Computing vibrational energy levels of CH₄ with a Smolyak collocation method

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Abstract

In this paper we demonstrate that it is possible to apply collocation to compute vibrational energy levels of a five-atom molecule using an exact kinetic energy operator (with cross terms and coordinate-dependent coefficients). This is made possible by using: 1) a pruned basis of products of univariate functions; 2) a Smolyak grid made from nested sequences of grids for each coordinate; 3) a collocation method that obviates the need to solve a generalized eigenvalue problem; 4) an efficient sequential transformation between the (nondirect product) grid and the (nondirect product) basis representations; and 4) hierarchical univariate functions that make it possible to avoid storing large intermediate vectors. The accuracy of the method is confirmed by computing 500 vibrational energy levels of methane.

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INTRODUCTION

When perturbation theory is not adequate, vibrational energy levels and wavefunctions are usually determined by solving an eigenvalue problem, $\mathbf{A}\mathbf{U} = \mathbf{B}\mathbf{U}$. For molecules with more than about four atoms, this is difficult for two reasons: 1) the matrix (matrices) $\mathbf{A}$ (and $\mathbf{B}$) is (are) large and therefore computing eigenvalues and eigenvectors is costly; 2) simply calculating matrix elements (or if an iterative eigensolver is used) and matrix-vector products is costly. In most calculations of this kind, $\mathbf{A} = \mathbf{H}$ represents the Hamiltonian operator in a chosen basis. [1–3] Such calculations are called variational (although they are not truly variational unless the Hamiltonian matrix elements are exact). Alternatively, $\mathbf{A}$ can be obtained by applying the Hamiltonian operator to basis functions and evaluating at points. This approach is called collocation. [4] Collocation reduces the cost of 2), i.e. the cost of computing matrix elements and matrix-vector products. In a series of papers, we have developed a collocation method for computing vibrational spectra. [5–8] In a variational method, the $\mathbf{H}$ elements are integrals. Collocation obviates the need to evaluate integrals. Collocation has other advantages: 1) errors in energy levels and wavefunctions can be systematically reduced by improving only the basis (it is not necessary to also improve the quadrature) [9]; 2) there is no need to choose coordinates and basis functions to facilitate evaluation of matrix elements of the kinetic energy operator (KEO); 3) whereas, in a variational calculation it is costly to compute matrix elements of coordinate-dependent $\mathbf{G}$ matrix elements, [10] in a collocation calculation it is only necessary to evaluate coordinate-dependent $\mathbf{G}$ matrix elements at points.

When the $\mathbf{A}$ and $\mathbf{B}$ matrices are large, it is necessary to use an iterative eigensolver. Iterative eigensolvers makes it possible to solve the eigenvalue problem without storing $\mathbf{A}$ and $\mathbf{B}$. They are *much* more efficient when $\mathbf{B} = \mathbf{I}$. For this reason, variational methods with orthonormal basis functions are popular. In standard collocation methods, elements of $\mathbf{B}$ are values of basis functions evaluated at points and therefore $\mathbf{B} \neq \mathbf{I}$. New collocation methods in which $\mathbf{B} = \mathbf{I}$ have opened the door to the use of collocation with iterative eigensolvers. [5–7] Collocation is essentially interpolation applied to the solution of differential equations. The new methods use an multidimensional interpolant built from a basis of functions selected from a direct product basis and an interpolation grid (there are as many points as functions) constructed using sparse-grid or Smolyak ideas. A Smolyak grid has also been used with

quadratures. [11–17]

In a recent paper, [8] we have demonstrated that it is possible to implement Smolyak collocation methods for solving the Schroedinger equation without storing vectors larger than the Smolyak grid. In our earlier papers, larger intermediate vectors were stored. [5, 6] Reducing the size of the vectors facilitated the solution of a 9D problem: the computation of vibrational states of CH_2NH using a normal coordinate Hamiltonian. [8] However, because the $\pi^T \mu \pi$ term in the normal coordinate KEO [18] was dropped, that paper fails to demonstrate that Smolyak collocation can be used with a complex KEO. Because the fact that collocation facilitates the use of a complicated KEO is one of its most important advantages, it is crucial to also do calculations with a KEO with cross terms and coordinate-dependent $\mathbf{G}$ elements. The equations required to use the normal-coordinate KEO without any approximations and results for methane are presented in this paper. Neither μ nor the potential is expanded into sum-of-products form. We also demonstrate that the collocation method is accurate by comparing to earlier calculations, on the same potential, done in polyspherical coordinates. [19] The rectilinear normal coordinates used here work well for methane. The exact normal coordinate KEO is very complicated because it has 37 non-zero terms with two momentum operators and 8 terms with a single momentum operator that all have complicated coordinate-dependent coefficients. Collocation has been used with complicated KEOs before, [5–7] but never for a 9D problem.

II. THE NORMAL COORDINATE HAMILTONIAN FOR METHANE

In this paper we use Smolyak Collocation to compute vibrational energy levels of methane. We choose rectilinear dimensionless normal coordinate. [20] Similar ideas have been used with curvilinear normal coordinates. [7] Rectilinear normal coordinates work well for a semi-rigid molecule like methane and have been used before.[21–23] In Ref [21], a direct product discrete variable representation (DVR) [24, 25] and a Lanczos eigensolver are used. The DVR works well, but to use it one must store in memory (at least two) vectors as large as the size of the direct product basis. In Ref [21], owing to the fact that Lanczos vectors are explicitly orthogonalized, one requires enough memory to store many vectors. Despite the advantages of iterative eigensolvers and even if one does not explicitly orthogonalize Lanczos vectors, direct product bases are too big to be used with a molecule with more than five

ns. In Refs. 22 and 23, a multimode approximation to the potential is used. It is quite accurate, but to compute numerically exact energy levels one must use the full potential energy surface (PES).

In this paper we used the PES fit by Wang and Carrington to experimental data. [19] It is an improved version of the CCSD(T)+ cc-pVTZ PES of Schwenke and Partridge (SP) [26] The PES routine accepts as input the polyspherical coordinates associated with four Radau vectors. [27] We use dimensionless normal coordinates; we must therefore convert to Radau coordinates from normal coordinates. From the eigenvectors of the mass-weighted Cartesian force constant matrix, $\mathbf{F}^{Cart}$, and the equilibrium geometry, we obtain Cartesian coordinates that correspond to a normal coordinate point, and from the Cartesian coordinates we can calculate the Radau coordinates to call the WC potential. We use the atomic masses used in Ref [19]. Eigenvectors of $\mathbf{F}^{Cart}$ are obtained from eigenvectors of $\mathbf{G}^s \mathbf{F}^s$, by using Eq. 3.3.10 of Papousek and Aliev. [28] This is done to ensure the orthogonality of the eigenvectors of the mass-weighted Cartesian force constant matrix that correspond to vibrational coordinates and the eigenvectors that correspond to rotational motion. We use the symmetry coordinates of Ref [29]. The equilibrium geometry is: $r_e = 2.052410803$ bohr, $\theta_e = 109.4712206^\circ$. $\mathbf{G}^s$ matrix elements are obtained by analytically evaluating derivatives of molecule-fixed Cartesian coordinates with respect to symmetry coordinates, using Mathematica. [30] The non-zero elements of $\mathbf{F}^s$ are computed from mass-weighted Cartesian force constants. The mass-weighted Cartesian force constants are determined by fitting. First, sixth-order polynomial 1D cut potentials are fit. This gives us diagonal Cartesian force constants. For each pair of Cartesian coordinates, two 1D cut potentials are subtracted from the full potential evaluated at equilibrium for all other Cartesian coordinates. Sixth-order 2D cut potentials are then fit for each pair. This gives us off-diagonal Cartesian force constants. For the 1D fits we use 21 equally spaced points. For the 2D fits we use 21^2 points. Equating the quadratic Cartesian potential with the quadratic symmetry-coordinate potential, we obtain the non-zero symmetry-coordinate force constants. To do this we must compute the transformation matrix with which symmetry-coordinate displacements are obtained from Cartesian displacements. [10] It is obtained from analytic derivatives calculated with Mathematica. [30] $\mathbf{G}^s \mathbf{F}^s$ has eigenvalues that are degenerate to 16 significant figures.

