Using collocation and solutions for a sum-of-product potential to compute vibrational energy levels for general potentials

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Abstract

It is easier to compute a vibrational spectrum when the potential energy surface (PES) is a sum-of-products (SOP). Many popular computational methods work only if the PES is a SOP. However, the most accurate PESs are not SOPs. We propose using collocation and solutions of the Schrödinger equation with a SOP PES to compute solutions on a corresponding general PES. This makes it possible to account for coupling and anharmonicity omitted from the SOP PES. We find that correcting energy levels computed on a SOP PES with collocation reduces differences with exact energy levels by about two orders of magnitude.

I. INTRODUCTION

Given a potential energy surface (PES), it is possible to solve the time-independent Schrödinger equation numerically exactly to compute the vibrational (or ro-vibrational) spectrum of a poly-atomic molecule [1–6]. Such calculations can be divided into two groups: those in which the potential energy surface (PES) has a special simplifying form and those in which the form of the PES is general. The two most common special simplifying forms are the sum-of-products (SOP) form [7–9] and the N-mode representation form [10–13]. When the PES has a special simplifying form, it is possible to do accurate calculations for molecules with tens of atoms [9, 14–16]. Calculations with general PESs are more difficult and only tractable for smaller molecules. In this Letter, we propose a method for cheaply obtaining good estimates of energies on a general PES using the results of a calculation done on a related PES with a special simplifying form. The special form we focus on is the SOP form.

The SOP form makes calculations easier because: 1) it obviates the need for full-dimensional quadrature [17]; 2) it reduces the cost the matrix-vector products (MVP) required to use an iterative eigensolver [18, 19] . To realize advantages 1) and 2), it is imperative that each basis function be a product of univariate functions of the coordinates used to represent the PES. Advantage 1) is obvious. With a SOP PES and a product basis, every Hamiltonian matrix element is a product of one-dimensional integrals. If the PES does not have SOP form then multidimensional quadrature is required. Multidimensional quadrature is costly and typically requires a large set of quadrature points. Advantage 2) is also important. If a basis has product structure it can be exploited when the PES is a SOP to efficiently evaluate MVPs by doing sums sequentially. The simplest such basis is a direct product basis and in this case the cost of a MVP scales as n^{D+1}, where D is the dimensionality and n is a representative number of basis functions for a single coordinate [20]. Similar ideas can be used with a non-direct product basis [21, 22]. These and related advantages have made it possible to do calculations on large molecules [9, 14, 15].

When the PES does not have a simple form, e.g. a SOP, it becomes necessary to use (in some form) quadrature and to solve

$$(\mathbf{K^{exact}} + \mathbf{V^{quad}})\mathbf{U} = \mathbf{S^{quad}UE} \,, \tag{1}$$

where $\mathbf{K^{exact}}$ is an exact matrix representation of the kinetic energy operator (KEO), $\mathbf{V^{quad}}$ is a quadrature approximation to the matrix representation of the PES, and $\mathbf{S^{quad}}$ is a quadrature approximation to the overlap matrix. If the basis functions are products of univariate functions then

it is common to use a direct product quadrature. Often one chooses the 1-D quadratures so that $\mathbf{S}^{\mathbf{quad}} = \mathbf{I}$. Non-direct product quadrature schemes are difficult to design [23]. The number of points in a direct product quadrature grid scales as n^D. If $D \gtrsim 9$ then storing the PES on the grid requires a lot of memory. A direct product discrete variable representation (DVR) calculation has similar memory requirements [20]. It is possible to use quadrature, but reduce the memory required, by dividing coordinates into two groups and solving two sub-problems. Some calculations use basis functions that are products of primitive functions for one group and eigenfunctions of one of the sub-problems [24, 25]. Others use basis functions that are products of the eigenfunctions of both sub-problems [26–28]. These calculations require tuning several parameters and using large direct product quadrature grids for the sub-problems.

In this Letter we bridge the dichotomy between the simplicity of the SOP PES world and the accuracy and generality of the general PES world. Probably the most natural way to do this is to use quadrature and basis functions for solving the Schrödinger equation with $H_{gen} = \hat{K} + V_{gen}$ that are eigenfunctions of $H_{sop} = \hat{K} + V_{sop}$. $\hat{K}$ is the kinetic energy operator (KEO); V_{gen} is a general PES; and V_{sop} is a SOP approximation to V_{gen}. These basis functions should be excellent in the sense that few will be required as long at $V_{sop} \sim V_{gen}$. How would one choose quadrature points and weights for computing matrix elements of H_{gen} in the basis of the eigenfunctions of H_{sop} ? The simplest idea is to use a direct product quadrature. It can be chosen so that $\mathbf{S}^{\mathbf{quad}} = \mathbf{I}$, but a direct product grid has many points In this letter, we shall instead use "rectangular collocation" [29–32]. Rectangular collocation (RC) has the disadvantage that it requires solving a generalized eigenvalue problem, but the advantage that it is not necessary to choose points (and there are no weights) with which quadrature approximations to integrals are accurate. We show that with RC and a point set much smaller than a direct product grid, it is straightforward to incorporate much of the effect of $V_{gen} - V_{sop}$ on the vibrational energies.

