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Cite as: J. Chem. Phys. **145**, 224110 (2016); <https://doi.org/10.1063/1.4971295>

Submitted: 29 September 2016 . Accepted: 18 November 2016 . Published Online: 15 December 2016

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Using an internal coordinate Gaussian basis and a space-fixed Cartesian coordinate kinetic energy operator to compute a vibrational spectrum with rectangular collocation

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(Received 29 September 2016; accepted 18 November 2016; published online 15 December 2016)

We demonstrate that it is possible to use basis functions that depend on curvilinear internal coordinates to compute vibrational energy levels without deriving a kinetic energy operator (KEO) and without numerically computing coefficients of a KEO. This is done by using a space-fixed KEO and computing KEO matrix elements numerically. Whenever one has an excellent basis, more accurate solutions to the Schrödinger equation can be obtained by computing the KEO, potential, and overlap matrix elements numerically. Using a Gaussian basis and bond coordinates, we compute vibrational energy levels of formaldehyde. We show, for the first time, that it is possible with a Gaussian basis to solve a six-dimensional vibrational Schrödinger equation. For the zero-point energy (ZPE) and the lowest 50 vibrational transitions of H₂CO, we obtain a mean absolute error of less than 1 cm⁻¹; with 200 000 collocation points and 40 000 basis functions, most errors are less than 0.4 cm⁻¹. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4971295>]

INTRODUCTION

To compute numerically exact vibrational energy levels of a molecule whose potential energy surface (PES) is not a sum-of-products, one must use either quadrature or collocation.^{1–5} Energy levels are determined by solving a matrix eigenvalue problem. The size of the Hamiltonian matrix (and possibly the overlap matrix) is the number of basis functions. To minimize the cost of the calculation, one must reduce both the number of basis functions and the number of quadrature/collocation points. In this paper, we use a basis of products of Gaussian functions that are the functions of bond length and bond angle coordinates. By choosing the positions and widths of the Gaussians, we ensure that the size of the basis is minimized. Gaussian basis functions have been previously used to calculate vibrational energy levels.^{6–10} However, Gaussian basis functions are usually used with a variational ansatz, with matrix elements of the kinetic energy operator (KEO) being computed exactly and matrix elements of the potential being computed with quadrature. Instead, we use quadrature, or “rectangular collocation” (see below), for the KEO, the overlap matrix, and the potential. Another novel feature of the method we present is the way we treat the KEO. The KEO is almost invariably written in terms of the coordinates on which the basis functions depend and is often very complicated. Many years ago, Handy presented a systematic procedure for deriving KEOs.¹¹ More recently, it has become

popular to evaluate coefficients of second (and first) derivatives numerically.^{12–20} In this paper, we go a step further and show that it is possible to use a KEO in space-fixed (SF) Cartesian coordinates and a basis in curvilinear internal coordinates. Using a space-fixed KEO, it is possible to compute a spectrum with basis functions that depend on curvilinear coordinates without either deriving an analytic KEO in curvilinear coordinates or numerically computing coefficients of the derivatives in the KEO. If the basis depends only on coordinates that specify the shape of the molecule, one obtains vibrational energy levels, regardless of the fact that the KEO depends on SF coordinates.

Using quadrature/collocation to compute both KEO and potential matrix elements has the important, and underappreciated, advantage that it sometimes makes it possible to reduce the number of points. If the wavefunctions one wishes to compute can be accurately represented as linear combinations of the functions in the basis, then a small number of points are sufficient.²¹ This means that when quadrature/collocation is used to compute KEO, overlap, and potential matrix elements, reducing the number of required basis functions also enables one to reduce the number of quadrature/collocation points. Often, basis functions that are the products of univariate functions are used. Even for molecules with only 4 atoms, the quadrature/collocation grid used with a direct product basis is so large that it is impossible to compute *ab initio* potential values at all the points. As a result, an analytic PES function is required. Analytic PESs are usually built by fitting *ab initio* data, which introduces an additional step.^{22–47} In this paper, we use a basis that is both small and good, and we are therefore able to use a correspondingly small set of quadrature/collocation points. For molecules with four atoms, it would be possible to compute *ab initio* potential values at

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the points. This obviates the need to build a PES. This is an important advantage, as PESs will never be made for the vast majority of materials studied in laboratories. On the other hand, *ab initio* codes are already widely used, even in experimental labs.

When quadrature is used for the overlap matrix, and for the KEO and potential matrix elements, the eigenvalues one computes are identical to those obtained from collocation.⁹ If there are more collocation points than basis functions, then the collocation problem is rectangular. To use collocation, wavefunctions are expanded in a basis

$$\psi_k(\mathbf{x}) = \sum_{n=1}^N c_{kn} g_n(\mathbf{x}), \quad (1)$$

where $g_n(\mathbf{x})$ is a basis function, and the coefficients are chosen so that the Schrödinger equation (SE) is satisfied at a set of points $\{\mathbf{x}_m\}$, $m = 1, \dots, M$. In our case, $M > N$ and the collocation equation is rectangular. The coefficients and the energies are the solutions of the matrix equation

$$\mathbf{M}\mathbf{c}'_k = E_k \mathbf{S}\mathbf{c}'_k, \quad (2)$$

where $S_{mn} = g_n(\mathbf{x}_m)$, $M_{mn} = \mathbf{T}g_n(\mathbf{x}_m) + V(\mathbf{x}_m)g_n(\mathbf{x}_m)$, and \mathbf{c}'_k is a vector of coefficients. \mathbf{T} is the KEO. This rectangular matrix equation can be solved by multiplying on the left with \mathbf{S}^T to obtain the square generalized eigenproblem,

$$\mathbf{S}^T \mathbf{M} \mathbf{c}_k = E_k \mathbf{S}^T \mathbf{S} \mathbf{c}_k, \quad (3)$$

where $\mathbf{c}_k \approx \mathbf{c}'_k$. Eq. (3) is the same equation obtained by using the variational method and evaluating integrals with a simple quadrature with unit weights. Quadrature can therefore be seen as a means of solving the rectangular collocation problem. In recent papers, we have used rectangular collocation with a rectangular eigensolver to compute vibrational levels.^{48–54} In this paper, we also have more points than basis functions, but use the square generalized eigenproblem.⁵⁵ A key advantage of collocation is that accurate energies may be obtained when it is not possible to devise an accurate (multidimensional) quadrature scheme. This idea is exploited in Refs. 56 and 57, but in those papers the number of points is equal to the number of basis functions. Here, we use more points than basis functions. The method of this paper is simple to program. Because it does not require a KEO in internal coordinates, it is general and easy to apply. It is easy to improve the accuracy by progressively adding more points, as is done here. In the current code, the $\mathbf{S}^T \mathbf{S}$ and $\mathbf{S}^T \mathbf{M}$ matrices are stored in memory.