The KEO is the well known Watson normal coordinate KEO. [18] π_α is obtained from the Coriolis ζ^α , which in turn is computed from the eigenvectors of the matrix of mass weighted

Gaussian force constants. If $\pi^T \mu \pi$ is not neglected, the Watson KEO is complicated. Collocation calculations are facilitated by re-arranging the part of the operator that contains derivatives so that it takes the form, [13]

$$\hat{K} = \sum_{s=1, t \geq s}^D A^{s,t}(^1q, ^2q, \dots, ^Dq) \frac{\partial^2}{\partial ^s q \partial ^t q} + \sum_{c=1}^D D^c(^1q, ^2q, \dots, ^Dq) \frac{\partial}{\partial ^c q} \quad (1)$$

Watson's extra potential term [18] is added to the potential. For methane, $\pi^T \mu \pi$ shifts many of the lowest 500 energy levels by tens of cm^{-1} . The coordinate dependence of μ has a small effect on levels, but it costs nothing to include it in our collocation calculation.

III. SMOLYAK COLLOCATION

Smolyak Collocation uses an interpolant made from a basis and a set of interpolation points. Each multidimensional basis function is a product of univariate functions. The univariate basis functions are “hierarchical” functions, $\tilde{\varphi}_{n_c}(^c q)$, that are linear combinations of primitive functions, $\varphi_{n_c}(^c q)$. The basis spans the space spanned by primitive functions that satisfy the condition

$$\sum_{c=1}^D G^c(n_c) \leq H, \quad (2)$$

where $G^c(n_c)$ are monotonically nondecreasing functions. In Section VC we specify the $G^c(n_c)$ used for methane. The interpolant is made using G^c and $i_c = 1, 2, \dots$, where i_c labels an interpolation level for coordinate $^c q$. An interpolated wavefunction is $I(D, H) \Psi_n(^1q, ^2q, \dots, ^Dq)$ and

$$I(D, H) = \sum_{G(i_1-1, i_2-1, \dots, i_D-1) \leq H} \Delta U^{i_1} \otimes \Delta U^{i_2} \otimes \dots \otimes \Delta U^{i_D}, \quad (3)$$

where D is the number of coordinates. The 1D ΔU^{i_c} are

$$\Delta U^{i_c} = U^{i_c} - U^{i_c-1}, \quad (4)$$

where $U^0 = 0$ and U^{i_c} is defined so that

$$\bar{f}(^c q) = U^{i_c} f(^c q) = \sum_{k_c=0}^{m_c(i_c)-1} a_{i_c, k_c}(^c q) f(^c q_{k_c}), \quad (5)$$

is a 1D interpolant. The pruning function $G(i_1 - 1, i_2 - 1, \dots, i_D - 1)$, H , and the number of points (functions), $m_c(i_c)$, control the quality of the interpolant. In this paper, $m_c(i_c)$ is

step to i_c . This is consistent with the use of the basis condition $\sum_{c=1}^D G^c(n_c) \leq H$, and the level condition $\sum_{c=1}^D G^c(i_c - 1) \leq H$. We use Eq. (3) with general Lagrange-type functions (LTF)

$$\begin{aligned} a_{i_c, k_c}(^c q) &= \sum_{n_c=0}^{m_c(i_c)-1} B_{k_c, n_c}^{i_c} \varphi_{n_c}(^c q) . \\ &= \sum_{n_c=0}^{m_c(i_c)-1} \tilde{B}_{k_c, n_c}^{i_c} \tilde{\varphi}_{n_c}(^c q) . \end{aligned} \quad (6)$$

B_{k_c, n_c} is an element of the inverse of the matrix whose elements are $\varphi_{n_c}(^c q_{k_c})$. $\tilde{B}^{i_c}$ is obtained from B^{i_c} and the transformation between the primitive and the hierarchical functions. $^c q_{k_c}, k_c = 0, 1, \dots, m_c(i_c) - 1$ are interpolation points. For more detail, readers are referred to Refs. 5–8

The collocation matrix eigenvalue problem is

$$\left(K_{k'_1, k'_2, \dots, k'_D; k_1, k_2, \dots, k_D} + V(^1 q_{k'_1}, ^2 q_{k'_2}, \dots, ^D q_{k'_D}) \delta_{k_1, k'_1} \delta_{k_2, k'_2} \dots \delta_{k_D, k'_D} \right) U_{k_1, k_2, \dots, k_D; n} = E_n U_{k'_1, k'_2, \dots, k'_D; n} ,$$

where $\mathbf{KU}$ is the matrix obtained by evaluating $\hat{K}I(D, H)\Psi_n(^1 q, ^2 q, \dots, ^D q)$ at $[^1 q_{k'_1}, ^2 q_{k'_2}, \dots, ^D q_{k'_D}]$; $\hat{K}$ is the KEO. To obtain $\mathbf{K}$, we use the fact that the Smolyak interpolant can be written as a restricted sum of products of hierarchical basis functions, $\tilde{\varphi}_{n_c}(^c q)$,

$$I(D, H)\Psi_n(^1 q, ^2 q, \dots, ^D q) = \sum_{G(n_1, n_2, \dots, n_D) \leq H} \tilde{\varphi}_{n_1}(^1 q) \tilde{\varphi}_{n_2}(^2 q) \dots \tilde{\varphi}_{n_D}(^D q) \tilde{\Gamma}_{n_1, n_2, \dots, n_D}^n \quad (7)$$

The $\tilde{\varphi}_{n_c}(^c q)$ are special linear combinations of the original basis functions $\varphi_{n_c}(x_c)$. [6] $\tilde{\Gamma}_{n_1, n_2, \dots, n_D}^n$ in Eq. (7) is related to $U_{k_1, k_2, \dots, k_D; n}$ by

$$\tilde{\Gamma}_{n_1, n_2, \dots, n_D}^n = \sum_{G(k_1, k_2, \dots, k_D) \leq H} \tilde{T}_{(n_1, n_2, \dots, n_D), (k_1, k_2, \dots, k_D)} U_{k_1, k_2, \dots, k_D; n} . \quad (8)$$