II.   RECTANGULAR COLLOCATION

As is typically the case, wavefunctions Ψ_n are represented as linear combinations of basis functions $\phi_i(\mathbf{x})$, $i = 1, \cdots, N$ that depend on coordinates $\mathbf{x}$. In collocation[33–35], the basis expansion coefficients are determined by demanding that the Schrödinger equation be satisfied at collocation points $\{\mathbf{x}_m\}$ for $m = 1,.., M$ and solving

$$(\mathbf{G} + \mathbf{VB})\tilde{\mathbf{U}} = \mathbf{B}\tilde{\mathbf{U}}\tilde{\mathbf{E}} , \qquad (2)$$

where elements of the diagonal matrix $\tilde{\mathbf{E}}$ are energies. In this equation, $G_{ji} = \hat{K}\phi_i(\mathbf{x}_j)$, $V_{jk} = V(\mathbf{x}_j)\delta_{kj}$, and $B_{ji} = \phi_i(\mathbf{x}_j)$. To solve this equation when $M > N$, we multiply on the left by $\mathbf{B^T}$ and obtain

$$(\mathbf{B^T G} + \mathbf{B^T VB})\mathbf{U} = (\mathbf{B^T B})\mathbf{UE} \ . \tag{3}$$

Using more points than basis functions is expected to yield more accurate energies because using more points constrains wavefunctions at more points. Using more points also improves the condition number of $(\mathbf{B^T B})$.

When it is not possible to write a wavefunction as an *exact* linear combination of the basis functions then the corresponding energy computed from Eq. 3 will depend on the choice of the collocation points. We call error introduced by the choice of the points point-set error. The error in an eigenvalue E_n is proportional [29] to $\varepsilon_{b_n}^2 + \varepsilon_{b_n}\varepsilon_{q_n}$, where

$$\varepsilon_{b_n} = ||\Psi_n - \psi_n^{best}|| \ , \tag{4}$$

with Ψ_n the exact wavefunction and ψ_n^{best} the best possible approximation to the wavefunction in the $\phi_i(\mathbf{x})$, $i = 1, \cdots N$ basis; and ε_{q_n} is a measure of point-set error. Clearly, using a basis that reduces ε_{b_n} should reduce the effect of ε_{q_n}. When $V_{sop} \sim V_{gen}$, it is reasonable to expect that ε_{b_n} will be small when the $\phi_i(\mathbf{x})$ are the eigenfunctions of H_{sop}. The number of $\phi_i(\mathbf{x})$ required to achieve accurate energy levels of $H_{gen} = \hat{K} + V_{gen}$ should be small. The idea we present is to use the simplicity of an SOP method as a stepping stone to solving for energies of H_{gen}, without needing to store large vectors or matrices. How well does this work for realistic V_{gen} and V_{sop}? To what extent are we able to account for the effect of $V_{gen} - V_{sop}$ on energy levels? For P$_2$O (HFCO), we find that we are able to compute fairly accurate energy levels from a basis with 150 (1000) functions.

III. CALCULATION DETAILS

We use dimensionless normal coordinates Q_k and the KEO

$$\hat{K} = \sum_k^D -\frac{\omega_k}{2}\frac{\partial^2}{\partial Q_k^2} \ . \tag{5}$$

The SOP method we use to generate eigenfunctions of H_{sop} is the pruned basis method of Brown and Carrington [36], although in principle any SOP method could be used. The method of Brown and Carrington starts with basis of harmonic oscillator basis (HOB) functions pruned by retaining

only functions whose total HOB index is less than some threshold value. This basis is then adaptively improved by adding the nearest neighbours of the basis functions deemed most important. Those deemed important are those for which the corresponding components of the eigenvectors are large. During and after the expansion of the basis, eigenvalues and eigenvectors are computed using `ARPACK` [37]. Eigenvectors of H_{sop} thus computed are stored. Elements of the eigenvectors are coefficients of a HOB representation of $\phi_i(\mathbf{Q})$, $i = 1, \cdots N$. Elements of the matrix $\mathbf{B}$ in Eq. 2 are obtained by evaluating $\phi_i(\mathbf{Q})$, $i = 1, \cdots N$ at the collocation points.

