
(0 0 0)	4638.31	2723.50	2723.50	2723.50	$3018.0\underline{4}$
(0 1 0)	1595.08	1616.08 (−21.00)	1616.08 (−21.00)	1616.08 (−21.00)	$2182.\underline{56}$ (−587.48)
(0 2 0)	3152.20	3197.45 (−45.26)	3197.45 (−45.26)	3197.45 (−45.26)	3697.43 (−545.23)
(0 0 1)	3755.73	3711.56 (44.17)	3711.56 (44.17)	3711.56 (44.17)	$438\underline{6.53}$ (−630.80)
(0 3 0)	4667.57	4739.03 (−71.46)	$4739.0\underline{6}$ (−71.49)	4739.03 (−71.46)	$5830.\underline{27}$ (−1162.70)
(0 1 1)	5331.51	5309.39 (22.12)	5309.39 (22.12)	5309.39 (22.12)	$663\underline{3.76}$ (−1302.25)
(0 4 0)	6135.08	6232.92 (−97.84)	$6233.4\underline{3}$ (−98.35)	6232.92 (−97.84)	7231.02 (−1095.94)
(0 2 1)	6872.15	6874.32 (−2.17)	$6874.3\underline{3}$ (−2.18)	6874.32 (−2.17)	$798\underline{2.54}$ (−1110.39)
(0 0 2)	7444.88	7257.58 (187.31)	7257.58 (187.31)	7257.58 (187.31)	$89\underline{50.92}$ (−1506.04)
(0 5 0)	7543.86	7665.34 (−121.49)	$7671.\underline{84}$ (−127.98)	7665.34 (−121.49)	$9314.\underline{84}$ (−1770.99)
(0 3 1)	8374.77	8402.03 (−27.26)	$8402.1\underline{4}$ (−27.37)	8402.03 (−27.26)	$1017\underline{1.87}$ (−1797.10)

[a] Converged 3D results obtained with the GENIUSH and DOPI (Ref. 17) algorithms. Exactly the same CVRQD PES and nuclear masses were applied in the two calculations.

[b] Results obtained with GENIUSH. $r_1(HO)=0.957\,82$ Å was fixed throughout the computations. Nuclear masses, $m_H=1.007\,276\,5$ u and $m_O=15.990\,526$ u, and an *xxy* body-fixed frame were used. Underlined digits did not converge upon the increase in the basis size due to the singularity of the Hamiltonian. Deviations from 3D results are given in parentheses, $(\tilde{\nu}(3D)-\tilde{\nu}(2D))$.

[c] The active internal coordinates were the second Jacobi distance, r_{2j} and $\cos\theta_j$ in the Podolsky-form of the vibrational Hamiltonian, given Eq. (19), used here. 30 PO-DVR grid points, optimized on a grid of 80 points and the interval [0.3, 2.5] Å, were used for r_{2j}, and 30 primitive Legendre-DVR points were used for the $\cos\theta_j$ coordinate.

[d] The active internal coordinates were $r_2(HO)$ and $r_3(HH)$. A (30,30) primitive grid was used on $r_2\in[0.3,2.0]$ Å and $r_3\in[0.8,3.2]$ Å intervals.

[e] 2D models constructed with reduction in **g**.

[f] 2D models constructed with reduction in **G**.

program developed by Lopata and Kiss,[64] which allows various definitions of simple internal coordinates. Furthermore, the three interatomic coordinates and the orthogonal Jacobi coordinates have also been implemented for the case of triatomic molecules. In general, any subroutine would be appropriate which provides the Cartesian coordinates in the body-fixed frame in terms of internal coordinates.

Then, the active and constrained sets of coordinates are specified. An interval must be defined for grid points along each active vibrational coordinate. The position of the grid points can be optimized (PO-DVR). Otherwise, primitive scaled and shifted (see Ref. 18) Hermite-DVR points are used. If there are constrained coordinates, their constrained value also needs to be specified. If there are special mathematical requirements on the range of internal coordinates, e.g., in the case of the three interatomic coordinates the triangle inequality, the range of internal coordinates is automatically tested. After construction of the direct-product grid, those grid points are omitted which do not fulfill the prescribed requirements, e.g., on the ranges of coordinates. Furthermore, not only geometrical restrictions but also energetical (potential energy) requirements can be employed in order to reduce the number of grid points involved in the computation.

Then, the step size for the numerical differentiation is to be defined. If internal coordinates are defined within the framework of a *Z* matrix, first, second, and third analytic derivatives are also available.

After appropriate choices have been made for all of the above options, the representation of the kinetic energy part is completely specified. The potential energy is obtained from electronic structure computations and usually available as a force field or a (semi)global PES as implemented in a subroutine. In order to call this subroutine a user-supplied interface might be required, which converts the values of the internal coordinates actually defined for the kinetic energy operator to the input coordinates of the potential energy subroutine. If the potential energy subroutine requires the Cartesian coordinates as input parameters, it can be automatically linked to GENIUSH.

A. H_2O

$H_2{}^{16}O$ was extensively studied during the validation of the code GENIUSH for two reasons. First, accurate benchmark results in full vibrational dimensionality are easily available for this system. Second, as the system is small, full- and reduced-dimensional calculations can be carried out very fast, and numerous internal coordinate choices are possible either in full or reduced dimensionality. It is important to emphasize that all these computations are done with a single code which constructs automatically the kinetic energy representation once the coordinates are defined. From a technical point of view it is not straightforward to have a numerically robust implementation of such a universal protocol (Sec. III B and Appendix), especially if one is interested in the energy levels with spectroscopic accuracy, ~0.01 cm^{-1}, which corresponds typically to six or seven significant digits.

In the light of the discussed numerical difficulties the accuracy and flexibility of the program were carefully tested. The most relevant results are collected in Tables II and III. In all computations the CVRQD PES (Ref. 21) and the corresponding nuclear masses were used. Three-dimensional (3D) benchmark data were obtained with the DOPI code[17,18] using the same PES and masses.