$\tilde{\mathbf{T}}$ transforms a vector labelled by points to a vector labelled by indices of hierarchical basis functions. This is like a DVR to FBR transformation (but neither the $\tilde{\varphi}_{n_1}(^1 q) \tilde{\varphi}_{n_2}(^2 q) \dots \tilde{\varphi}_{n_D}(^D q)$ basis nor the $k_1, k_2, \dots, k_D$ grid is a direct product). Putting Eq. (8) into Eq. (7) and then applying $\hat{K}$ to it and at evaluating at $[^1 q_{k'_1}, ^2 q_{k'_2}, \dots, ^D q_{k'_D}]$, one obtains the regular (not

generalized) matrix eigenvalue problem

$$\sum_{G(k_1, k_2, \dots, k_D) \leq H} \left(\sum_{G(n_1, n_2, \dots, n_D) \leq H} [\hat{K} \tilde{\varphi}_{n_1}(^1q) \tilde{\varphi}_{n_2}(^2q) \cdots \tilde{\varphi}_{n_D}(^Dq)] |_{[^1q=^1q_{k'_1}, ^2q=^2q_{k'_2}, \dots, ^Dq=^Dq_{k'_D}]} \right. \\ \left. \tilde{T}_{(n_1, n_2, \dots, n_D), (k_1, k_2, \dots, k_D)} + V(^1q_{k'_1}, ^2q_{k'_2}, \dots, ^Dq_{k'_D}) \delta_{k_1, k'_1} \delta_{k_2, k'_2} \cdots \delta_{k_D, k'_D} \right) \\ U_{k_1, k_2, \dots, k_D; n} = E_n U_{k'_1, k'_2, \dots, k'_D; n}, \\ [\mathbf{K} + \mathbf{V}] \mathbf{U} = \mathbf{U} \mathbf{E}, \quad (9)$$

which is solved using ARPACK. [31] ARPACK is a re-started Arnoldi method. This requires evaluating matrix-vector products, $\mathbf{w} = (\mathbf{K} + \mathbf{V})\mathbf{z}$, where $\mathbf{z}$ is an Arnoldi vector. $\tilde{\mathbf{T}}$ is multiplied onto $\mathbf{z}$ by evaluating sums over $k_D, k_{D-1}, \dots, k_1$ sequentially. [6] The KEO is then applied by sequentially evaluating sums over $n_1, n_2, \dots, n_D$.

IV. MATRIX-VECTOR PRODUCTS FOR A GENERAL KEO: 9D EXAMPLE

We must evaluate the matrix-vector product (MVP) $(\mathbf{K} + \mathbf{V})\mathbf{z}$. The rows and columns of $\mathbf{K}$ and $\mathbf{V}$ and the components of $\mathbf{z}$ are labelled by points on the Smolyak grid. Because $\mathbf{V}$ is diagonal the only costly MVP is done with $\mathbf{K}$. In a previous paper, it was shown that the $\mathbf{K}$ MVP is best done by first transforming $\mathbf{z}$ from the grid to a (pruned) hierarchical basis expansion and then, in a second step, applying $\hat{K}$ and evaluating at points on the Smolyak grid. [6] Transforming $\mathbf{z}$ from the grid to an hierarchical pruned basis expansion requires one set of D constrained sums and each term of the KEO requires another set of D constrained sums. When using a direct product basis, it is well-established, with or without quadrature, that it is best to evaluate the sums sequentially. [25, 32–39] The same idea can be used with a pruned basis. [40] Every sum is done by executing $D + 1$ loops and storing intermediate vectors. For a single set of sums, the computer program therefore contains D sets of $D + 1$ nested loops. In Ref [8], we demonstrated that if the KEO is simple, it is not necessary to store vectors with more elements than the Smolyak grid (or the pruned basis). In this paper, the KEO has cross terms and it is therefore necessary to store one vector with more elements than the Smolyak grid (see below).

As explained in Ref [8], the transformation that converts $\mathbf{z}$ to a vector labelled by hierarchical basis functions in 9 dimensions is,

$$\tilde{\mathbf{v}}^{\text{out}}(n_1, n_2, n_3, n_4, n_5, n_6, n_7, n_8, n_9) = \sum_{k_9=0}^{k_9^{\text{max}}} \Delta \tilde{B}_{k_9, n_9}^{n_9+1} \sum_{k_8=0}^{k_8^{\text{max}}} \Delta \tilde{B}_{k_8, n_8}^{n_8+1} \sum_{k_7=0}^{k_7^{\text{max}}} \Delta \tilde{B}_{k_7, n_7}^{n_7+1} \sum_{k_6=0}^{k_6^{\text{max}}} \Delta \tilde{B}_{k_6, n_6}^{n_6+1} \sum_{k_5=0}^{k_5^{\text{max}}} \Delta \tilde{B}_{k_5, n_5}^{n_5+1} \sum_{k_4=0}^{k_4^{\text{max}}} \Delta \tilde{B}_{k_4, n_4}^{n_4+1} \sum_{k_3=0}^{k_3^{\text{max}}} \Delta \tilde{B}_{k_3, n_3}^{n_3+1} \sum_{k_2=0}^{k_2^{\text{max}}} \Delta \tilde{B}_{k_2, n_2}^{n_2+1} \sum_{k_1=0}^{k_1^{\text{max}}} \Delta \tilde{B}_{k_1, n_1}^{n_1+1} \mathbf{v}^{\text{in}}(k_1, k_2, k_3, k_4, k_5, k_6, k_7, k_8, k_9), \quad (10)$$

where $\mathbf{z} = \mathbf{v}^{\text{in}}$. The points on the grid are restricted by $\sum_{c=1}^9 G^c(k_c) \leq H$, and $\Delta \tilde{B}_{k_c, n_c}^{n_c+1} = \tilde{B}_{k_c, n_c}^{n_c+1} - \tilde{B}_{k_c, n_c}^{n_c}$. In terms of ${}^c\mathbf{T}^T = \Delta \tilde{\mathbf{B}}^{n_c+1}$, Eq. (10) is

$$\tilde{\mathbf{v}}^{\text{out}}(n_1, n_2, n_3, n_4, n_5, n_6, n_7, n_8, n_9) = \sum_{k_9=0}^{k_9^{\text{max}}} {}^9T_{n_9, k_9} \sum_{k_8=0}^{k_8^{\text{max}}} {}^8T_{n_8, k_8} \sum_{k_7=0}^{k_7^{\text{max}}} {}^7T_{n_7, k_7} \sum_{k_6=0}^{k_6^{\text{max}}} {}^6T_{n_6, k_6} \sum_{k_5=0}^{k_5^{\text{max}}} {}^5T_{n_5, k_5} \sum_{k_4=0}^{k_4^{\text{max}}} {}^4T_{n_4, k_4} \sum_{k_3=0}^{k_3^{\text{max}}} {}^3T_{n_3, k_3} \sum_{k_2=0}^{k_2^{\text{max}}} {}^2T_{n_2, k_2} \sum_{k_1=0}^{k_1^{\text{max}}} {}^1T_{n_1, k_1} \mathbf{v}^{\text{in}}(k_1, k_2, k_3, k_4, k_5, k_6, k_7, k_8, k_9), \quad (11)$$

The intermediate vector obtained by computing the sum over k_c is denoted $\tilde{\mathbf{v}}^c$; $\tilde{\mathbf{v}}^{\text{out}} = \tilde{\mathbf{v}}^9$.