There are many ways to choose collocation points. In this Letter, we report energies that we compute with points in slabs surrounding d-dimensional subspaces. Many authors represent a $D-$dimensional PES as a sum of d-dimensional terms. In chemistry, the ideas are associated with the terms "N-mode representation" and "high dimensional model representation" [10, 12]. When fitting a PES with a sum of terms each of which involves d coordinates, the simplest thing to do is to use a d-dimensional grid for each of the terms [38]. In Ref. 39, we used related sets of points to compute energy levels with RC and a Gaussian basis. Here the same type of points are used but the basis functions are eigenfunctions of H_{sop}. We shall call the points N-mode representation (NMR) points. NMR points in d-dimensional slabs are a good choice for computing wavefunctions if coupling between different sets of d coordinates is weak. For example, if an exact wavefunction is nearly a product of 1-D functions, then the wavefunction computed by putting collocation points in slabs along coordinate axes will be accurate because if the wavefunction is accurate in the slabs then all derivatives of the wavefunction are also accurate. Note that our NMR points are selected from one set of points in the full $D-$dimensional space. They are not on a grid.

We denote a set of points in a $d-$dimensional slab as NMR(d). We start with a quasi-random multi-dimensional Sobol sequence [40] within a hypercube. Coordinate ranges are chosen to include the Gauss Hermite points associated with the primitive HOB used to compute the eigenfunctions of H_{sop}. We then retain points if

$$\frac{V_{ceil} - V(\mathbf{Q}) + \Delta}{V_{ceil} + \Delta} > rand \,, \tag{6}$$

where rand is a (uniformly distributed) random number in [0, 1]. We use $\Delta = 500 \text{ cm}^{-1}$ and put V_{ceil} equal to at least $10,000 \text{ cm}^{-1}$ above the largest desired energy level. This set of filtered Sobol points is reduced by retaining only points that satisfy

$$\sum_{i=1}^{D} H \left(abs \left(\frac{Q_i - Q_i^{eq}}{Q_i^{max} - Q_i^{min}} \right) - s \right) \leq d \tag{7}$$

where H is the Heaviside step function. The thickness of the slabs is determined by s.

To solve the eigenvalue problem

$$(\mathbf{B^T G} + \mathbf{B^T V B})\mathbf{U} = \mathbf{B^T B U E} , \tag{8}$$

we do not build the $M \times N$ matrices $\mathbf{B}$ and $\mathbf{G}$, nor the $M \times M$ matrix $\mathbf{V}$. Instead, we sum over points to compute

$$
\begin{aligned}
(B^T B)_{ij} &= \sum_{m=1}^{M} \phi_i(\mathbf{Q}_m)\phi_j(\mathbf{Q}_m) \\
(B^T G)_{ij} &= \sum_{m=1}^{M} \phi_i(\mathbf{Q}_m)\hat{K}\phi_j(\mathbf{Q}_m) \\
(B^T V B)_{ij} &= \sum_{m=1}^{M} \phi_i(\mathbf{Q}_m)\phi_j(\mathbf{Q}_m)V(\mathbf{Q}_m),
\end{aligned}
\tag{9}
$$

and store only $N \times N$ matrices. In our calculations, $N \ll M$

IV. RESULTS

We have done two tests of these ideas: one with a very good V_{sop} for P_2O and one with a poorer V_{sop} for HFCO. In both cases, collocation with the $\phi_i(\mathbf{x})$ basis captures much of the difference between V_{sop} and V_{gen}. Of course, energies are more accurate if V_{sop} is close to V_{gen}.

A. P_2O

For P_2O, V_{sop} is the quartic SOP of Ref. 41. V_{gen} is made from V_{sop} by extending it so that the cubic and some quartic derivatives of V_{gen} are equal to those of V_{sop}. To do this, we invert Taylor series for the variables $z_1 = (1 - e^{-\beta_1 Q_1^2})^{1/2}$ and $y_k = 1 - e^{-\alpha_k Q_k}$ for $k = 2,3$ to obtain the Q_k as power series in either z_1 or y_k respectively [42]. By choosing

$$\beta_1 = \frac{-F_{1111}}{6\omega_1} \quad \text{and} \quad \alpha_k = \frac{-F_{kkk}}{3\omega_k}, \quad k = 2,3 \quad, \tag{10}$$