1. Three-dimensional results

In Table II full 3D results obtained with GENIUSH using valence, Jacobi, and interatomic coordinates and an *xxy* body-fixed frame are compared with independent benchmark data. To switch between the different sets of coordinates used, only the coordinate definition was changed; the representation of the Hamiltonian was generated automatically by the program.

The numerical results meet the fundamental physical expectation that the converged values of computed vibrational energy levels are independent of the actual coordinate representation, and they also reproduce the benchmark data. However, it is important to point out that the convergence properties of the different sets of coordinates are different. The required number of grid points and the computational effort to achieve an expected accuracy differ significantly. In this case, the convergence is fastest for the Jacobi coordinates.

2. Two-dimensional results

Table III contains the most interesting reduced-dimensional test results. Fixing one of the O–H distances and letting the rest of the molecule move freely does not provide a numerically valuable approximation to the 3D results. Nevertheless, important theoretical relationships are reflected by these numerical results—they provide a valuable tool for checking the accuracy and consistency of reduced-dimensional models automatically constructed by GENIUSH for a given choice of coordinates.

Reductions introduced in **g** and **G** (Secs. II C and II E) were studied in these two-dimensional (2D) numerical examples. Theoretically, the reduction in **g** corresponds to fixing the constrained coordinates at given values, while reduction in **G** is merely another possible mathematical route to neglect the coupling terms between sets of coordinates. The results presented in Table III reflect this difference. If the reduction is introduced in **g**, the converged energy levels are independent of the actual choice of coordinates if the same constraints are introduced. However, if the **G** matrix is used to construct a reduced-dimensional model, the results do depend on the choice of the active coordinates even if the same coordinates were fixed at a given value. Thus, these numerical results exemplify the preference of constructing reduced-dimensional models via the **g** matrix.

Due to the difference of reduction in **g** and **G** the results of the two reduction strategies are, in general, different even if the same set of coordinates is used. The case of Jacobi coordinates with constraining the first Jacobi distance to a given value is an exception. This specific coordinate is decoupled from the rest both in the vibrational and in the rovibrational block of the **g** (**G**) matrix. The special behavior of this coordinate is reproduced by the reduced-dimensional results of GENIUSH.

B. NH_3

The inversion-tunneling motion makes ammonia an interesting molecule for spectroscopic and dynamical studies.[36,65–69] Reliable computations are straightforward only with properly chosen body-fixed frames and curvilinear internal coordinates. In the present computations the body-fixed frame was the *xxy* (scattering) frame and the primitive internal coordinates are given in Table IV. A dummy atom, X, is introduced in order to define the inversion coordinate, θ, symmetrically.[44] Symmetry adapted stretching coordinates are introduced in terms of the primitive stretching coordinates as

TABLE IV. *Z*-matrix representation of the internal coordinates of NH_3.

N						
X	N	1.0				
H1	N	r_1	X	θ		
H2	N	r_2	X	θ	H1	β_1
H3	N	r_3	X	θ	H1	$-\beta_2$

$$s_1 = \frac{1}{\sqrt{3}}(r_1 + r_2 + r_3), \quad s_2 = \frac{1}{\sqrt{6}}(2r_1 - r_2 - r_3),$$

$$s_3 = \frac{1}{\sqrt{2}}(r_2 - r_3).$$

It is worth emphasizing that only the number of degrees of freedom and the coordinate definitions were changed to specify the kinetic energy part for ammonia, which was then automatically generated by the program. In all computations the "refined" PES of Ref. 67 and the corresponding atomic masses were employed.

The effect of couplings of stretching coordinates to the tunneling-inversion motion was monitored through the comparison of inversion splittings, resulting from the low inversion barrier,[68,69] obtained from 1D, 2D, four-dimensional (4D), and (full) six-dimensional (6D) vibrational models.

1. Six-dimensional results

The full, 6D variational results obtained with GENIUSH for $^{14}NH_3$ are presented in Table V. For comparison, approximate variational results are also given there, taken from the reference publication of the actually employed PES.[67] Our converged results (convergence on the order of 0.05 cm^{-1}) up to ~6000 cm^{-1} are the first benchmark results with this PES, without introducing any approximation in the variational treatment. They improve the approximate variational results of Ref. 67 only slightly for the first few vibrational band origins (VBOs); however, for higher-lying vibrational levels substantial improvements can be observed.

2. Reduced inversion models

In Table VI 1D, 2D, and 4D reduced inversion models are compared with our full, 6D benchmark results. Reduced-dimensional models were constructed by reducing the **g** matrix, as this is the preferred route based on both theoretical (Secs. II C and II E) and numerical (Sec. IV A) observations discussed above.

In the 1D model, the only active coordinate was the θ inversion angle; the rest of the internal coordinates were fixed at their equilibrium values (their values at the minimum of the PES employed). For convenience, a 2D model was also introduced by adding the s_1 symmetric stretching coor-

TABLE V. ZPVE and VBOs of $^{14}NH_3$, in cm^{-1}, obtained with GENIUSH using a full, 6D vibrational model and the refined PES of Ref. 67 compared to approximate variational results of Ref. 67.