In Ref [8], it is explained that because ${}^c\mathbf{T}$ is lower triangular, the number of elements of the $\tilde{\mathbf{v}}^c$ vectors is only as large as the Smolyak grid. In general, the indices of $\tilde{\mathbf{v}}^c$ are constrained by

$$G^9(k_9) + \dots + G^{c+1}(k_{c+1}) + G^c(n_c) + \dots + G^1(n_1) \leq H \quad (12)$$

and the indices of $\tilde{\mathbf{v}}^{c-1}$ are constrained by $G^c(k_c) \leq H - \sum_{c''=1}^{c-1} G^{c''}(n_{c''}) - \sum_{c''=c+1}^9 G^{c''}(k_{c''})$. From the constraint on the indices of $\tilde{\mathbf{v}}^{c-1}$, one determines a restriction on k_c^{max} . It is,

$$k_c^{\text{max}} \leq (G^c)^{-1} \left[H - \sum_{c''=1}^{c-1} G^{c''}(n_{c''}) - \sum_{c''=c+1}^9 G^{c''}(k_{c''}) \right], \quad (13)$$

where $(G^c)^{-1}(a)$ is the inverse function of $G^c(k_c)$. In practice, $(G^c)^{-1}(a)$ is the largest value of k_c for which $G^c(k_c) \leq a$. It is also advantageous to limit the values of k_c so that $k_c \leq n_c$ because otherwise $\Delta \tilde{B}_{k_c, n_c}^{n_c+1} = 0$. Therefore,

$$k_c^{\text{max}} = \text{MIN} \left[(G^c)^{-1} \left[H - \sum_{c''=1}^{c-1} G^{c''}(n_{c''}) - \sum_{c''=c+1}^9 G^{c''}(k_{c''}) \right], n_c \right]. \quad (14)$$

From the constraint on the indices of $\tilde{\mathbf{v}}^c$ one determines n_c^{max} ,

$$n_c^{max} = (G^c)^{-1} [H - \sum_{c''=1}^{c-1} G^{c''}(n_{c''}) - \sum_{c''=c+1}^9 G^{c''}(k_{c''})], \quad (15)$$

Knowing the k_c^{max} in Eq. (11) and that n_c assumes the values $0, 1, \dots, n_c^{max}$, it is possible to compute $\tilde{\mathbf{v}}^{out}$.

In the final step of the calculation of $\mathbf{Hz}$, one multiplies $\tilde{\mathbf{v}}^{out}$, which is labelled by basis indices, on the left by $[\hat{K} \tilde{\varphi}_{n_1}(^1q) \tilde{\varphi}_{n_2}(^2q) \dots \tilde{\varphi}_{n_D}(^Dq)]_{[^1q=^1q_{k'_1}, ^2q=^2q_{k'_2}, \dots, ^Dq=^Dq_{k'_D}]}$ and sequentially sums over the basis indices. This is done separately for each term in the KEO. For terms with a first or a second derivative with respect to q , the output vector is computed by evaluating a D-fold sum for which the summand is a product of D factors and $\tilde{\mathbf{v}}^{out}$. $D - 1$ of the factors are collocation matrices whose elements are ${}^c C_{k'_c, n_c} = \tilde{\varphi}_{n_c}({}^c q_{k'_c})$, $c' \neq c$. The D th factor is a matrix whose elements are ${}^c S_{k'_c, n_c} = \frac{d^2}{dc^2} \tilde{\varphi}_{n_c}(^c q)_{q_{k'_c}}$ or $\frac{d}{dc} \tilde{\varphi}_{n_c}(^c q)_{q_{k'_c}}$. It is useful to order the factors, and the sums, so that ${}^c \mathbf{S}$ is on the right. The sum is, for example for the $\frac{\partial^2}{\partial c^2}$ term

$$\begin{aligned} & \sum_{n_1=0}^{n_1^{max}} \sum_{n_2=0}^{n_2^{max}} \dots \sum_{n_{c-1}=0}^{n_{c-1}^{max}} \sum_{n_{c+1}=0}^{n_{c+1}^{max}} \dots \sum_{n_9=0}^{n_9^{max}} \sum_{n_c=0}^{n_c^{max}} \frac{\partial^2}{\partial c^2} \tilde{\varphi}_{n_1}(^1q) \tilde{\varphi}_{n_2}(^2q) \tilde{\varphi}_{n_3}(^3q) \tilde{\varphi}_{n_4}(^4q) \tilde{\varphi}_{n_5}(^5q) \tilde{\varphi}_{n_6}(^6q) \tilde{\varphi}_{n_7}(^7q) \tilde{\varphi}_{n_8}(^8q) \\ & \times \tilde{\varphi}_{n_9}(^9q) \Big]_{[^1q=^1q_{k'_1}, ^2q=^2q_{k'_2}, ^3q=^3q_{k'_3}, ^4q=^4q_{k'_4}, ^5q=^5q_{k'_5}, ^6q=^6q_{k'_6}, ^7q=^7q_{k'_7}, ^8q=^8q_{k'_8}, ^9q=^9q_{k'_9}]} \tilde{\mathbf{v}}^{out}(n_1, n_2, n_3, n_4, n_5, n_6, n_7, n_8, n_9) = \\ & \sum_{n_1=0}^{n_1^{max}} {}^1 C_{k'_1, n_1} \sum_{n_2=0}^{n_2^{max}} {}^2 C_{k'_2, n_2} \dots \sum_{n_{c-1}=0}^{n_{c-1}^{max}} {}^{c-1} C_{k'_{c-1}, n_{c-1}} \sum_{n_{c+1}=0}^{n_{c+1}^{max}} {}^{c+1} C_{k'_{c+1}, n_{c+1}} \dots \sum_{n_9=0}^{n_9^{max}} {}^9 C_{k'_9, n_9} \sum_{n_c=0}^{n_c^{max}} {}^c S_{k'_c, n_c} \\ & \tilde{\mathbf{v}}^{out}(n_1, n_2, n_3, n_4, n_5, n_6, n_7, n_8, n_9). \quad (16) \end{aligned}$$

We denote $\tilde{\mathbf{z}}^c$ the intermediate vector obtained after evaluating the sum over n_c . Since the ${}^{c'} \mathbf{C}$ factors are upper triangular [6] the indices of $\tilde{\mathbf{z}}^c$ are constrained by $G^c(k'_c) + \sum_{c''=1 \neq c}^9 G^{c''}(n_{c''}) \leq H$ and the indices of $\tilde{\mathbf{z}}^{c' \neq c}$ are constrained by $G^c(k'_c) + \sum_{c''=c' \neq c}^9 G^{c''}(k'_{c''}) + \sum_{c''=1 \neq c}^{c'-1} G^{c''}(n_{c''}) \leq H$. To evaluate Eq. (16), one must know n_c^{max} , k_c^{max} , $n_{c'}^{max}$, $c' \neq c$, and