Collocation is a useful alternative to variational methods. When the number of collocation points is equal to the number of basis functions, a spectrum can be computed by solving a matrix eigenvalue problem $\mathbf{A}\mathbf{U} = \mathbf{B}\mathbf{U}E$, in which the matrices \mathbf{A} and \mathbf{B} both have rows labelled by points and columns labelled by functions. It has recently been understood that by combining collocation with Lagrange-type basis functions, pseudo-Gauss collocation points, and sparse-grid interpolation ideas, it is possible to make $\mathbf{B} = \mathbf{I}$ and at the same time minimize the size of \mathbf{A} .^{56–58} When the number of collocation points is greater than the number of basis functions, a spectrum can be computed by solving a matrix eigenvalue problem $\mathbf{A}\mathbf{U} = \mathbf{B}\mathbf{U}E$, in which the matrices \mathbf{A}

and \mathbf{B} both have rows and columns labelled by basis functions (Eq. (3)). Another option, used in previous papers, is to use a rectangular eigensolver.^{48–54} In these papers, a fitted Gaussian basis was used to solve three-dimensional (3D) problems, including isolated H_2O ⁴⁸ and H_2O adsorbed on Pt.⁴⁹ For molecules with more atoms, a parameterized harmonic basis was used to impose an approximate nodal structure on the wavefunctions.⁵¹ In this way, it was possible to solve the SE for a molecule-surface system (AcOH on TiO_2) in 7D^{53,54} and for a molecule (UF_6) in 15D⁵⁵ with extremely small bases and sets of points (as few as 2.1 points per coordinate).

We use a space-fixed Cartesian KEO with basis functions that depend on curvilinear coordinates. This idea could be employed in many contexts. In addition, we use Gaussian basis functions, for the first time, to solve a 6D vibrational SE. We use a quasi-random point placement scheme (on the order of 100 000 points), up to 40 000 Gaussian basis functions, and a simple heuristic for the choice of the Gaussian widths to achieve accuracy better than 1 cm^{-1} on the first 50 levels of H_2CO . The calculations described in this article can be done on a powerful desktop computer.

METHODS

In this paper, we use internal curvilinear coordinates.^{59–61} They are better than normal coordinates unless vibrations are small amplitude. We use Gaussian basis functions. They have the advantage that they are localized in configuration space and can be placed where one expects wavefunctions to have significant amplitude. They can also be used with any coordinates. On the other hand, there is some evidence that to optimize Gaussians one requires more parameters than would be needed with a harmonic basis and that when used with collocation more functions and points are required than would be necessary with a harmonic basis.⁵¹

The Gaussian basis functions we use are⁶

$$g_n(\mathbf{x}) = \prod_{d=1}^D (2\sigma_d^2\pi)^{-\frac{1}{2}} e^{-\frac{(x_d - x_d^{0,n})^2}{2\sigma_d^2}}, \quad (4)$$

where $D = 6$ is the number of dimensions. The x_d are coordinates that specify the shape of the molecule. The N basis function centers $\mathbf{x}^{0,n}$ are the first N of the M collocation points. Sobol⁶² points are used because they fill the energetically accessible space and ensure that basis functions are not too close to each other, which is important for numeric stability. The widths σ_d^n are the same for all n but depend on d . They should be chosen to avoid near linear dependence, but so that the basis spans the relevant part of Hilbert space. We choose widths proportional to the corresponding coordinate's range Δx_d , $\sigma_d = \alpha N^{-\frac{1}{D}}$, where $\alpha \approx 1.2\Delta x_d$ for bond lengths and $\alpha \approx 0.6\Delta x_d$ for angles. $N^{\frac{1}{D}}$ is the number of functions we would have in coordinate d if the centers were on a direct product grid and, if the distribution of centers is fairly close to uniform, it is proportional to the range of the coordinate. Near-optimal values of α are easily found by doing test calculations with moderate numbers of points and basis functions and choosing α to reduce the residual, R (see below).

Practically, we find that the optimal width is just less than the width at which numeric instability sets in, as expected. Many authors have used Gaussian basis functions.^{6–10} An important difference between most Gaussian basis function methods and ours is the fact that we do not use exact equations for the KEO matrix elements. This makes it possible to monitor the quality of the solution by using the residual

$$R = \sum_{k=1}^K \|(\mathbf{M} - E_k \mathbf{S}) \mathbf{c}_k\|, \quad (5)$$

where K is the number of desired levels. To reduce the memory cost of the calculation, elements of the square matrices $\mathbf{S}^T \mathbf{M}$ in Eq. (3) are accumulated by multiplying blocks of \mathbf{S}^T with blocks of \mathbf{M} and summing the results. The same thing is done for $\mathbf{S}^T \mathbf{S}$. In this fashion the number of points can be systematically increased.

The complexity of internal-coordinate KEOs is a serious problem. All (exact) internal-coordinate KEOs are complicated. If the π - π terms of the Watson normal-coordinate KEO⁶³ are not neglected, it is *more* complicated than many internal-coordinate KEOs. If the internal coordinates are polyspherical, there are several simple and general ways of writing the KEO.^{64–67} Unfortunately, coupling in polyspherical coordinates is sometimes large. Of course, the KEO in space-fixed (SF) Cartesian coordinates is simple, but one does not want to use basis functions that depend on SF Cartesian coordinates. Here we show that it is possible to use basis functions that are the functions of internal curvilinear coordinates in conjunction with a space-fixed (SF) *Cartesian* KEO. This obviates the need to obtain (analytically or numerically) an internal-coordinate KEO and greatly simplifies computing a spectrum and will also simplify the optimization of basis parameters (not done in this paper). The key idea is not to transform the SF KEO, but instead to find a way of applying the SF KEO to a basis function that depends on internal curvilinear coordinates.

We apply the methods of this section to formaldehyde using as coordinates the CO bond length, the two CH bond lengths, the two HCO angles, and the book angle between the two HCO planes.^{68,69} It is only possible to use the SF Cartesian KEO if KEO matrix elements are evaluated numerically. This is not a problem, however, because if the basis is good and the quadrature is not excellent, it is better not to use exact KEO matrix elements.²¹ Using the space-fixed KEO does have the disadvantage that matrix elements of the KEO in a product basis are not factorizable, even when the curvilinear coordinate KEO is a sum of products. If the Hamiltonian matrix is small enough, this does not impede calculations.