we ensure that after truncating the Taylor series for V_{gen} after the terms with four powers of Q_k, third derivatives of V_{gen} with respect to Q_k for $k = 2,3$ and the fourth derivative of V_{gen} with respect to Q_1 are exactly equal to the corresponding force constants in V_{sop}.
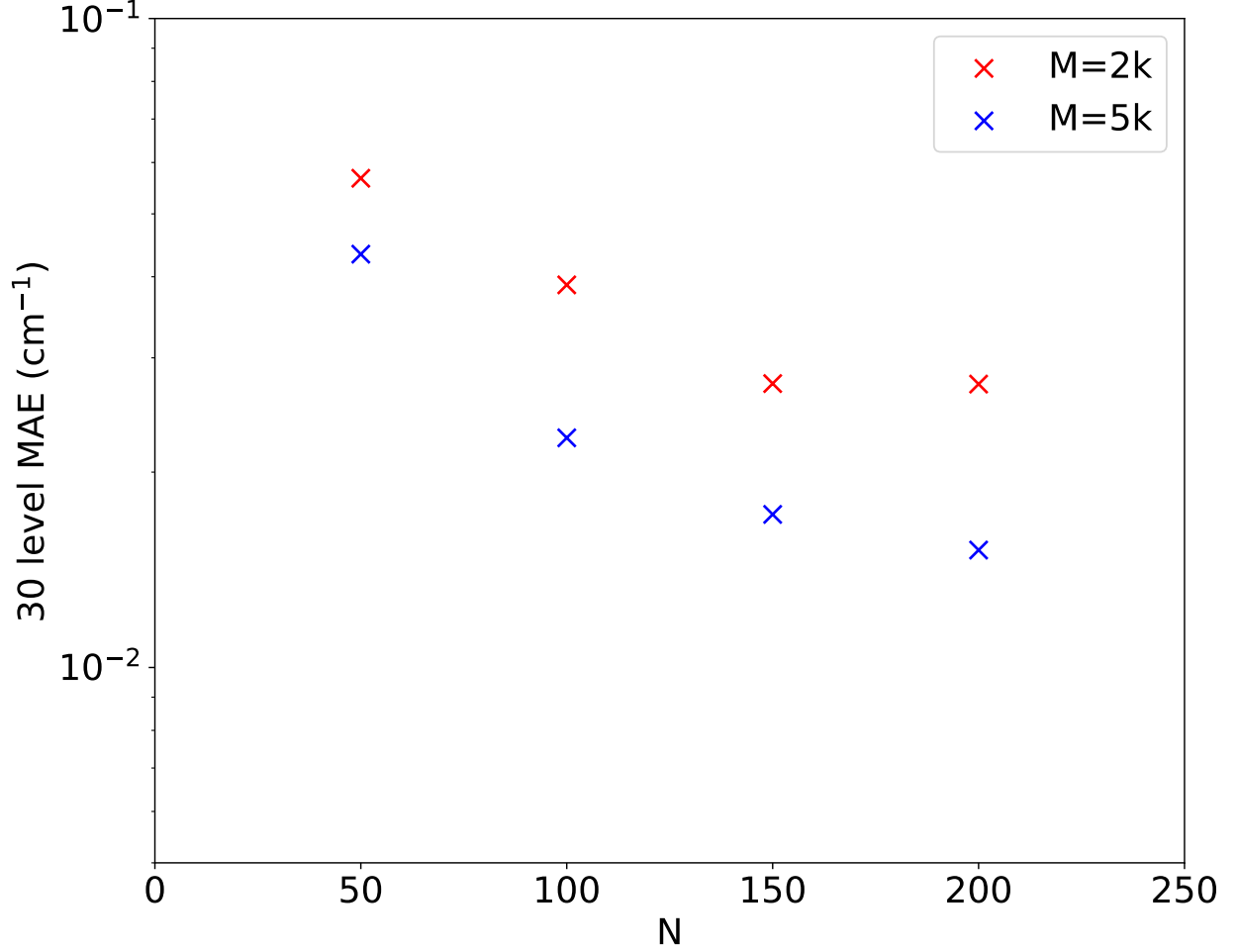
FIG. 1: Mean absolute error of the lowest 30 collocation-corrected energies of P_2O as a function of basis size

The error, $\Delta^{RC} = |E_n^{RC} - E_n^{exact}|$, where E_n^{RC} is an energy computed with RC and E_n^{exact} is an eigenvalue of H_{gen}, (calculated using a direct-product ARPACK method)[37] is smaller than the SOP error, $\Delta^{sop} = |E_n^{sop} - E_n^{exact}|$, where E_n^{sop} is the energy computed on the SOP PES. The mean absolute error (MAE) of the lowest 30 energies of H_{gen} computed with $V_{ceil} = 14,000\,\mathrm{cm}^{-1}$, $d = 2$, and $s = 0.1$ is shown in Fig. 1 for increasing basis size N and point set size M. s values below 0.1 work less well. V_{gen} and V_{sop} are very similar: the mean absolute difference (MAD) of the lowest 30 exact energies for the two potentials is about 2.72 cm^{-1}. Δ^{RC} is about two order of magnitude smaller than Δ^{sop}.