$k_c'^{max}, c' \neq c$:

$$n_c^{max} = (G^c)^{-1}[H - \sum_{c''=1 \neq c}^9 G^{c''}(n_{c''})], \quad (17)$$

$$k_c'^{max} = (G^c)^{-1}[H - \sum_{c''=1 \neq c}^9 G^{c''}(n_{c''})] \quad (18)$$

$$n_{c'}^{max} = MIN[(G^{c'})^{-1}[H - G^c(k_c') - \sum_{c''=1, \neq c}^{c'-1} G^{c''}(n_{c''}) - \sum_{c''=c'+1, \neq c}^9 G^{c''}(k_{c''}')], k_c'], \quad (19)$$

$$k_{c'}'^{max} = (G^{c'})^{-1}[H - G^c(k_c') - \sum_{c''=1, \neq c}^{c'-1} G^{c''}(n_{c''}) - \sum_{c''=c'+1, \neq c}^9 G(k_{c''}')]. \quad (20)$$

$n_{c'}^{max}$ is the minimum of two values because ${}^{c'}\tilde{\varphi}_{n_{c'}}({}^{c'}q_{k_c'}) = 0$ if $n_{c'} > k_{c'}'$,

The KEO of Eq.(1) also has terms with derivatives with respect to two different coordinates, tq and sq . In this case $D - 2$ of the factors in the summand are upper triangular collocation matrices and the two rightmost factors, ${}^sS_{k_s', n_s} = \frac{d}{d{}^sq} \tilde{\varphi}_{n_s}({}^sq)]_{q_{k_s'}}$ and ${}^tS_{k_t', n_t} = \frac{d}{d{}^tq} \tilde{\varphi}_{n_t}({}^tq)]_{q_{k_t'}}$ are not upper triangular. It is useful to order the factors, and the sums, so that sS and tS are on the right and so that from left to right the sums are over $n_1, n_2, \dots, n_{s-1}, n_{s+1}, \dots, n_{t-1}, n_{t+1}, \dots, n_s, n_t$. The sum is, for example for the $\frac{\partial^2}{\partial {}^sq \partial {}^tq}$ term

$$\begin{aligned} & \sum_{n_1=0}^{n_1^{max}} \sum_{n_2=0}^{n_2^{max}} \dots \sum_{n_{s-1}=0}^{n_{s-1}^{max}} \sum_{n_{s+1}=0}^{n_{s+1}^{max}} \dots \sum_{n_{t-1}=0}^{n_{t-1}^{max}} \sum_{n_{t+1}=0}^{n_{t+1}^{max}} \dots \sum_{n_9=0}^{n_9^{max}} \sum_{n_s=0}^{n_s^{max}} \sum_{n_t=0}^{n_t^{max}} \frac{\partial^2}{\partial {}^sq \partial {}^tq} \tilde{\varphi}_{n_1}({}^1q) \tilde{\varphi}_{n_2}({}^2q) \tilde{\varphi}_{n_3}({}^3q) \tilde{\varphi}_{n_4}({}^4q) \tilde{\varphi}_{n_5}({}^5q) \\ & \times \tilde{\varphi}_{n_6}({}^6q) \tilde{\varphi}_{n_7}({}^7q) \tilde{\varphi}_{n_8}({}^8q) \tilde{\varphi}_{n_9}({}^9q) \Big]_{[{}^1q={}^1q_{k_1'}, {}^2q={}^2q_{k_2'}, {}^3q={}^3q_{k_3'}, {}^4q={}^4q_{k_4'}, {}^5q={}^5q_{k_5'}, {}^6q={}^6q_{k_6'}, {}^7q={}^7q_{k_7'}, {}^8q={}^8q_{k_8'}, {}^9q={}^9q_{k_9'}]} \\ & \times \tilde{v}^{out}(n_1, n_2, n_3, n_4, n_5, n_6, n_7, n_8, n_9) = \sum_{n_1=0}^{n_1^{max}} {}^1C_{k_1', n_1} \sum_{n_2=0}^{n_2^{max}} {}^2C_{k_2', n_2} \dots \sum_{n_{s-1}=0}^{n_{s-1}^{max}} {}^{s-1}C_{k_{s-1}', n_{s-1}} \\ & \sum_{n_{s+1}=0}^{n_{s+1}^{max}} {}^{s+1}C_{k_{s+1}', n_{s+1}} \dots \sum_{n_{t-1}=0}^{n_{t-1}^{max}} {}^{t-1}C_{k_{t-1}', n_{t-1}} \sum_{n_{t+1}=0}^{n_{t+1}^{max}} {}^{t+1}C_{k_{t+1}', n_{t+1}} \dots \sum_{n_9=0}^{n_9^{max}} {}^9C_{k_9', n_9} \sum_{n_s=0}^{n_s^{max}} {}^sS_{k_s', n_s} \sum_{n_t=0}^{n_t^{max}} {}^tS_{k_t', n_t} \\ & \tilde{v}^{out}(n_1, n_2, n_3, n_4, n_5, n_6, n_7, n_8, n_9) \end{aligned} \quad (21)$$

For the vector $\tilde{\mathbf{z}}^s$, the elements are constrained by

$$G^s(k_s') + G^t(k_t') + \sum_{c''=1, \neq s, t}^9 G^{c''}(n_{c''}) \leq H. \quad (22)$$

k_s^{max} is therefore

$$k_s'^{max} = (G^s)^{-1}[H - G^t(k_t') - \sum_{c''=1, \neq s, t}^9 G^{c''}(n_{c''})]. \quad (23)$$

n_t^{max} is obtained from the constraint on $\tilde{\mathbf{z}}^t$. There are two constraints on $\tilde{\mathbf{z}}^t$, because k'_t and the n_c indices are constrained separately, owing to the fact that tS is not upper triangular. The two restrictions on the indices of $\tilde{\mathbf{z}}^t$ are

$$G^t(k'_t) + \sum_{c''=1, \neq t}^9 G^{c''}(0) \leq H \text{ and } \sum_{c''=1, \neq t}^9 G^{c''}(n_{c''}) + G^t(0) \leq H. \quad (24)$$

Therefore

$$n_s^{max} = (G^s)^{-1}[H - G^t(0) - \sum_{c''=1, \neq t, s}^9 G^{c''}(n_{c''})]. \quad (25)$$

$k'_t{}^{max}$ is obtained from the first part of Equation 24,

$$k'_t{}^{max} = (G^t)^{-1}[H - \sum_{c''=1, \neq t}^9 G^{c''}(0)] \quad (26)$$

n_t^{max} is obtained from the constraint on $\tilde{\mathbf{z}}^{\text{in}}$ which is $\sum_{c''=1}^9 G^{c''}(n_{c''}) \leq H$.

$$n_t^{max} = (G^t)^{-1}[H - \sum_{c''=1, \neq t}^9 G^{c''}(n_{c''})] \quad (27)$$