The space-fixed KEO is

$$\mathbf{T}^{SF} = - \sum_{k=1}^{3N_{atoms}} \frac{1}{2m_k} \frac{\partial^2}{\partial X_k^2}. \quad (6)$$

We want to apply \mathbf{T}^{SF} to a basis function $g_n(q)$, where q represents $3N_{atoms} - 6$ internal curvilinear coordinates (the same coordinates as those represented by x in the Introduction), and to evaluate the resulting function at a particular collocation point q^m . If \mathbf{T}^{SF} is re-written¹¹ in terms of three coordinates for the center of mass, three Euler angles, and $3N - 6$ shape coordinates (N is the number of atoms), one obtains

$$\begin{aligned} \mathbf{T}^{int} = & \mathbf{T}^{CM} + \sum_{ij} \mathbf{A}_{ij} \mathbf{p}_i \mathbf{p}_j + \sum_i \mathbf{B}_i \mathbf{p}_i + \sum_{ab} \mathbf{C}_{ab} \mathbf{J}_a \mathbf{J}_b \\ & + \sum_a \mathbf{D}_a \mathbf{J}_a + \sum_{ia} \mathbf{E}_{ia} \mathbf{p}_i \mathbf{J}_a, \end{aligned}$$

where \mathbf{A} , \mathbf{B} , \mathbf{C} , \mathbf{D} , and \mathbf{E} are the coordinate-dependent matrices, $\mathbf{p}_i = \frac{\partial}{\partial q_i}$, and \mathbf{T}^{CM} is the kinetic energy of the center of mass. Eigenvalues of a matrix representing $\mathbf{T}^{int} + V$ and $\mathbf{T}^{SF} + V$ in a basis of functions that depend only on shape coordinates approximate vibrational energy levels because when \mathbf{T}^{CM} and \mathbf{J}_a are applied to a basis function one obtains zero. To compute $\mathbf{T}^{SF} g_n(q)$ at q^m , we write q in terms of the Cartesian coordinates, \tilde{x} , of a rotated space-fixed (RSF) frame whose origin is on the C atom, whose y axis is along the CO bond, and whose x axis is in the plane containing C, O, and one of the H nuclei. We denote this axis system a rotated space-fixed (RSF) frame for the point q^m . It is straightforward to write the q on which $g_n(q)$ depend as functions of the RSF coordinates. In the same fashion, one can determine the RSF coordinates, \tilde{x}^m , of the collocation point at which the derivative is evaluated. We use the RSF coordinates as a tool in order to apply \mathbf{T}^{SF} to a basis function $g_n(q(\tilde{x}))$. \mathbf{T}^{SF} could be applied to $g_n(q(X))$ directly, without the RSF frame, but it is more convenient to exploit the invariance of the Laplacian under orthogonal transformations. To simplify the coordinate transformation, a different RSF is used for each collocation point. Note that we are not writing the KEO in RSF coordinates. Second derivatives of $g_n(q(\tilde{x}))$ at \tilde{x}^m are computed using a finite difference method. This requires $g_n(q(\tilde{x}^m + d\tilde{x}^m))$. It is crucial that the orientation of the RSF is *identical* for $\tilde{x}^m + d\tilde{x}^m$ and \tilde{x}^m . Note that in a standard molecule-fixed (MF) frame, the orientation of the frame depends on the shape of the molecule and that therefore two points in MF Cartesian space have MF frames with *different* orientations. The RSF frame is not a MF frame. Using these ideas, we compute

$$\mathbf{T} g_n = - \sum_{k=1}^{3N_{atoms}} \frac{1}{2m_k} \frac{\partial^2}{\partial \tilde{x}_k^2} g_n \left(q \left(\tilde{x} \right) \right), \quad (7)$$

where N_{atom} is the number of atoms, and k indexes the Cartesian coordinates \tilde{x} . We use a five-point finite difference stencil with $dx = 1 \times 10^{-5}$ a.u. which gives converged results. We were unable to find a step size that gave accurate derivatives with a three-point stencil.

The calculations were done in Matlab⁷⁰ and the code is provided in the [supplementary material](#). The code is about 200 lines long. Calculating 50 levels of formaldehyde takes between a few minutes and dozens of minutes when using multiple cores (on a 12-core AMD processor). The bottleneck is the memory required to solve the eigenproblem for which Matlab's *eigs* function was used. For the largest calculation presented here, with 40 000 basis functions, the memory required to store $\mathbf{S}^T \mathbf{M}$ and $\mathbf{S}^T \mathbf{S}$ is 24 GB. Sub-cm⁻¹ accuracy on many levels can be obtained with 25 000–30 000 functions. Modern personal computers have this amount of memory and the necessary central processing unit (CPU) power. This means that it is possible to calculate 50 accurate levels of a 6D Hamiltonian

TABLE I. The lowest 50 vibrational levels of H₂CO computed with 25 000 basis functions and different numbers of points. For each set of points, the ZPE and the difference between the ZPE and the reference value are given at the top of the table. The lowest 49 excited states, from which the ZPE is subtracted, are also given. All results are in cm⁻¹. The mean absolute error and the residual *R* (Eq. (5)) are also given. The last columns include available experimental energies, deviations from them (for the calculation with the largest number of points) as well as the mean absolute deviation.