Label		Ref. 67	$\tilde{\nu}$ (6D)[a]		
ZPVE	A_1'	–[b]	7436.82		–
ZPVE	A_2''	0.79	0.79		(0.00)
v_2	A_1'	932.46	932.41		(0.05)
v_2	A_2''	968.14	968.15		(−0.01)
$2v_2$	A_1'	1597.38	1597.26		(0.11)
v_4	E_1'	1626.22	1625.62	[0.00]	(0.60)
v_4	E_1''	1627.33	1626.73	[0.00]	(0.60)
$2v_2$	A_2''	1882.09	1882.18		(−0.09)
$3v_2$	A_1'	2384.06	2384.20		(−0.14)
v_2+v_4	E_1'	2540.27	2539.61	[0.00]	(0.67)
v_2+v_4	E_1''	2585.94	2585.39	[0.00]	(0.55)
$3v_2$	A_2''	2895.50	2895.74		(−0.24)
$2v_2+v_4$	E_1'	3189.80	3189.11	[0.00]	(0.68)
$2v_4$	A_1'	3215.55	3214.47		(1.09)
$2v_4$	A_2''	3217.23	3216.15		(1.07)
$2v_4$	E_1'	3239.85	3238.55	[0.00]	(1.29)
$2v_4$	E_1''	3241.34	3240.05	[0.00]	(1.28)
v_1	A_1'	3336.04	3335.78		(0.26)
v_1	A_2''	3337.10	3336.84		(0.26)
v_3	E_1'	3443.68	3443.92	[0.00]	(−0.24)
v_3	E_1''	3444.02	3444.27	[0.00]	(−0.24)
$4v_2$	A_1'	3462.69	3463.00		(−0.31)
$2v_2+v_4$	E_1''	3502.85	3502.44	[0.00]	(0.41)
$3v_2+v_4$	E_1'	4008.38	4008.04	[0.00]	(0.33)
$4v_2$	A_2''	4062.10	4062.47		(−0.37)
v_2+2v_4	A_1'	4113.78	4112.42		(1.36)
v_2+2v_4	E_1'	4134.67	4133.22	[0.00]	(1.45)
v_2+2v_4	A_2''	4172.03	4171.08		(0.95)
v_2+2v_4	E_1''	4192.28	4191.09	[0.00]	(1.20)
v_1+v_2	A_1'	4294.26	4294.13		(0.13)
v_1+v_2	A_2''	4319.95	4319.77		(0.18)
v_2+v_3	E_1'	4416.71	4416.94	[0.00]	(−0.24)
v_2+v_3	E_1''	4435.33	4435.58	[0.00]	(−0.25)
$3v_2+v_4$	E_1''	4531.53	4531.32	[0.00]	(0.21)
$5v_2$	A_1'	4695.51	4695.92		(−0.41)
$2v_2+2v_4$	A_1'	4754.99	4753.71		(1.28)
$2v_2+2v_4$	E_1'	4773.61	4772.19	[0.01]	(1.42)
$3v_4$	E_1'	4798.66	4796.02	[0.00]	(2.64)
$3v_4$	E_1''	4800.92	4798.30	[0.01]	(2.62)
$3v_4$	A_1'	4840.78	4838.67		(2.11)
$3v_4$	A_2'	4841.68	4838.83		(2.86)
$3v_4$	A_2''	4842.73	4840.64		(2.09)
$3v_4$	A_1''	4843.70	4840.88		(2.83)
v_3+v_4	E_1'	4955.37	4954.10	[0.00]	(1.27)
v_3+v_4	E_1''	4956.62	4955.35	[0.00]	(1.27)
v_1+2v_2	A_1'	4999.36	4999.21		(0.15)
v_1+v_4	A_2'	5049.93	5049.17		(0.76)
v_1+v_4	A_1''	5050.57	5049.82		(0.76)
v_3+v_4	E_1'	5052.31	5051.78	[0.00]	(0.53)
v_3+v_4	E_1''	5052.90	5052.37	[0.00]	(0.53)
v_3+v_4	A_2''	5066.32	5065.64		(0.68)
v_3+v_4	A_1'	5066.33	5065.65		(0.68)
$2v_2+2v_4$	A_2''	5093.43	5092.98		(0.45)
$4v_2+v_4$	E_1'	5106.36	5106.21	[0.00]	(0.15)
$2v_2+2v_4$	E_1''	5113.71	5112.82	[0.01]	(0.89)
v_1+2v_2	E_1'	5143.62	5143.77	[0.00]	(−0.15)
v_1+2v_2	A_2''	5233.03	5232.82		(0.21)
v_1+2v_2	E_1''	5352.59	5352.86	[0.00]	(−0.27)
$5v_2$	A_2''	5362.03	5362.51		(−0.47)

TABLE V. (*Continued.*)

Label		Ref. 67	$\tilde{\nu}$ (6D)[a]		
$3v_2+2v_4$	A_1'	5604.17	5603.91		(0.26)
$3v_2+2v_4$	E_1'	5624.11	5623.30	[0.02]	(0.81)
v_2+3v_4	E_1'	5676.16	5672.94	[0.01]	(3.22)
$4v_2+v_4$	E_1''	5709.68	5709.42	[0.01]	(0.25)
v_2+3v_4	A_1'	5714.66	5712.38		(2.28)
v_2+3v_4	A_2'	5717.11	5713.59		(3.53)
$3v_2+v_1$	A_1'	5736.80	5736.53		(0.28)
v_2+3v_4	E_1''	5752.79	5750.80	[0.02]	(2.00)
v_2+3v_4	A_2''	5786.64	5784.87		(1.76)
v_2+3v_4	A_1''	5788.34	5785.52		(2.82)
$3v_2+v_3$	E_1'	5855.40	5855.64	[0.00]	(−0.24)

[a] Results obtained with GENIUSH. Number of optimized grid points along the actual internal coordinates $(r_1,r_2,r_3,\theta,\beta_1,\beta_2)$ was (13,13,13,27,13,13). Each set of points was optimized on a primitive grid of 80 points and on $r_1,r_2,r_3 \in [0.35,2.00]$ Å, $\theta \in [5,175]^{\circ}$, and $\beta_1,\beta_2 \in [20,220]^{\circ}$ intervals. Atomic masses, $m_{\mathrm{H}} = 1.007\,825$ u and $m_{\mathrm{N}} = 14.003\,074$ u, and an *xxy* body-fixed frame were employed. Deviations between degenerate levels due to the incomplete convergence are given in brackets, $[\tilde{\nu}(\text{higher}) - \tilde{\nu}(\text{lower})]$. Deviations from approximate variational results of Ref. 67, $(\tilde{\nu}(\text{Ref. } 67) - \tilde{\nu}(\text{6D}))$, are given in parentheses.