The elements of $\tilde{\mathbf{z}}^c$ vectors with $c \neq s, t$ are constrained by

$$G^s(k'_s) + G^t(k'_t) + G^c(k'_c) + \sum_{c''=1, \neq s, t}^{c-1} G^{c''}(n_{c''}) + \sum_{c''=c+1, \neq s, t}^9 G^{c''}(k'_{c''}) \leq H. \quad (28)$$

k_c^{max} , $c \neq s, t$ is obtained from the constraint on $\tilde{\mathbf{z}}^c$

$$k_c^{max} = (G^c)^{-1}[H - G^t(k'_s) - G^s(k'_t) - \sum_{c''=1, \neq s, t}^{c-1} G^{c''}(n_{c''}) - \sum_{c''=c+1, \neq s, t}^9 G^{c''}(k'_{c''})]. \quad (29)$$

n_c^{max} , $c \neq s, t$ is obtained from the constraint on vector whose components are summed to obtain $\tilde{\mathbf{z}}^c$.

$$n_c^{max} = \text{MIN} \left[(G^c)^{-1} \left[H - G^t(k'_s) - G^s(k'_t) - \sum_{c''=1, \neq s, t}^{c-1} G^{c''}(n_{c''}) - \sum_{c''=c+1, \neq s, t}^9 G^{c''}(k'_{c''}) \right], k'_c \right]. \quad (30)$$

CALCULATING ENERGY LEVELS OF CH₄

A. Original basis functions

We use as original basis functions eigenfunctions of the 1D operators

$$\hat{H}_c = -\frac{\omega_c}{2} \frac{d^2}{d^2 q} + \frac{\omega_c}{2} q^2. \quad (31)$$

i.e. the basis functions are

$$\varphi_{n_c}(q) = H_{n_c}(q) e^{-\frac{q^2}{2}}, \quad (32)$$

where $H_n(q)$ is a Hermite polynomial of degree n and q is a dimensionless coordinate. [20] The harmonic frequencies are 3160.689, 3160.689, 3160.689, 3038.399, 1571.950, 1571.950, 1343.130, 1343.130 and 1343.1300 cm⁻¹. The dimensionless normal coordinates are ordered with respect to their harmonic frequencies from the largest (coordinate q_1) to the smallest (coordinate q_9). The hierarchical basis functions $\tilde{\varphi}_{n_c}(q)$ are determined from the original basis functions after choosing 1D interpolation/collocation points. [6] Other hierarchical functions have also been used. [41–46]

B. Choosing collocation points

The basis functions of the previous subsection are organized into levels. The functions $n_c = 0, 1, \dots, i_c - 1$ are used to make U^{i_c} . To use the collocation method of section III, one must also choose, for each coordinate, a nested set of points with $m_c(i_c) = i_c$ points in level i_c . In a nested set of points, the points used to make U^{i_c} are also used for U^{i_c+1} . Using nested points and functions makes it possible to evaluate matrix-vector products efficiently. [6] It is best to have a sequence in which the number of points increases slowly as i_c is increased. In this paper we use Leja points associated with the harmonic oscillator functions of the previous subsection. [8, 47–52] Since we use dimensionless normal coordinates, the $\varphi_{n_c}(q)$ are the same for all coordinates and the Leja sequence of interpolation points is the same for every coordinate. The Leja points we use are determined as in Ref [8]. We use equations written in terms of hierarchical (not harmonic) basis functions, $\tilde{\varphi}_{n_c}(q)$, however, the Leja points work equally well when using the hierarchical functions.

Leja points are obtained for the harmonic basis from the equation

$$q_k = \arg \max_{(-\infty, +\infty)} \left\{ \varphi_k(q) - U^{k-1}(q_1, q_2, \dots, q_{k-1})[\varphi_k(q)] \right\}. \quad (33)$$

One is free to choose the $k = 0$ point. In this paper, $q_0 = 0$. Since the $\varphi_n(q)$ are even or odd, the other interpolation points should be plus/minus pairs. Therefore when we use Eq. 33, we restrict the Leja points so that $q_{k+1} = -q_k$ for $k = 1, 3, 5, \dots$ as in Ref [8].

For example, $q_2 = -q_1$ and q_1 is determined by maximizing the function,

$$(\varphi_1(q) - C_{1,0}\varphi_0(q))^2 + (\varphi_2(q) - C_{2,0}\varphi_0(q))^2, \quad (34)$$

where $C_{1,0}\varphi_0(q)$ is the interpolant for $\varphi_1(q)$ computed with the single basis function $\varphi_0(q)$ and the single point q_0 and $C_{2,0}\varphi_0(q)$ is the interpolant for $\varphi_2(q)$ computed with the single basis function $\varphi_0(q)$ and the single point q_0 . Similarly, $q_4 = -q_3$ and q_3 is determined by maximizing the function

$$(\varphi_3(q) - C_{3,0}\varphi_0(q) - C_{3,1}\varphi_1(q) - C_{3,2}\varphi_2(q))^2 + (\varphi_4(q) - C_{4,0}\varphi_0(q) - C_{4,1}\varphi_1(q) - C_{4,2}\varphi_2(q))^2, \quad (35)$$

where $C_{3,0}\varphi_0(q) + C_{3,1}\varphi_1(q) + C_{3,2}\varphi_2(q)$ is the interpolant for $\varphi_3(q)$ made with the basis $\{\varphi_0(q), \varphi_1(q), \varphi_2(q)\}$ and the points $\{q_0, q_1, q_2\}$ and $C_{4,0}\varphi_0(q) + C_{4,1}\varphi_1(q) + C_{4,2}\varphi_2(q)$ is the interpolant for $\varphi_4(q)$ made with the basis $\{\varphi_0(q), \varphi_1(q), \varphi_2(q)\}$ and the points $\{q_0, q_1, q_2\}$

Points are added to the Leja sequence in groups of two, however, to make interpolation rules we use $m_c(i_c) = i_c$, i.e., U^k has one more point than U^{k-1} . The points included in interpolation rules U^k , $k = 1, 2, 3, \dots$ are

$$(q_0), (q_0, q_1), (q_0, q_1, q_2 = -q_1), (q_0, q_1, q_2 = -q_1, q_3), (q_0, q_1, q_2 = -q_1, q_3, q_4 = -q_3) \dots (36)$$

C. $G^c(n_c)$ for CH_4

The $G^c(n_c)$ determine how many and which basis functions and points are used to make the interpolant for a particular value of H . As in previous papers, we use $G^c(n_c)$ that are step functions. We do calculations with two sets of $G^c(n_c)$: set A and set B. They are designed for the calculation of the lowest 500 vibrational levels of methane. Both are obtained from primitive $G_{\text{prim}}^c(n_c) = n_c$ by adding an increment, $G_{\text{incmt}}^c(n_c) = G_{\text{prim}}^c(n_c) + I_c$. Two principles are used to guide the choice of I_c . [8] When n_c is small, I_c is positive and smaller when n_c is larger. This choice is made to avoid including basis functions with many non-zero n_c . When n_c is large, I_c is negative and its absolute value is larger when n_c is larger. This choice is made to ensure that that some basis functions have large values of

44 I_c is a multiple of 0.1 and so that $G^c(n_c)$ is an integer we use $G^c(n_c) = 10 * G_{incmt}^c(n_c)$. To ensure that $G^c(n_c)$ can be used with different H , we add an H dependent shift to some $G^c(n_c)$.