Number of PES points													
25 000		50 000		100 000		150 000		200 000		250 000			
ZPE													
Level	Δref	Level	Δref	Level	Δref	Level	Δref	Level	Δref	Level	Δref		
5775.2	−0.05	5775.2	−0.11	5775.4	0.15	5775.4	0.11	5775.3	0.01	5775.3	−0.01		
Frequencies													
f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	Expt.	ΔExpt.
1168.2	1.41	1168.0	1.24	1168.0	1.22	1167.8	1.07	1167.7	0.97	1167.7	0.94	1167.3	0.4
1251.3	0.69	1250.7	0.16	1250.6	0.01	1250.4	−0.13	1250.6	0.03	1250.6	−0.02	1249.1	1.5
1500.3	0.23	1501.3	1.25	1501.6	1.56	1501.7	1.63	1501.7	1.61	1501.6	1.55	1500.2	1.4
1747.0	0.38	1747.0	0.35	1747.4	0.76	1747.4	0.71	1747.3	0.69	1747.5	0.81	1746.1	1.4
2326.6	−0.67	2326.4	−0.93	2326.4	−0.86	2326.6	−0.72	2326.7	−0.60	2326.7	−0.56	2327.5	−0.8
2422.2	0.44	2421.5	−0.24	2421.4	−0.37	2421.4	−0.37	2421.6	−0.17	2421.7	−0.08	2422.4	−0.7
2497.8	−0.22	2497.8	−0.17	2497.8	−0.16	2497.7	−0.26	2498.1	0.09	2498.1	0.08	2496.1	2.0
2666.4	0.06	2666.8	0.47	2666.2	−0.12	2666.0	−0.37	2665.9	−0.40	2665.9	−0.42	2667.1	−1.2
2719.9	0.19	2720.9	1.19	2721.1	1.43	2721.4	1.69	2721.5	1.80	2721.2	1.47	2718.6	2.6
2780.3	−0.99	2780.3	−1.02	2780.5	−0.85	2780.4	−0.88	2780.6	−0.74	2780.5	−0.86	2782.5	−2.0
2841.7	−0.94	2841.7	−0.91	2841.6	−1.09	2841.5	−1.12	2841.9	−0.79	2841.9	−0.71	2843.4	−1.5
2906.2	0.30	2905.2	−0.70	2905.4	−0.48	2904.9	−0.92	2904.9	−0.97	2905.0	−0.86	2906.0	−1.0
3001.1	2.06	3000.2	1.16	3000.4	1.37	3000.4	1.36	3000.6	1.56	3000.6	1.49	2998.1	2.5
3007.6	6.28	3005.9	4.63	3005.1	3.85	3003.8	2.55	3003.4	2.13	3002.8	1.48	3000.6	2.2
3242.9	4.06	3243.5	4.66	3241.8	2.98	3241.0	2.18	3240.7	1.91	3240.1	1.33	3239.0	1.1
3472.4	0.60	3472.8	0.96	3472.8	0.99	3473.2	1.40	3473.6	1.84	3474.1	2.30	3471.6	2.5
3481.9	−2.52	3481.5	−2.93	3481.4	−3.03	3481.2	−3.23	3481.4	−3.03	3481.3	−3.11	3480.7	0.6
3587.0	0.48	3586.7	0.21	3586.6	0.07	3586.5	−0.01	3586.7	0.19	3586.5	0.01	3586.6	−0.1
3674.1	−0.77	3674.2	−0.64	3674.2	−0.71	3674.1	−0.81	3674.3	−0.56	3674.5	−0.37	3673.0	1.5
3744.5	2.35	3742.9	0.78	3743.1	1.03	3743.0	0.92	3743.3	1.16	3743.2	1.14		
3828.4	3.34	3830.3	5.24	3828.3	3.23	3828.1	3.00	3828.0	2.96	3828.0	2.91	3825.3	2.7
3885.9	−1.34	3886.7	−0.54	3886.6	−0.58	3887.2	−0.03	3887.1	−0.08	3887.2	−0.02	3886.5	0.7
3940.6	2.92	3940.1	2.38	3940.0	2.34	3940.2	2.56	3939.7	2.02	3939.6	1.89	3937.4	2.2
3940.8	0.43	3940.1	−0.32	3940.4	0.06	3940.7	0.29	3941.0	0.64	3940.9	0.51	3940.2	0.7
3996.5	0.76	3996.2	0.46	3995.5	−0.24	3995.5	−0.26	3995.6	−0.09	3995.5	−0.19	3995.8	−0.3
4034.2	1.09	4033.3	0.17	4033.1	−0.02	4033.0	−0.18	4032.9	−0.21	4032.7	−0.49		
4058.4	−0.49	4056.9	−1.96	4057.8	−1.13	4057.5	−1.39	4057.6	−1.25	4057.6	−1.31	4058.3	−0.7
4088.1	2.52	4088.7	3.18	4088.2	2.65	4087.8	2.21	4087.4	1.86	4087.0	1.45	4083.1	3.9
4163.5	−0.42	4161.4	−2.52	4161.7	−2.23	4161.8	−2.05	4162.2	−1.67	4162.5	−1.34	4163.9	−1.4
4172.3	7.87	4169.0	4.58	4169.4	4.98	4169.2	4.77	4169.1	4.70	4168.0	3.50		
4198.0	3.73	4201.2	6.88	4200.4	6.07	4199.5	5.20	4199.8	5.50	4200.0	5.72		
4250.8	0.32	4250.4	−0.11	4251.1	0.58	4250.7	0.23	4250.5	0.05	4250.7	0.25	4248.7	2.0
4250.8	−2.28	4250.4	−2.71	4251.1	−2.01	4250.7	−2.36	4251.4	−1.66	4251.0	−2.06	4253.8	−2.8
4333.7	−2.96	4336.3	−0.36	4337.7	1.09	4338.0	1.39	4338.5	1.82	4338.4	1.69	4335.1	3.3
4402.2	4.77	4399.7	2.24	4397.4	−0.09	4397.4	−0.08	4397.2	−0.27	4396.5	−0.96	4397.5	−1.0
4465.8	−1.65	4468.5	1.09	4467.7	0.25	4468.1	0.65	4468.5	1.07	4468.5	1.07	4466.8	1.7
4506.3	10.20	4514.5	18.45	4517.2	21.07	4520.1	24.02	4518.7	22.61	4516.2	20.10		
4522.9	−5.27	4523.1	−5.07	4524.3	−3.88	4523.5	−4.70	4524.4	−3.78	4524.7	−3.48	4529.4	−4.7
4568.8	−3.91	4569.3	−3.37	4570.1	−2.62	4569.4	−3.25	4570.0	−2.72	4569.7	−2.95	4571.5	−1.8
4625.0	0.96	4624.4	0.35	4623.3	−0.70	4623.8	−0.23	4623.8	−0.23	4623.4	−0.60	4624.3	−0.9
4630.9	−16.11	4631.3	−15.73	4631.4	−15.71	4631.2	−15.83	4631.4	−15.63	4631.4	−15.62	4629.0	2.4
4728.9	−0.65	4726.3	−3.20	4730.4	0.93	4731.9	2.43	4732.5	3.02	4731.8	2.26	4730.8	1.0
4731.9	−2.51	4732.0	−2.46	4733.4	−1.03	4732.2	−2.25	4732.5	−1.89	4731.8	−2.65	4733.8	−2.0
4746.7	−2.55	4746.4	−2.82	4744.7	−4.52	4744.4	−4.78	4744.2	−4.97	4743.7	−5.51	4741.9	1.8
4841.8	−1.79	4842.8	−0.72	4843.1	−0.50	4843.2	−0.42	4843.4	−0.21	4843.1	−0.50	4842.0	1.1
4929.1	2.92	4927.5	1.27	4926.4	0.14	4925.9	−0.33	4925.9	−0.30	4925.7	−0.54		
4953.3	−2.79	4958.1	2.00	4955.6	−0.46	4954.5	−1.61	4954.5	−1.56	4953.0	−3.04	4955.2	−2.2

TABLE I. (Continued.)