B. HFCO

V_{gen} for HFCO is the 12th order SOP in the supplementary material of Ref. 43. To make V_{sop} we remove from V_{gen} all terms whose degree is larger than four. We then remove four of the remaining terms that cause holes in our calculations. Tab. I shows a comparison between the 4th and 12th-order exact energies calculated with a DVR basis and the `ARPACK` eigensolver and the RC results. 1000 eigenfunctions of V_{sop} and 100,000 NMR points with $d = 5$, $s = 0.1$, and $V_{ceil} = 23,000$ cm^{-1} were used. For HFCO, V_{gen} is much further from V_{sop}; the MAD for the first 25 levels is 103.00 cm^{-1}. Nevertheless, RC reduces energy level errors by almost two orders of magnitude. The MAEs of the first 10 and 25 collocation-corrected energies (with respect to the 12th order energies) are 1.69 and 5.15 cm^{-1} respectively, both are about two orders of magnitude smaller than the corresponding MADs of exact levels computed on V_{sop} and V_{gen}.

V. CONCLUSION

There are many methods with which it is possible to solve the Schrödinger equation to compute a vibrational spectrum that work only if the PES is a SOP. For a large molecule it is often the case that the best available PES is a SOP. For a molecule with fewer than about 6 atoms, it is now fairly straightforward to fit an accurate non-SOP PES to ab initio data. This can be done either by using physically motivated fitting functions or general machine learning methods [44, 45]. An accurate PES is rarely a SOP in the coordinates in which one wants to solve the Schrödinger equation. Solving the Schrödinger equation on a non-SOP PES requires a very different numerical approach and some form of quadrature or collocation. In this Letter we point out that by using eigenfunctions of an SOP Hamiltonian as basis functions and rectangular collocation it is possible to compute energies that are much closer to exact energies than the energies of the SOP Hamiltonian. The number of basis functions required for HFCO is about an order of magnitude larger than the number for P$_2$O. This is not due to HFCO being a larger molecule, but to the fact that the SOP PES for HFCO is much further from the accurate potential. Similar ideas could be applied to other approximate eigenfunctions, e.g. those obtained from a semi-classical calculation [46].

TABLE I: Comparison of HFCO energies. Columns 1 and 2 are exact energies computed on the 12th and 4th order PESs. Column 3 is the difference between columns 1 and 2. Column 4 contains collocation-corrected energies computed using NMR points. Column 5 is errors in the collocation-corrected energies

4th-Order	12th-Order	| 4th-12th |	Coll.	| Coll - 12th |
4588.335	4524.684	63.651	4524.712	0.028
5249.686	5186.070	63.616	5186.861	0.792
5640.448	5530.125	110.323	5536.911	6.785
5662.681	5584.570	78.110	5585.601	1.030
5910.231	5846.412	63.819	5847.595	1.184
5982.431	5865.012	117.419	5866.657	1.646
6294.265	6190.265	104.000	6191.845	1.579
6322.704	6238.159	84.545	6240.167	2.008
6423.445	6358.821	64.624	6359.555	0.734
6569.854	6505.626	64.228	6506.716	1.090
6643.155	6525.396	117.759	6532.084	6.688
6682.350	6531.084	151.266	6545.942	14.857
6710.152	6585.799	124.353	6594.471	8.672
6733.084	6631.509	101.575	6632.959	1.451
6947.240	6849.342	97.898	6855.046	5.704
6981.857	6871.854	110.004	6881.059	9.205
7008.759	6890.594	118.166	6895.183	4.589
7058.651	6913.830	144.821	6920.435	6.605
7078.594	7014.638	63.956	7019.441	4.803
7228.427	7163.604	64.824	7168.595	4.991
7302.872	7183.060	119.812	7189.020	5.960
7329.446	7188.078	141.368	7199.932	11.854
7357.967	7191.810	166.157	7205.534	13.724
7362.584	7238.030	124.555	7245.467	7.437
7391.750	7277.498	114.252	7282.879	5.382

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