Set A is:

$$\begin{aligned} G^c(0) &= 0, G^c(1) = 17, G^c(2) = 26, G^c(3) = 35, G^c(4) = 44, G^c(5) = 53, G^c(6) = 62, \\ G^c(7) &= 71, G^c(8) = 80, G^c(9) = 90, G^c(10) = 100, G^c(11) = 110, G^c(12) = 120, \\ G^c(13) &= 130, G^c(14) = 140, G^c(15) = 150, G^c(16) = 160, G^c(17) = 169, G^c(18) = 178, \\ G^c(19) &= 187, G^c(20) = 196, G^c(21) = 205, G^c(22) = 214, G^c(23) = 223, G^c(24) = 232, \\ G^c(25) &= 241, G^c(26) = 250, \end{aligned} \quad (37)$$

for coordinates 1,2, 3 and 4; and

$$\begin{aligned} G^c(0) &= 0, G^c(1) = 15, G^c(2) = 24, G^c(3) = 33, G^c(4) = 42, G^c(5) = 51, G^c(6) = 60, \\ G^c(7) &= 70, G^c(8) = 80, G^c(9) = 90, G^c(10) = 100, G^c(11) = 110, G^c(12) = 120, G^c(13) = 130, \\ G^c(14) &= 139, G^c(15) = 148, G^c(16) = 157, G^c(17) = 166, G^c(18) = 175, G^c(19) = 184, \\ G^c(20) &= 193, G^c(21) = 202, G^c(22) = 211, G^c(23) = 220, G^c(24) = 229, G^c(25) = 238, \\ G^c(26) &= 247, \end{aligned} \quad (38)$$

for coordinates 5,6,7,8 and 9. Different values are used because coordinates 1,2, 3 and 4 have significantly higher frequencies. After adding the H dependent shift, we obtain the final $G^c(n_c)$:

$$G^c(n_c, h) = G^c(n_c) + h(H) \text{ if } 1 \leq n_c \leq 4; \quad G^c(n_c, h) = G^c(n_c) - h(H) \text{ if } n_c \geq 13. \quad (39)$$

$h(H)$ is an increasing function of H . Values for different calculations are given in the Results section.

Set B is:

$$\begin{aligned} G^c(0) &= 0, G^c(1) = 17, G^c(2) = 17, G^c(3) = 35, G^c(4) = 35, G^c(5) = 53, G^c(6) = 53, G^c(7) = 71, \\ G^c(8) &= 71, G^c(9) = 89, G^c(10) = 89, G^c(11) = 109, G^c(12) = 109, G^c(13) = 130, G^c(14) = 130, \\ G^c(15) &= 150, G^c(16) = 150, G^c(17) = 169, G^c(18) = 169, G^c(19) = 187, G^c(20) = 187, \\ G^c(21) &= 205, G^c(22) = 205, G^c(23) = 223, G^c(24) = 223, G^c(25) = 241, G^c(26) = 241, \end{aligned} \quad (40)$$

for coordinates 1,2, 3 and 4; and

$$\begin{aligned}
 G^c(0) &= 0, G^c(1) = 15, G^c(2) = 15, G^c(3) = 33, G^c(4) = 33, G^c(5) = 51, G^c(6) = 51, \\
 G^c(7) &= 69, G^c(8) = 69, G^c(9) = 89, G^c(10) = 89, G^c(11) = 110, G^c(12) = 110, \\
 G^c(13) &= 130, G^c(14) = 130, G^c(15) = 148, G^c(16) = 148, G^c(17) = 166, G^c(18) = 166, \\
 G^c(19) &= 184, G^c(20) = 184, G^c(21) = 202, G^c(22) = 202, G^c(23) = 220, \\
 G^c(24) &= 220, G^c(25) = 248, G^c(26) = 248,
 \end{aligned} \tag{41}$$

for coordinates 5,6,7,8 and 9 The $G^c(n_c)$ of set B are made using the same principles, however, pairs of $G^c(n_c)$ values are forced to be equal. This is done to ensure that if the Smolyak interpolant includes, ${}^1q_{k_1}, \dots, {}^{c-1}q_{k_{c-1}}, {}^c q_{k_c}, {}^{c+1}q_{k_{c+1}}, \dots, {}^D q_{k_D}$ then it also includes ${}^1q_{k_1}, \dots, {}^{c-1}q_{k_{c-1}}, -{}^c q_{k_c}, {}^{c+1}q_{k_{c+1}}, \dots, {}^D q_{k_D}$

Set B makes it possible to exploit symmetry. Each of the multidimensional product basis functions is either symmetric or antisymmetric with respect to the operator that permutes two hydrogen atoms, P_{12} . [53] It is surely possible to use a group larger than $G_2 = \{E, P_{12}\}$, but G_2 allows us to demonstrate the ideas. P_{12} divides configuration space into a symmetrically unique region, its image region, and a boundary. The points on the Smolyak grid can be divided into three groups: those in the symmetrically unique region, those in its image region and those on the boundary between the two. P_{12} maps points in the symmetrically unique region onto points in the image region. We use Arnoldi vectors with as many components as the sum of the number of points in the symmetrically unique region and the number of points on the boundary. Each vector is then expanded so that it includes as many components as there are points on the full Smolyak grid. A vector is expanded by adding components at image points that are equal to ± 1 times components at the symmetrically unique points. When it is plus, the vector represents a symmetric function; when it is minus, the vector represents an antisymmetric function. After expanding the vector we evaluate MVPs in the usual fashion. [6, 8] Note that because we expand the vectors we do not reduce the size of the largest vectors we must store. In this respect this symmetry adaption method is similar to the symmetry adapted Lanczos method. [54, 55] To find the image point of $\mathbf{q}$, we first convert normal to Cartesian coordinates and then permute the Cartesian coordinates of hydrogen atoms 1 and 2. We then find the point on the Smolyak grid whose corresponding interatomic distances are the same as those of the permuted Cartesian point.

Exploiting symmetry makes it possible to label wavefunctions as symmetric or antisymmetric. It also has the advantage that it reduces error. Why? The energy levels we compute from collocation are exactly equal to those that one would obtain by solving $\mathbf{H}\mathbf{U} = \mathbf{S}\mathbf{U}\mathbf{E}$, where $\mathbf{H}$ is a matrix representation of the Hamiltonian and $\mathbf{S}$ is an overlap matrix, if *all* of the $\mathbf{H}$ and $\mathbf{S}$ matrix elements are evaluated by a quadrature whose points are the collocation points. [9] This means that choosing collocation points to make $\mathbf{H}$ and $\mathbf{S}$ matrix elements more accurate will increase the accuracy of the corresponding collocation energy levels and wavefunctions. $\mathbf{H}$ and $\mathbf{S}$ matrix elements between symmetric and antisymmetric functions will be exact (and zero) when evaluated on the grid determined from set B. They are zero because symmetric (antisymmetric) basis functions evaluated at a point in the symmetrically unique set and evaluated at its image point are equal (differ only in sign). Unfortunately, the same G^c must be used for both the grid and the basis and the G^c required (with $G^c(2n_c - 1) = G^c(2n_c)$) to ensure that the full grid is divisible into symmetrically unique, image, and boundary subsets may give a basis that is less good. The error in energy levels computed by collocation can always be attributed to a combination of quadrature error and completeness error. [9]

VI. RESULTS

To test the convergence of the vibrational levels we compare levels computed with different values of H and h . Increasing H increases simultaneously the size of the basis and the interpolation grid.