Frequencies													
f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	Expt.	ΔExpt.
4974.8	−5.46	4977.9	−2.42	4975.5	−4.76	4975.9	−4.40	4975.4	−4.87	4975.0	−5.32	4977.1	−2.1
4983.4	0.52	4983.3	0.41	4983.7	0.85	4983.6	0.74	4984.0	1.11	4983.8	0.93		
Mean absolute error ZPE + 50 transitions vs reference												mae vs expt.	
2.36		2.35		2.16		2.28		2.20		2.17		1.44	
R													
4381		4340		2875		1585		1798		1367			

TABLE II. The lowest 50 vibrational levels of H₂CO computed with 30 000 basis functions and different numbers of points. Otherwise the format is the same as in Table I.

Number of PES points													
30 000		60 000		120 000		180 000		240 000		300 000			
ZPE													
Level	Δref	Level	Δref	Level	Δref	Level	Δref	Level	Δref	Level	Δref		
5775.1	−0.21	5775.2	−0.08	5775.2	−0.10	5775.1	−0.18	5775.1	−0.21	5775.1	−0.21		
Frequencies													
f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	Expt.	ΔExpt.
1167.5	0.78	1167.3	0.54	1167.3	0.58	1167.4	0.59	1167.2	0.44	1167.1	0.33	1167.3	−0.2
1251.5	0.95	1251.0	0.48	1250.9	0.32	1250.7	0.17	1250.7	0.15	1250.7	0.09	1249.1	1.6
1501.7	1.66	1502.0	1.92	1501.9	1.84	1501.7	1.65	1501.7	1.60	1501.4	1.34	1500.2	1.2
1747.5	0.83	1747.8	1.17	1747.6	0.96	1747.6	0.97	1747.5	0.90	1747.4	0.76	1746.1	1.3
2327.2	−0.12	2326.9	−0.39	2326.8	−0.53	2326.7	−0.54	2326.7	−0.58	2326.6	−0.65	2327.5	−0.9
2423.1	1.31	2422.4	0.66	2422.2	0.44	2422.2	0.44	2422.1	0.31	2422.0	0.26	2422.4	−0.4
2499.3	1.35	2498.8	0.83	2498.6	0.64	2498.4	0.43	2498.3	0.27	2498.2	0.16	2496.1	2.1
2666.7	0.40	2666.8	0.46	2666.6	0.21	2666.3	−0.03	2666.2	−0.11	2666.1	−0.27	2667.1	−1.0
2722.0	2.26	2722.0	2.28	2722.2	2.49	2721.9	2.23	2722.1	2.38	2721.9	2.22	2718.6	3.3
2780.8	−0.52	2780.3	−0.97	2780.3	−1.02	2780.4	−0.94	2780.3	−0.99	2780.3	−1.02	2782.5	−2.2
2843.1	0.48	2842.6	−0.09	2842.2	−0.49	2841.9	−0.72	2841.8	−0.80	2841.8	−0.88	2843.4	−1.6
2906.6	0.75	2905.9	0.02	2905.7	−0.19	2905.8	−0.12	2905.5	−0.35	2905.4	−0.47	2906.0	−0.6
3002.7	3.66	3001.2	2.16	3000.6	1.52	3000.7	1.60	3000.7	1.67	3001.0	1.91	2998.1	2.9
3004.0	2.68	3002.9	1.66	3002.9	1.62	3002.8	1.55	3002.7	1.43	3002.7	1.39	3000.6	2.1
3240.5	1.72	3241.2	2.45	3240.0	1.16	3240.1	1.31	3240.3	1.46	3240.2	1.38	3239.0	1.2
3473.3	1.51	3475.1	3.28	3474.0	2.21	3473.2	1.37	3473.0	1.19	3472.7	0.92	3471.6	1.1
3481.8	−2.58	3481.1	−3.28	3480.8	−3.57	3480.8	−3.61	3480.9	−3.47	3480.9	−3.52	3480.7	0.2
3588.1	1.56	3587.6	1.10	3587.0	0.50	3586.9	0.37	3586.7	0.19	3586.7	0.17	3586.6	0.1
3675.6	0.73	3675.2	0.35	3675.4	0.52	3675.3	0.44	3675.1	0.27	3675.0	0.14	3673.0	2.0
3744.0	1.87	3743.5	1.42	3743.4	1.29	3743.1	1.03	3743.0	0.89	3742.9	0.82		
3828.6	3.53	3829.1	4.10	3828.7	3.66	3828.4	3.34	3828.1	3.02	3827.8	2.78	3825.3	2.5
3888.2	0.98	3888.0	0.77	3887.9	0.67	3887.9	0.64	3888.2	0.99	3888.2	0.94	3886.5	1.7
3940.0	2.37	3939.7	1.98	3939.8	2.09	3939.8	2.14	3939.7	2.02	3939.4	1.73	3937.4	2.0
3941.3	0.93	3941.4	1.05	3941.4	0.98	3941.1	0.70	3940.8	0.46	3940.6	0.24	3940.2	0.4
3997.6	1.91	3996.1	0.41	3995.7	−0.06	3995.3	−0.45	3995.1	−0.68	3995.0	−0.74	3995.8	−0.8
4033.7	0.57	4032.8	−0.33	4033.0	−0.18	4032.6	−0.52	4032.6	−0.55	4032.6	−0.51		
4058.9	−0.04	4057.9	−1.01	4058.0	−0.85	4058.3	−0.60	4058.1	−0.76	4057.9	−0.98	4058.3	−0.4
4087.3	1.77	4086.0	0.48	4085.9	0.33	4085.5	−0.08	4085.4	−0.20	4085.1	−0.43	4083.1	2.0
4166.7	2.77	4164.0	0.15	4164.0	0.11	4164.0	0.07	4163.5	−0.38	4163.4	−0.52	4163.9	−0.5
4170.4	6.00	4168.9	4.42	4169.2	4.78	4170.1	5.66	4170.1	5.70	4170.5	6.09		
4200.9	6.55	4200.1	5.81	4199.6	5.25	4199.2	4.86	4198.6	4.34	4198.0	3.65		
4250.4	−0.10	4250.5	0.02	4250.5	0.00	4250.6	0.08	4250.6	0.07	4250.5	0.02	4248.7	1.8
4252.0	−1.05	4252.1	−0.98	4252.1	−0.95	4252.2	−0.92	4252.8	−0.25	4252.7	−0.40	4253.8	−1.1

TABLE II. (Continued.)