[b] ZPVE was not reported in Ref. 67.

dinate while restricting $s_2 = s_3 = 0$, which is also equivalent to requiring $r_1 = r_2 = r_3$. A next step to increment this 2D model is to add all the stretching vibrations either by using (θ, s_1, s_2, s_2) or the (θ, r_1, r_2, r_3) set of the coordinates. The converged results are independent of the active coordinates as the reduction was introduced in the **g** matrix.

Concerning the splittings resulting from these reduced-dimensional models, it can be observed that already the 1D results are reliable in a semiquantitative sense. Not surprisingly, adding the symmetric stretching and then all the stretching coordinates improve the inversion splittings and the absolute value of the VBOs [referenced to the corresponding zero-point vibrational energies (ZPVEs)]. Interestingly, the inversion splittings of the lower-lying levels $(v_2, 2v_2, 3v_2)$ changes unpredictably, whereas splittings of highly excited levels $(4v_2, 5v_2)$ are clearly improved by turning on the stretching contributions.

C. CH_4

CH_4 is a typical semirigid molecule with a single well-defined and deep minimum on its ground-state PES. Accurate variational computation of the VBOs is still not a straightforward task[25,70] because of the molecule's nine fully coupled vibrational degrees of freedom.

In the previous sections the accuracy and flexibility of the GENIUSH code was demonstrated by computations presented for water and ammonia both in full and reduced vibrational dimensionality and using a variety of internal coordinates. Besides these virtues, a universal code must be numerically efficient not to be constrained to low-dimensional systems. Results of a full, 9D computation are presented in Table VIII in order to demonstrate the largest system (the maximally coupled vibrational degrees of freedom) whose study is computationally feasible with the current version of GENIUSH. For convenience, bond lengths, angles, and torsions, defined in Table VII, were employed as internal coordinates. It is worth emphasizing again that only the coordinate definitions are to be specified; the representation of the kinetic energy is automatically generated by the program for the computation of energy levels and wave functions. Table VIII shows VBOs of the largest feasible computation for CH_4 using the T8 force field;[71] they are converged to about 0.5 cm^{-1}.

In order to improve these results one can (a) further increase the size of the direct-product grid until convergence; (b) introduce another set of internal coordinates in the hope of an increased convergence rate; (c) make use of the high symmetry of the actual system to split up the whole problem into independent subproblems, thus reducing the size of matrices; and (d) adopt sophisticated contraction techniques in order to make the representation more compact. Along all these four directions work is in progress. It is also worth pointing out that the DEWE code,[39,61] working in normal coordinates, produces converged energy levels using a relatively small direct-product grid. This result shows that normal coordinates and the corresponding basis are very well suited for the vibrational computations on this semirigid molecule having a single, well-defined potential energy minimum.

V. SUMMARY AND CONCLUSIONS

Using the variational method with a full-dimensional vibrational Hamiltonian the numerically exact vibrational energy levels and wave functions can be obtained, limited only by the accuracy of the actual representation of the PES and the BO approximation. Due to the exponential scaling of the size of the problem with the number of degrees of freedom, accurate variational treatment in full vibrational dimensionality is still a challenge for systems containing more than four nuclei. Apart from the enormous size, the versatility of the possible choices of body-fixed frames and internal coordinates for systems consisting more than four particles has also been a source of difficulty in dynamical computations. The unfavorable scaling means that the choice of physically

TABLE VI. ZPVE and VBOs of $^{14}NH_3$, in cm^{-1}, as obtained with GENIUSH using full- and reduced-dimensional inversion models (constructed by reduction in the **g** matrix) and the refined PES of Ref. 67.

Label		$\tilde{\nu}$ (6D)^{a,b}		$\tilde{\nu}$ (1D)^{a,c}		$\tilde{\nu}$ (2D)^{a,d}		$\tilde{\nu}$ (4D)^{a,e}	
ZPVE	A'_1	7436.82		521.43		2256.74		5828.91	
ZPVE	A''_2	0.79	{0.79}	1.13	{1.13}	1.28	{1.28}	0.58	{0.58}
v_2	A'_1	932.41		930.57		900.48		945.65	
v_2	A''_2	968.15	{35.74}	979.80	{49.23}	952.80	{52.31}	973.89	{28.23}
$2v_2$	A'_1	1597.26		1586.98		1537.60		1626.11	
$2v_2$	A''_2	1882.18	{284.91}	1918.86	{331.88}	1868.39	{330.78}	1884.43	{258.32}
$3v_2$	A'_1	2384.20		2439.66		2375.33		2383.23	
$3v_2$	A''_2	2895.74	{511.55}	2986.24	{546.58}	2906.55	{531.22}	2882.32	{499.09}
v_1	A'_1	3335.78		—		3442.02		3337.87	
v_1	A''_2	3336.84	{1.06}	—		3443.99	{1.97}	3338.97	{1.11}
v_3	E'_1	3443.92		—		—		3458.51	
v_3	E''_1	3444.27	{0.35}	—		—		3458.75	{0.25}
$4v_2$	A'_1	3463.00		3586.52		3488.33		3441.38	
$4v_2$	A''_2	4062.47	{599.47}	4225.87	{639.35}	4102.63	{614.31}	4033.36	{591.97}
v_1+v_2	A'_1	4294.13		—		4376.79		4313.56	
v_1+v_2	A''_2	4319.77	{25.64}	—		4412.84	{36.05}	4332.32	{18.76}
v_2+v_3	E'_1	4416.94		—		—		4442.40	
v_2+v_3	E''_1	4435.58	{18.64}	—		—		4456.17	{13.77}
$5v_2$	A'_1	4695.92		4901.01		4750.52		4660.07	
v_1+2v_2	A'_1	4999.21		—		5041.58		5040.47	
v_1+2v_2	E'_1	5143.77		—		—		5190.63	
v_1+2v_2	A''_2	5232.82	{233.61}	—		5322.62	{281.04}	5241.47	{201.00}
v_1+2v_2	E''_1	5352.86	{209.10}	—		—		5372.45	{181.82}
$5v_2$	A''_2	5362.51	{666.59}	5608.26	{707.24}	5429.90	{679.38}	5320.99	{660.92}

[a] Results obtained with GENIUSH. Inversion splittings are given in braces $\{\nu_i(\text{upper})-\nu_i(\text{lower})\}$. Atomic masses, $m_H=1.007\,825$ u and $m_N=14.003074$ u, and an *xxy* body-fixed frame were used in the calculations.