For the A set of $G^c(n_c)$, we did four calculations: A1 with $H = 230, h = 3$ and 6'415'430 basis functions; A2 with $H = 240, h = 4$ and 7'952'746 basis functions; A3 with $H = 250, h = 4$ and 11'578'547 basis functions; and A4 with $H = 260, h = 5$ and 14'425'734 basis functions. The average absolute difference and the maximum absolute difference of the lowest 500 levels in each of these calculations with respect to the levels in calculation A4 are: for A1 (0.016,0.08) cm^{-1} ; for A2 (0.012,0.08) cm^{-1} ; for A3 (0.003,0.05) cm^{-1} . Even with fewer than 10 million basis functions, the 500 levels are well converged.

For the B set of $G^c(n_c)$, we also did four calculations: B1 with $H = 180$ and 3460531 basis functions (the symmetry blocks have dimensions of 1'749'008); B2 with $H = 190$ and 6'770'037 basis functions (the symmetry blocks have dimensions of 3'413'185), B3 with

$H = 200$ and $8'314'069$ basis functions (the symmetry blocks have dimension of $4'190'161$); and B4 with $H = 210$ and $13'918'903$ basis functions (the symmetry blocks have dimensions $7'006'630$). The average absolute difference and the maximum absolute difference of the lowest 500 levels in each of these calculations with respect to the levels in calculation B4 are: for B1 (0.06,0.35) cm^{-1} , for B2 (0.018,0.17) cm^{-1} , for B3 (0.009,0.07) cm^{-1} . Because the B set makes it possible to exploit symmetry it reduces the number of Arnoldi vectors that must be stored. We store 500, for each symmetry. For the A calculations, we store 700 Arnoldi vectors.

The average absolute difference and maximum absolute difference between calculations A4 and B4 are 0.004, and 0.03 cm^{-1} . This is a good measure of the error in the energy levels in calculations A4 and B4. The B set of $G^c(n_c)$ is designed to reduce the quadrature error. The A set of $G^c(n_c)$ is designed to reduce the completeness error. Agreement between the A and B calculations confirms their accuracy. The accuracy of the collocation calculations is also confirmed by comparing with Ref [19]. The average absolute difference and maximum absolute difference between the energies of calculations A4 and B4 and the energies of Ref [19] with basis b3s1 (which has 954 bend functions and 260 stretch functions) are (0.022,0.12) and (0.022,0.12) cm^{-1} .

It has been suggested that when integrals are evaluated exactly the condition

$$n_1 + n_2 + n_3 + n_4 + n_5 + n_6 + n_7 + n_8 + n_9 \leq H \quad (42)$$

is excellent. [56] (In Ref [56] exact integrals are possible because the PES is a sum of products.) We have therefore also done calculations with Eq. (42) with $H = 180, 190, 200$. These three calculations, denoted C1, C2, and C3, have basis sizes 4686825, 6906900, 10015005, respectively. The average absolute difference and maximum absolute difference between calculations C1, C2, and C3 and A4 are (0.04,0.2), (0.02,0.08), (0.007,0.06) cm^{-1} . The quality of the collocation energies for calculations A4, B4, and C3 (the largest of each type) are similar, despite the fact that the degree of completeness and the quadrature error must be slightly different in all three cases.

It is also possible to compare with previous methane calculations also done in normal coordinates. [57] We cannot compare energy levels with those of Ref [57] because it used a different PES. We can compare basis sizes. In Ref [57] a basis of $241'864'704$ is used to compute about levels up to 6125 cm^{-1} . Most of the convergence errors reported are less than

cm^{-1} . Pruning the basis (and the grid) enable us to compute 500 levels (all levels up to 7437 cm^{-1}) with errors of about 0.1 cm^{-1} using a basis with less than 10 million functions. The pruning is clearly very helpful.

VII. CONCLUSION

Why is it important to develop a collocation method for computing spectra of molecules with five (or fewer) atoms with an exact KEO? If the PES is a sum-of-products or multimode expansion, in the coordinates with which the spectrum is computed, then there is no need for collocation. There are excellent methods designed to work well when the PES has one of these simple forms. [56, 58–61] For a general PES, it is necessary to use either quadrature or collocation. Of course, the first challenge is to find a basis with which one can compute the desired energy levels and wavefunctions but whose favourable properties, e.g. its small size or its simple structure, make solving the required matrix eigenvalue problem not too costly. However, for a general potential a good basis is not enough. One must also obviate the need to store the potential on a huge (collocation or quadrature grid). When contracted basis functions are used, one option is to use the F matrix idea of Ref [62–64]. Contracted bases are also used with PESs simple enough that a grid is not necessary. [65] If rather than contracting the basis, one prunes a direct product basis, [66] it is likewise necessary to find a way of doing quadrature or collocation that avoids the need for a huge grid. Nondirect product Smolyak grid quadrature methods make this possible. [12–17] They work, so why should one care about collocation? Spectra computed with the Smolyak quadrature methods are only accurate if the quadrature is good enough that the overlap matrix computed by quadrature is correct. It is not simple to devise nested 1D grids from which one can build a Smolyak quadrature grid that satisfies this condition. To do this, we used [12–15] harmonic oscillator basis functions and extended the grids of Heiss and Winschel [67]. Other authors prefer to use non-nested points and compute MVPs for every contributing grid in the Smolyak quadrature sum. [16, 17] This is costly. Finding nested sets of quadrature points with which the overlap matrix is exact is even more difficult if one uses general (not harmonic) basis functions. For many molecules, 1D cut eigenfunctions are much better basis functions.

Using collocation, it is possible to compute accurate energy levels using 1D basis functions

and points for which the overlap matrix computed by quadrature is poor. The collocation grid, like the quadrature grid, is made, from families of 1D grids, with the Smolyak recipe. A collocation method was proposed in Ref [6]. In that paper, to circumvent the problem of needing a basis and a quadrature good enough to yield an accurate overlap matrix, it was necessary to store many intermediate vectors that were significantly larger than basis. In Ref [8] it was shown that when the KEO has no mixed momentum terms and no coordinate dependent coefficients it is possible to obviate the need to store vectors larger than the basis. However, for molecules with more than three atoms, *all* KEOs have mixed momentum terms and coordinate dependent coefficients, and they cannot be ignored if one wishes to do numerically exact calculations. In this paper, we show that for such complicated KEOs similar ideas can be used. It is necessary to store only one vector larger than the basis and it is not much larger than the basis. It is important to be able to cope with complicated KEOs because this allows one to use optimal coordinates. Using a variational/quadrature method with a general complicated KEO is costly because it is necessary to evaluate matrix elements of all the G matrix elements by quadrature. When using a collocation method, with a KEO written so that derivatives are on the right, the coordinate dependence of the G matrix elements is easy to deal with because the G matrix elements need only be evaluated at points. Using collocation in conjunction with optimized coordinates will make it possible to do calculations for many interesting molecules.

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