Frequencies													
f	Δ_{ref}	f	Δ_{ref}	f	Δ_{ref}	f	Δ_{ref}	f	Δ_{ref}	f	Δ_{ref}	Expt.	$\Delta_{\text{Expt.}}$
4336.7	0.03	4337.0	0.34	4337.3	0.60	4337.4	0.77	4337.4	0.76	4337.5	0.87	4335.1	2.4
4401.3	3.89	4399.9	2.44	4398.0	0.56	4397.9	0.48	4397.7	0.28	4397.3	-0.20	4397.5	-0.2
4469.2	1.83	4469.3	1.88	4468.6	1.19	4468.7	1.28	4468.8	1.38	4468.2	0.77	4466.8	1.4
4520.6	24.49	4516.7	20.60	4515.2	19.11	4515.2	19.12	4512.7	16.65	4511.7	15.60		
4524.4	-3.78	4526.1	-2.05	4525.5	-2.61	4525.7	-2.42	4525.9	-2.22	4526.1	-2.06	4529.4	-3.3
4569.1	-3.58	4570.1	-2.62	4569.6	-3.13	4569.6	-3.14	4570.1	-2.64	4570.2	-2.48	4571.5	-1.3
4628.5	4.49	4626.9	2.91	4626.5	2.49	4626.0	2.03	4625.4	1.36	4625.0	0.96	4624.3	0.7
4631.2	-15.84	4630.7	-16.32	4629.9	-17.18	4629.8	-17.25	4629.8	-17.30	4629.7	-17.33	4629.0	0.7
4727.9	-1.60	4729.1	-0.42	4725.9	-3.57	4725.8	-3.72	4725.9	-3.64	4725.6	-3.89	4730.8	-5.2
4735.5	1.05	4735.7	1.29	4734.1	-0.28	4733.7	-0.72	4733.6	-0.82	4733.3	-1.13	4733.8	-0.5
4747.4	-1.80	4746.0	-3.18	4745.2	-3.98	4744.9	-4.32	4745.0	-4.25	4745.0	-4.25	4741.9	3.1
4844.4	0.80	4844.5	0.91	4844.3	0.69	4844.1	0.55	4843.8	0.24	4843.7	0.15	4842.0	1.7
4928.0	1.77	4927.2	0.96	4927.1	0.92	4926.8	0.61	4926.7	0.48	4926.5	0.28		
4953.0	-3.06	4954.0	-2.03	4952.3	-3.74	4950.7	-5.40	4951.4	-4.62	4951.9	-4.13	4955.2	-3.3
4977.9	-2.35	4977.6	-2.66	4977.4	-2.92	4977.1	-3.21	4976.9	-3.37	4976.7	-3.61	4977.1	-0.4
4984.5	1.63	4984.3	1.38	4984.0	1.16	4984.0	1.11	4983.9	1.03	4984.0	1.09		
Mean absolute error ZPE + 50 transitions vs reference												mae vs expt.	
2.57		2.18		2.12		2.13		2.00		1.93		1.29	
R													
3651		2738		1938		2436		1014		1749			

TABLE III. The lowest 50 vibrational levels of H₂CO computed with 40 000 basis functions and different numbers of points. Otherwise the format is the same as in Table I.

Number of PES points													
40 000		80 000		160 000		240 000		320 000		400 000			
ZPE													
Level	Δref	Level	Δref	Level	Δref	Level	Δref	Level	Δref	Level	Δref		
5775.4	0.08	5775.3	0.06	5775.4	0.08	5775.3	0.06	5775.3	0.05	5775.3	0.03		
Transition (frequencies)													
f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	Expt.	ΔExpt.
1167.2	0.44	1167.0	0.23	1167.0	0.21	1166.9	0.15	1166.9	0.17	1166.9	0.15	1167.3	−0.4
1251.0	0.44	1250.8	0.25	1250.7	0.15	1250.7	0.10	1250.6	0.06	1250.6	0.04	1249.1	1.5
1499.9	−0.22	1499.9	−0.15	1499.7	−0.34	1499.7	−0.35	1499.7	−0.41	1499.7	−0.38	1500.2	−0.5
1747.3	0.66	1747.3	0.62	1747.1	0.41	1747.1	0.42	1747.0	0.34	1747.0	0.33	1746.1	0.9
2327.4	0.07	2327.1	−0.17	2327.0	−0.24	2326.9	−0.35	2326.9	−0.40	2326.8	−0.44	2327.5	−0.7
2422.9	1.10	2422.3	0.52	2422.1	0.37	2422.1	0.31	2422.0	0.29	2422.0	0.22	2422.4	−0.4
2498.6	0.57	2498.4	0.41	2498.3	0.31	2498.2	0.24	2498.2	0.19	2498.2	0.17	2496.1	2.1
2666.1	−0.22	2666.2	−0.13	2666.1	−0.25	2666.3	−0.08	2666.3	−0.04	2666.3	−0.03	2667.1	−0.8
2721.3	1.57	2720.9	1.23	2720.8	1.11	2720.7	1.03	2720.6	0.95	2720.6	0.93	2718.6	2.0
2781.1	−0.26	2780.9	−0.46	2780.9	−0.46	2780.9	−0.43	2780.9	−0.43	2780.9	−0.43	2782.5	−1.6
2842.8	0.20	2842.3	−0.30	2842.4	−0.22	2842.4	−0.24	2842.4	−0.26	2842.4	−0.28	2843.4	−1.0
2906.6	0.73	2906.0	0.18	2906.0	0.12	2906.0	0.09	2906.0	0.11	2906.0	0.15	2906.0	0.0
3000.4	1.30	3000.5	1.38	3001.2	2.11	3001.5	2.41	3001.4	2.30	3001.5	2.38	2998.1	3.4
3002.2	0.87	3002.1	0.81	3002.2	0.96	3002.1	0.80	3002.1	0.80	3002.1	0.78	3000.6	1.5
3240.3	1.46	3240.2	1.45	3240.3	1.55	3240.4	1.60	3240.3	1.51	3240.3	1.48	3239.0	1.3
3472.9	1.08	3472.6	0.81	3472.6	0.82	3472.8	1.02	3472.8	0.96	3472.6	0.85	3471.6	1.0
3481.8	−2.66	3481.2	−3.18	3481.0	−3.40	3480.9	−3.51	3480.8	−3.62	3480.7	−3.74	3480.7	0.0
3587.8	1.24	3587.2	0.64	3586.8	0.23	3586.6	0.09	3586.5	−0.01	3586.4	−0.11	3586.6	−0.2
3675.8	0.88	3675.5	0.58	3675.3	0.41	3675.3	0.38	3675.2	0.37	3675.2	0.37	3673.0	2.2

TABLE III. (Continued.)