[b] Results obtained with a 6D vibrational model, see Table V.

[c] Results obtained with a 1D vibrational model. The single active internal coordinate was θ. Converged results were obtained by using 40 grid points optimized on a primitive grid of 100 points and on a $\theta \in [5,175]^\circ$ interval. Constrained coordinates were fixed at $r_1=r_2=r_3=1.010\,31$ Å and $\beta_1=\beta_2=120°$.

[d] Results obtained with a 2D vibrational model. The active internal coordinates were θ and s_1. (25,15) PO-DVR grid points, each optimized on a primitive grid of 80 points and on $\theta \in [5,175]^\circ$ and $s_1 \in \sqrt{3}[0.35,2.5]$ Å intervals, were utilized. The rest of the coordinates were fixed at $s_2=0$, $s_3=0$, and $\beta_1=\beta_2=120°$.

[e] Results obtained with a 4D vibrational model. The active internal coordinates were θ and r_1, r_2, r_3. (25,15,15,15) PO-DVR grid points, each optimized on a primitive grid of 80 points and on $\theta \in [5,175]^\circ$ and r_1, r_2, $r_3 \in (0.35,2.5)$ Å intervals, were utilized. The rest of the coordinates were fixed at $\beta_1=\beta_2=120°$.

meaningful and thus efficient body-fixed frames and internal coordinates is of extreme importance when one is aimed at tackling medium-sized systems.

In this paper a simple but universal strategy is presented allowing variational vibrational computations using arbitrarily defined embeddings and internal coordinates and full- or reduced-dimensional models, all this in a single code. A highly desirable feature of the GENIUSH protocol, where GENIUSH stands for general (GE) (ro)vibrational code with numerical (N), internal-coordinate (I), user-specified Hamiltonians (USH), is that the vibrational Hamiltonian of arbitrarily chosen body-fixed frame and internal coordinates is constructed automatically during the course of the calculation through numerical evaluations. This means that there is no need to know the often complicated form of the kinetic energy operator in internal coordinates *a priori*. The matrices corresponding to this Hamiltonian are constructed using a DVR on a direct-product or truncated (preoptimized) DVR grid. The useful features of DVR allow a straightforward and exact inclusion of an arbitrary representation of the potential energy surface (PES), as well as terms of the kinetic energy operator corresponding to the actual coordinate choice. Eigenvalues and eigenvectors of the huge but sparse Hamiltonian matrix are provided by an iterative eigensolver.

Concerning the technical details of the implementation, we found that the **t**-vector formalism is much better adaptable to our scheme than the **s**-vector one,[9,48] though the two are equivalent from a theoretical point of view. In the **t**-vector formalism the rearranged form of the vibrational Hamiltonian, Eq. (20) is often used.[44,46] In order to construct the kinetic energy part of the Hamiltonian matrix of this form, first, second, and third derivatives of the Cartesian coordinates in terms of the internal coordinates must be computed with increased numerical precision if derivatives are evaluated numerically. Otherwise, analytic derivatives are required. In the current version of GENIUSH numerical derivatives of any kind of coordinate choice can be evaluated using 128 bit reals (quadruple precision in FORTRAN), and analytic derivatives are available for the *xxy* (scattering) frame and a *Z*-matrix-type definition of internal coordinates.

The DVR allows an efficient implementation of the Podolsky-form, Eq. (19), of the (ro)vibrational Hamiltonian, which requires only the computation of the first coordinate derivatives on the expense of a slightly higher memory requirement and CPU usage in the eigensolver part. Evaluation of only the first derivatives of body-fixed Cartesian coordi-

TABLE VII. *Z*-matrix representation of internal coordinates of CH_4.

C						
H1	C	r_1				
H2	C	r_2	H1	θ_1		
H3	C	r_3	H2	θ_2	H1	β_1
H4	C	r_4	H3	θ_3	H1	$-\beta_2$

nates in terms of the internal coordinates is not only computationally less expensive but requires a less robust numerical procedure than that for second and especially third derivatives.

Test vibrational computations for H_2O were carried out in full and reduced vibrational dimensionality. Validation of the results was made by comparing the 3D results with independent benchmark data and by checking the fulfillment of fundamental theoretical relationships. If numerical derivatives were computed only with 64 bit reals (double precision in FORTRAN) an error of a couple of wavenumbers appeared in the results compared to the accurate reference data or results obtained with increased precision (128 bit reals) numerical or standard precision (64 bit reals) but exact, analytic derivatives.

Due to the universal ideas lying behind the GENIUSH algorithm, the implementation of reduced-dimensional vibrational models is straightforward. Reduced-dimensional models can be constructed either by reducing the **g** or the **G** matrices. Both routes are implemented in GENIUSH; however, theoretical considerations and their numerical demonstrations through 2D models of H_2O indicate that reduction in **g** should be the preferred route. A simple physical requirement, the independence of the converged eigenpairs from the choice of the active coordinates, holds only if the reduced model is constructed by reducing the **g** matrix but fails, in general, if the **G** matrix is reduced.