Transition (frequencies)													
f	Δ_{ref}	f	Δ_{ref}	f	Δ_{ref}	f	Δ_{ref}	f	Δ_{ref}	f	Δ_{ref}	Expt.	$\Delta_{\text{Expt.}}$
3743.2	1.08	3742.8	0.69	3742.5	0.45	3742.5	0.37	3742.4	0.27	3742.3	0.24		
3825.6	0.54	3825.7	0.66	3825.7	0.60	3825.7	0.65	3825.6	0.59	3825.5	0.46	3825.3	0.2
3888.6	1.41	3888.2	1.01	3887.8	0.61	3887.7	0.51	3887.7	0.43	3887.7	0.45	3886.5	1.2
3939.7	1.99	3940.1	2.44	3939.6	1.91	3939.4	1.69	3939.3	1.64	3939.2	1.56	3937.4	1.8
3940.8	0.39	3940.6	0.19	3940.4	0.06	3940.3	-0.05	3940.3	-0.05	3940.3	-0.05	3940.2	0.1
3996.7	1.02	3995.9	0.18	3996.1	0.33	3995.9	0.13	3995.8	0.09	3995.8	0.08	3995.8	0.0
4034.0	0.83	4033.4	0.27	4033.2	0.09	4033.1	-0.02	4033.1	-0.08	4033.0	-0.10		
4058.5	-0.44	4058.3	-0.64	4058.2	-0.66	4058.3	-0.57	4058.2	-0.67	4058.2	-0.69	4058.3	-0.1
4086.0	0.42	4085.7	0.15	4085.6	0.00	4085.5	-0.05	4085.4	-0.11	4085.5	-0.06	4083.1	2.4
4166.1	2.19	4165.0	1.14	4164.7	0.85	4164.6	0.76	4164.4	0.56	4164.4	0.51	4163.9	0.5
4166.1	1.62	4167.7	3.25	4167.6	3.16	4166.9	2.45	4166.6	2.15	4166.3	1.86		
4196.7	2.36	4197.0	2.74	4196.9	2.63	4196.8	2.52	4196.5	2.21	4196.4	2.12		
4250.6	0.09	4251.0	0.54	4251.1	0.62	4251.0	0.51	4250.9	0.38	4250.9	0.38	4248.7	2.2
4252.3	-0.77	4252.9	-0.23	4252.8	-0.28	4253.2	0.13	4253.2	0.13	4253.4	0.31	4253.8	-0.4
4338.3	1.61	4337.7	1.07	4337.9	1.21	4337.8	1.19	4337.7	1.00	4337.6	0.96	4335.1	2.5
4399.0	1.59	4398.7	1.24	4398.1	0.66	4398.0	0.56	4398.0	0.51	4397.8	0.31	4397.5	0.3
4467.5	0.14	4468.4	1.03	4467.8	0.43	4467.7	0.30	4467.4	0.00	4467.3	-0.10	4466.8	0.5
4507.7	11.65	4508.8	12.74	4507.1	11.01	4506.5	10.41	4507.3	11.20	4507.6	11.54		
4527.4	-0.81	4527.6	-0.52	4527.6	-0.54	4527.9	-0.30	4527.8	-0.34	4527.9	-0.31	4529.4	-1.5
4571.6	-1.14	4571.9	-0.79	4571.7	-0.98	4571.7	-0.99	4571.7	-0.99	4571.6	-1.12	4571.5	0.1
4624.8	0.75	4624.0	-0.01	4624.2	0.17	4624.1	0.09	4624.1	0.13	4624.1	0.07	4624.3	-0.2
4630.7	-16.32	4630.1	-16.96	4629.9	-17.17	4629.8	-17.28	4629.7	-17.41	4629.5	-17.55	4629.0	0.5
4728.0	-1.47	4728.9	-0.62	4729.5	0.02	4729.8	0.30	4730.4	0.86	4730.4	0.86	4730.8	-0.4
4734.0	-0.47	4734.5	0.04	4734.2	-0.22	4734.2	-0.27	4734.0	-0.38	4734.1	-0.35	4733.8	0.3
4747.2	-2.00	4746.3	-2.96	4745.7	-3.56	4745.5	-3.73	4745.3	-3.87	4745.2	-3.98	4741.9	3.3
4844.5	0.90	4844.2	0.64	4843.7	0.13	4843.6	0.03	4843.5	-0.06	4843.5	-0.07	4842.0	1.5
4927.5	1.28	4926.8	0.62	4926.7	0.52	4926.6	0.43	4926.6	0.38	4926.6	0.35		
4955.6	-0.50	4955.6	-0.47	4954.0	-2.10	4953.8	-2.23	4953.3	-2.80	4953.1	-2.92	4955.2	-2.1
4976.5	-3.75	4976.2	-4.06	4976.2	-4.05	4976.6	-3.72	4976.7	-3.61	4976.7	-3.56	4977.1	-0.4
4984.6	1.69	4983.7	0.85	4983.8	0.94	4983.8	0.92	4983.6	0.77	4983.6	0.72		
Mean absolute error ZPE + 50 transitions vs reference												mae vs expt.	
1.54		1.45		1.39		1.34		1.34		1.34		0.90	
R													
4827		4771		1525		2112		1904		1627			

with our method on a desktop computer using commercial (i.e., Matlab) software. Calculations were done using the analytic formaldehyde PES of Ref. 69 to gauge the accuracy of the method. The spectrum computed in Ref. 43 on the same PES was used as a reference. The reference levels were computed with a large product basis and the Lanczos algorithm. It is assumed that they are well converged and are considered exact for the purposes of this work (except one level as described below).

The collocation points are chosen within ranges limited by maximum displacements of each coordinate at $V_{\text{max}} = 15\,000\text{ cm}^{-1}$ (we set the equilibrium value of the potential to zero). We use a Sobol sequence⁶² within these ranges, and points are accepted if $(V(\mathbf{x}) < V_{\text{max}})$ and $(V(\mathbf{x}) < V_{\text{max}} \times 1.2\text{rand})$, where *rand* is a random number. This is done to weight more lower-energy points.⁴³ Due to randomness in the point selection scheme, changing the random seed changes levels by about 0.01 cm^{-1} (for M and N values used here). We

therefore report only the first decimal place in our computed levels.