Once the main technical difficulties in the implementation of such a universal vibrational algorithm were properly addressed and solved, the inversion tunneling in ammonia was examined through a variety of full- and reduced-dimensional models. The freedom of using a range of vibrational models strongly relies on the automatic construction of the actual kinetic energy representation provided by GENIUSH. Our computations show that already the 1D inversion-only model provides a semiquantitative approximation to the exact inversion splittings (the constrained coordinates are fixed at their equilibrium values). Incrementing this 1D model by stretching coordinates allows the construction of 2D and 4D stretching-inversion models. Improvement in the splittings of lower-lying states is not systematic, while the higher excited states are clearly improved. Furthermore, our 6D results are the first benchmark data, without introducing any approximations, obtained with the actually employed refined PES of Ref. 67.

Based on our experience, in molecules most reduced-dimensional vibrational models provide only a semiquantitative approximation to the full-dimensional results. We expect that the main virtues of reduced-dimensional models can be exploited in at least two ways. First, wave functions of reduced-dimensional Hamiltonians can serve as a kind of "preoptimized basis" to the solution of the full-dimensional problem. This philosophy has already been exploited in the present work via usage of preoptimized DVR points (PO-DVR). In order to carry out such a preoptimization in higher dimensions one would likely adopt one of the well-known contraction techniques[25,72] using two- or multiple-stage contractions. Our preliminary results on contraction techniques adopted in GENIUSH indicate that this is a promising way of

TABLE VIII. ZPVE and VBOs of $^{12}CH_4$, in cm^{-1}, obtained with GENIUSH using a full, 9D, vibrational model and the T8 force field of Ref. 71.

Label		DEWE[a,c]	$\tilde{\nu}$ (9D)[b,c]		
(00)(00)	A_1	9691.54	9691.39		(0.14)
(00)(01)	F_2	1311.74	1311.74	[0.03]	(0.01)
(00)(10)	E	1533.25	1533.23	[0.00]	(0.01)
(00)(02)	A_1	2589.77	2589.10		(0.67)
(00)(02)	F_2	2616.23	2616.10	[0.26]	(0.13)
(00)(02)	E	2627.29	2626.90	[0.00]	(0.39)
(00)(11)	F_2	2831.52	2830.92	[0.34]	(0.60)
(00)(11)	F_1	2846.90	2846.84	[0.15]	(0.07)
(10)(00)	A_1	2913.76	2912.52		(1.24)
(01)(00)	F_2	3013.60	3012.53	[0.02]	(1.07)
(00)(20)	A_1	3063.48	3062.87		(0.61)
(00)(20)	E	3065.00	3064.66	[0.00]	(0.35)

[a] Converged results obtained with the DEWE program (Ref. 39) using eight grid points for the bending-type and seven grid points for the stretching-type normal coordinates.

[b] Results obtained with GENIUSH. 7 PO-DVR points for the stretching, r_1, r_2, r_3, r_4, 7 PO-DVR points for the bending $\theta_1, \theta_2, \theta_3$, and 11 PO-DVR points for the torsion coordinates, β_1, β_2, were used. Each set of points was optimized on a primitive grid of 80 points and on $r_1, r_2, r_3, r_4 \in [0.3, 2.5]$ Å, $\theta_1, \theta_2, \theta_3 \in [1, 179]^o$, and $\beta_1, \beta_2 \in [50, 190]^o$ intervals. An *xxy* body-fixed frame was employed. Deviations between degenerate levels due to the incomplete convergence are given in brackets $[\tilde{\nu}(\text{largest}) - \tilde{\nu}(\text{lowest})]$. Deviations from the converged results obtained with DEWE are given in parentheses, $(\tilde{\nu}(\text{DEWE}) - \tilde{\nu}(\text{9D}))$.

[c] Nuclear masses, $m_C = 11.996\,709$ u and $m_H = 1.007\,276\,0$ u were used throughout the computations.

extending our current limits toward larger systems treatable in full vibrational dimensionality. As for the current computational limitations, a maximum of nine coupled vibrational degrees of freedom can be handled, as was demonstrated for methane. Second, a possible fruitful application of reduced-dimensional models could be the study of intramolecular dynamics of complexes consisting of semirigid monomer units. For such systems, reliable results can be expected from an approximate model in which the vibrational degrees of freedom of the monomers are fixed (or perhaps relaxed along the active dimensions) and only the intramolecular degrees of freedom are included explicitly.

The present implementation of GENIUSH suffers from two bottlenecks. We think the main deficiency of the current version is that symmetry properties of the molecular systems are not exploited. At this point, it is worth emphasizing that in spite of the fact that our actual test systems have symmetry, all computations were carried out as if the symmetry operators of the systems corresponded to the C_1 point group. Working in DVR, exploitation of symmetry in a universal code is not as straightforward as it is in finite basis representation.[48] Nevertheless, we are currently working, for example, on the usage of eigenfunctions of reduced-dimensional model Hamiltonians as a preoptimized basis for the full problem. Such preoptimized basis functions carry the symmetry properties of the reduced Hamiltonians; consequently, utilization of symmetry properties for the solution of the full problem is expected to be more straightforward. Besides the apparent gain in the required computational resources (memory, disk, CPU), exploitation of symmetry would provide symmetry labels to the computed vibrational levels that is also of considerable utility.

As to the second deficiency, one could point out that in this study vibration-only computations have been presented. However, we do not consider this point as a serious deficiency, as we are not aware of any fundamental limitation which would prohibit the extension of the current approach to the computation of rotational-vibrational energy levels and the subsequent determination of, for example, line-by-line absorption intensities. Work is in progress along this line, as well.

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APPENDIX: COMPUTATION OF THE EXTRAPOTENTIAL TERM

Logarithmic derivatives can be determined very efficiently by using Gauss elimination,[46] $k=1,2,\ldots,D+2$,

$$g_{ij}^{(k+1)} := g_{ij}^{(k)} - \frac{g_{ik}^{(k)}}{g_{kk}^{(k)}} g_{kj}^{(k)}, \quad i=1,2,\ldots,D+3, \quad j=k+1,\ldots,D+3, \tag{A1}$$

and $\mathbf{g}^{(1)}=\mathbf{g}$. In the course of the Gauss elimination steps derivatives of $\ln \tilde{g}$ and $\ln \tilde{G}$ are computed iteratively, as

$$\frac{\partial \ln \tilde{g}}{\partial q_m} = \frac{\partial}{\partial q_m} \ln \prod_{k=1}^{D+3} g_{kk}^{(k)} = \frac{\partial}{\partial q_m} \sum_{k=1}^{D+3} \ln g_{kk}^{(k)} = \sum_{k=1}^{D+3} \frac{1}{g_{kk}^{(k)}} \frac{\partial g_{kk}^{(k)}}{\partial q_m} \tag{A2}$$

and

$$\begin{aligned}\frac{\partial^2 \ln \tilde{g}}{\partial q_n \partial q_m} &= \frac{\partial}{\partial q_n} \sum_{k=1}^{D+3} \frac{1}{g_{kk}^{(k)}} \frac{\partial g_{kk}^{(k)}}{\partial q_m} \\ &= \sum_{k=1}^{D+3} \left[\frac{1}{g_{kk}^{(k)}} \frac{\partial^2 g_{kk}^{(k)}}{\partial q_n \partial q_m} - \frac{1}{(g_{kk}^{(k)})^2} \frac{\partial g_{kk}^{(k)}}{\partial q_n} \frac{\partial g_{kk}^{(k)}}{\partial q_m} \right].\end{aligned} \tag{A3}$$

In the kth step of the Gauss elimination, the $\partial \mathbf{g}^{(k+1)}/\partial q_m$ and $\partial^2 \mathbf{g}^{(k+1)}/\partial q_n \partial q_m$ matrices are computed by using the elements of $\partial \mathbf{g}^{(k)}/\partial q_m$ and $\partial^2 \mathbf{g}^{(k)}/\partial q_n \partial q_m$ matrices. In the kth step the $(k+1)$th elements of the expressions in Eqs. (A2) and (A3) are evaluated. In each elimination step always only the kth and $(k+1)$th derivative matrices are stored, so the procedure has only a modest memory requirement.

$$\frac{\partial g_{ij}^{(k+1)}}{\partial q_m} = \frac{\partial g_{ij}^{(k)}}{\partial q_m} - \frac{\partial g_{ik}^{(k)}}{\partial q_m} \frac{g_{kj}^{(k)}}{g_{kk}^{(k)}} + \frac{g_{ik}^{(k)}}{(g_{kk}^{(k)})^2} \frac{\partial g_{kk}^{(k)}}{\partial q_m} g_{kj}^{(k)} - \frac{g_{ik}^{(k)}}{g_{kk}^{(k)}} \frac{\partial g_{kj}^{(k)}}{\partial q_m}, \tag{A4}$$

$$\begin{aligned}\frac{\partial^2 g_{ij}^{(k+1)}}{\partial q_n \partial q_m} = {} & \frac{\partial^2 g_{ij}^{(k)}}{\partial q_n \partial q_m} - \frac{\partial^2 g_{ik}^{(k)}}{\partial q_n \partial q_m} \frac{g_{kj}^{(k)}}{g_{kk}^{(k)}} + \frac{\partial g_{ik}^{(k)}}{\partial q_m} \frac{\partial g_{kk}^{(k)}}{\partial q_n} \frac{g_{kj}^{(k)}}{(g_{kk}^{(k)})^2} \\ & - \frac{\partial g_{ik}^{(k)}}{\partial q_m} \frac{1}{g_{kk}^{(k)}} \frac{\partial g_{kj}^{(k)}}{\partial q_n} + \frac{\partial g_{ik}^{(k)}}{\partial q_n} \frac{g_{kj}^{(k)}}{(g_{kk}^{(k)})^2} \frac{\partial g_{kk}^{(k)}}{\partial q_m} \\ & - 2 \frac{g_{ik}^{(k)}}{(g_{kk}^{(k)})^3} \frac{\partial g_{kk}^{(k)}}{\partial q_n} \frac{\partial g_{kk}^{(k)}}{\partial q_m} g_{kj}^{(k)} + \frac{g_{ik}^{(k)}}{(g_{kk}^{(k)})^2} \frac{\partial^2 g_{kk}^{(k)}}{\partial q_n \partial q_m} g_{kj}^{(k)} \\ & + \frac{g_{ik}^{(k)}}{(g_{kk}^{(k)})^2} \frac{\partial g_{kk}^{(k)}}{\partial q_m} \frac{\partial g_{kj}^{(k)}}{\partial q_n} - \frac{\partial g_{ik}^{(k)}}{\partial q_n} \frac{1}{g_{kk}^{(k)}} \frac{\partial g_{kj}^{(k)}}{\partial q_m} \\ & + \frac{g_{ik}^{(k)}}{(g_{kk}^{(k)})^2} \frac{\partial g_{kk}^{(k)}}{\partial q_n} \frac{\partial g_{kj}^{(k)}}{\partial q_m} - \frac{g_{ik}^{(k)}}{g_{kk}^{(k)}} \frac{\partial^2 g_{kj}^{(k)}}{\partial q_n \partial q_m},\end{aligned} \tag{A5}$$

where $i=1,2,\ldots,D+3$, $j=k+1,\ldots,D+3$, and $n,m=1,2,\ldots,D$. In some cases the form Eq. (22) is more favorable to use (see the reduced-dimensional models). The quantities $\partial \ln \tilde{G}/\partial q_m$ and $\partial^2 \ln \tilde{G}/\partial q_n \partial q_m$ are evaluated similarly to the procedure described in Eqs. (A1)–(A5).