RESULTS

Tables I–III present differences between the computed vibrational levels and the computed zero-point energy (ZPE) for different numbers of points and basis functions, as well as the computed ZPE values. The energy differences and the ZPE are compared to reference and, for energy differences, experimental values. At the bottom of the tables, we also report residuals, R , and mean absolute errors (*mae*). Because integrals are evaluated by quadrature, there is no reason to expect that, for a fixed M , errors will decrease monotonically as the basis size is increased. As M is increased, R will approach a limit determined by the basis size; however, R may not decrease monotonically. The method is not variational. It has been noted in previous papers about using Gaussian basis sets that the

condition number of $S^T S$ is sometimes a problem. For the calculation with 40 000 basis functions and 400 000 points, the condition number of $S^T S$ is about 2×10^{10} . It is small enough that it does not impede accurate calculation of the eigenvalues. The following conclusions can be made from these results:

- (i) About 40 000 basis functions are sufficient to achieve an accuracy of 1 cm^{-1} . The *mae* with respect to the reference energies is about 1.4 cm^{-1} with about 100 000 points and can be improved by adding more points. 100 000 points are few enough that they could be computed *ab initio*. The accuracy of the ZPE (which is often more difficult to converge than level differences) is better than 0.1 cm^{-1} . The majority of levels are reproduced to better than 1 cm^{-1} when more than 100 000 PES points are used. There is one level with a deviation from the reference level of about 17 cm^{-1} . It is unaltered by changing the centers of the Gaussians and the point positions. The deviation is, however, not due to the method we introduce in this paper. In the Lanczos calculation, convergence of that level is impeded by a constraint introduced to avoid holes in the PES. Our energy agrees well with the experimental value. Overall, our levels are very close to their experimental counterparts; *mae* = 0.90 cm^{-1} . The median absolute deviation vs. the reference levels is 0.38 cm^{-1} .
- (ii) There is a clear advantage to using more points than basis functions. Because the most computationally costly part of the calculation is the solution of the matrix eigenproblem, accuracy can be improved by adding more points without increasing the basis size and without significantly increasing the CPU or memory cost. This is achieved by accumulating elements of square matrices and without having to compute matrix products of full rectangular matrices whose size is determined by the number of points.
- (iii) The number of collocation points required to converge the calculation is, as expected, larger when the basis is larger: With 25 000 basis functions, there is little improvement after $M = 50\,000$; with 30 000 functions, errors decrease by increasing the number of points up to about 200 000; with 40 000 functions, errors decrease by increasing the number of points up to about 300 000. There is a general trend of improvement in the residual, R , with improvement in *mae*. In the absence of reference levels, R could be used to guide the selection of α . The value of R can easily be changed by a factor of two by changing the points and it is therefore trends in R rather than absolute values that are important. R is sensitive to the points because many points are in regions in which wavefunctions are small. If needed, R could be redefined to make it less sensitive, e.g., by weighing the residuals of individual points by wavefunction values.

CONCLUSION

In this paper, we propose a method that makes it possible to use basis functions that depend on curvilinear internal coordinates to compute vibrational energy levels without

deriving a KEO and without numerically computing coefficients of a KEO. For decades it has been known that using curvilinear coordinates reduces the number of basis functions required to represent vibrational wavefunctions. Unfortunately, curvilinear KEOs are very messy. This causes two problems: (1) derivation of the operators is tricky and error-prone; (2) the number of terms and the complicated nature of some of the individual terms make using the operator difficult. The first problem no longer impedes progress. Computers can be made to derive KEOs.^{11,71} Alternatively, coefficients of derivative operators in the KEO can be evaluated numerically. A general and versatile program for this purpose exists.¹⁶ Despite these developments, the second problem can be important. Using the space-fixed KEO obviates both problems.

The idea of using a space-fixed Cartesian KEO to compute vibrational energy levels is unorthodox. It works only if matrix elements of the KEO are calculated numerically. Needing to calculate KEO matrix elements numerically may seem like a significant disadvantage. For decades the standard paradigm has been to exploit exact analytic KEOs to derive equations for the KEO matrix elements. Although this might be more elegant, it will not necessarily lead to more accurate solutions of the Schrödinger equation. If the basis is good, more accurate solutions are obtained by computing KEO, potential, and overlap matrix elements with quadrature.²¹ We point out that this is a form of “rectangular collocation” and that the accuracy of the solutions of the Schrödinger equation can be assessed by computing a residual.

In this paper, these ideas are used with a Gaussian basis⁶ and bond coordinates. Gaussian basis functions have the advantage that they can be easily placed in dynamically important regions of configuration space and are not linked to the quality of a zeroth-order Hamiltonian. Other basis functions and coordinates could also be used with the space-fixed Cartesian KEO, but they make the method general and easy to implement. The implementation is surprisingly easy: the Matlab code is about 200 lines. With this Matlab code, we were able to calculate accurate vibrational levels of formaldehyde (a 6D Hamiltonian) on a desktop computer; however, it is not the cost of the calculation that is most important, but the simplicity and the generalizability of the code. Our results demonstrate that the ideas work. The first 50 vibrational levels of formaldehyde are computed with an average error less than 1 cm^{-1} using about 10^5 points and about 10^4 basis functions. Most levels are within 0.4 cm^{-1} of the reference values. To the best of our knowledge, this is the first accurate 6D calculation using a Gaussian basis. We clearly showed the advantage of using more points than basis functions. The number of points is small enough that they could be computed with *ab initio* methods.

When it is possible to use the polyspherical coordinates associated with a set of “orthogonal” vectors, then the polyspherical KEO is simple enough that it is easy to use for a molecule with 4 or 5 atoms. Calculations for larger molecules are possible, but the number of terms in the KEO increases quickly and the cost scales linearly with the number of terms. If the vectors are not orthogonal, the number of terms is even larger. For such problems, the space-fixed KEO approach of this paper should be advantageous.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the Matlab code used in the calculations.

ACKNOWLEDGMENTS

This research was supported by the NSERC of Canada (T.C.) and the Ministry of Education of Singapore (S.M.). We thank Xiaogang Wang for providing the reference energy levels and confirming that the level with a large deviation was not converged in the Lanczos calculation (probably due to a constraint imposed on the PES to avoid holes).

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