Next, derivatives $\partial \mathbf{G}/\partial q_m$ and, if Eq. (22) is used, also $\partial^2 \mathbf{G}/\partial q_n \partial q_m$ must be considered. Exploiting the relationship $\mathbf{G}=\mathbf{g}^{-1} \in \mathcal{R}^{(D+3)\times(D+3)}$, the missing derivatives can be expressed as

$$\frac{\partial \mathbf{G}}{\partial q_m} = -\mathbf{G} \frac{\partial \mathbf{g}}{\partial q_m} \mathbf{G}, \tag{A6}$$

$$\frac{\partial^2 \mathbf{G}}{\partial q_n \, \partial q_m} = \mathbf{G}\frac{\partial \mathbf{g}}{\partial q_n}\mathbf{G}\frac{\partial \mathbf{g}}{\partial q_m}\mathbf{G} + \mathbf{G}\frac{\partial \mathbf{g}}{\partial q_m}\mathbf{G}\frac{\partial \mathbf{g}}{\partial q_n}\mathbf{G} - \mathbf{G}\frac{\partial^2 \mathbf{g}}{\partial q_n \, \partial q_m}\mathbf{G}. \tag{A7}$$

Then the matrices $\partial \mathbf{g}/\partial q_m$ and $\partial^2 \mathbf{g}/\partial q_n \partial q_m$ also involved in the above formulae are left to be considered,

$$\frac{\partial g_{kl}}{\partial q_m} = \sum_{i=1}^{N} m_i \sum_{a} \left(\frac{\partial t_{iak}}{\partial q_m} t_{ial} + t_{iak} \frac{\partial t_{ial}}{\partial q_m} \right), \tag{A8}$$

$$\frac{\partial^2 g_{kl}}{\partial q_n \, \partial q_m} = \sum_{i=1}^{N} m_i \sum_{a} \left(\frac{\partial^2 t_{iak}}{\partial q_n \, \partial q_m} t_{ial} + \frac{\partial t_{iak}}{\partial q_n} \frac{\partial t_{ial}}{\partial q_m} + \frac{\partial t_{iak}}{\partial q_m} \frac{\partial t_{ial}}{\partial q_n} + t_{iak} \frac{\partial^2 t_{ial}}{\partial q_n \, \partial q_m} \right), \tag{A9}$$

where $n,m=1,2,\ldots,D$ and $k,l=1,2,\ldots,D+3$.

Now, all the terms in the kinetic energy operator are expressed in terms of $\mathbf{t}_{im}$, $\partial \mathbf{t}_{im}/\partial q_l$, $\partial^2 \mathbf{t}_{im}/\partial q_k \partial q_l$, $i=1,2,\ldots,N$, $m=1,2,\ldots,D+3$, $k,l=1,2,\ldots,D$ ($\mathbf{t}$-vector formalism). For the vibrational part, i.e., k, l, $m=1,2,\ldots,D$, the $\mathbf{t}$ vectors and their derivatives are

$$\mathbf{t}_{im} = \frac{\partial \mathbf{x_i}}{\partial q_m}, \tag{A10}$$

$$\frac{\partial \mathbf{t}_{im}}{\partial q_l} = \frac{\partial^2 \mathbf{x_i}}{\partial q_l \, \partial q_m}, \tag{A11}$$

$$\frac{\partial^2 \mathbf{t}_{im}}{\partial q_k \, \partial q_l} = \frac{\partial^3 \mathbf{x_i}}{\partial q_k \, \partial q_l \, \partial q_m}, \tag{A12}$$

whereas for the rotational part, $m=D+1,\ D+2,\ D+3$, $k,l=1,2,\ldots,D$ they are

$$\mathbf{t}_{im} = \mathbf{e}_m \times \mathbf{x_i}, \tag{A13}$$

$$\frac{\partial \mathbf{t}_{im}}{\partial q_l} = \mathbf{e}_m \times \frac{\partial \mathbf{x_i}}{\partial q_l}, \tag{A14}$$

$$\frac{\partial^2 \mathbf{t}_{im}}{\partial q_k \, \partial q_l} = \mathbf{e}_m \times \frac{\partial^2 \mathbf{x_i}}{\partial q_k \, \partial q_l}, \tag{A15}$$

where $\mathbf{x}_i=(x_{ix},x_{iy},x_{iz})$ are the Cartesian coordinates in the body-fixed frame. First, second, and third derivatives, $\partial x_{ia}/\partial q_m$, $\partial^2 x_{ia}/\partial q_l \partial q_m$, and $\partial^3 x_{ia}/\partial q_k \partial q_l \partial q_m$ are determined numerically or analytically.

Let us first consider the numerical procedure. The procedure evaluating numerical derivatives uses an expression (a subroutine) which provides the Cartesian coordinates in the body-fixed frame, x_{ia}, in terms of the internal coordinates, q_m ($m=1,2,\ldots,D$). Primarily, the central difference formula is used to compute the numerical derivatives.

In the case of numerical differentiation the accuracy is a central question. For instance, if the terms in Eq. (21) were directly computed by means of inserting their arguments in the finite difference formulas, numerical instabilities or limited accuracy of the results might arise. In GENIUSH, the flexible type declaration of FORTRAN 90 is employed; thus, the accuracy of the numerical representation of the variables involved in the computation of $\partial x_{ia}/\partial q_m$, $\partial^2 x_{ia}/\partial q_l \partial q_m$, and $\partial^3 x_{ia}/\partial q_k \partial q_l \partial q_m$ can be easily increased to the required level. In this work $<0.01\ \mathrm{cm}^{-1}$ was the prescribed accuracy of the computed eigenvalues. The step of differentiation and the number representation were chosen accordingly, typically 10^{-5} and ~33 digits (similar to quadruple precision) turned out to be safe and appropriate choices.

Although the numerical derivative routines provide a perfectly black-box treatment of the actual choice of internal coordinates and the body-fixed frame, they are generally slower than their analytic counterparts. Due to efficiency reasons, first, second, and third analytic derivatives of Cartesian coordinates in the body-fixed frame in terms of internal coordinates are also implemented in GENIUSH for the case of an arbitrary *Z*-matrix and the *xyz* frame. The analytic derivative part of the program relies on the chain rule, and it is based on the collection of derivative subroutines of several elementary functions (product, ratio, sine, cosine, etc.), providing a modular and easily expandable structure.

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