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Using multi-dimensional Smolyak interpolation to make a sum-of-products potential

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We propose a new method for obtaining potential energy surfaces in sum-of-products (SOP) form. If the number of terms is small enough, a SOP potential surface significantly reduces the cost of quantum dynamics calculations by obviating the need to do multidimensional integrals by quadrature. The method is based on a Smolyak interpolation technique and uses polynomial-like or spectral basis functions and 1D Lagrange-type functions. When written in terms of the basis functions from which the Lagrange-type functions are built, the Smolyak interpolant has only a modest number of terms. The ideas are tested for HONO (nitrous acid). © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4926651>]

I. INTRODUCTION

In this paper, we report a new interpolation idea for making potential energy surfaces (PESs) in sum of products (SOP) form. The interpolation technique is related to the interpolation approach in Ref. 1 and the collocation method of Ref. 2. When using collocation to solve the Schrodinger equation, one determines values of unknown wavefunctions at points by demanding that the Schrodinger equation be satisfied at a set of points. When a potential (or any other function) is known at a set of points and one wishes to determine a function that passes through those points, it is only necessary to interpolate. The interpolation method we propose exploits the smoothness of the function to produce a SOP PES with a small number of terms. This is done without solving a linear system whose size is determined by the number of terms in the SOP.

Some methods for solving the Schrodinger equation that describes the motion of nuclei require a SOP PES.^{3–8} There are well established methods for converting an existing PES into SOP form, but the factors of the SOP they determine are known only at points.^{9,10} There are also neural network approaches that have been used to re-fit PESs to obtain SOP PESs.^{11–15} In these methods, the factors of the SOP are known everywhere. They could be used to make a SOP PES directly from a set of points. The method we propose in this paper can also be used to make a SOP PES from a set of *ab initio* energies at points.

In principle, the methods cited above are unnecessary because one can always obtain an interpolated SOP PES from a set of points by using a direct product basis and solving linear equations. This is done by imposing the form,

$$V^{SOP}(x_1, x_2, \dots, x_D) = \sum_{n_1=0}^{n_1^{max}} \sum_{n_2=0}^{n_2^{max}} \cdots \sum_{n_D=0}^{n_D^{max}} C_{n_1, n_2, \dots, n_D} \times \varphi_{n_1}(x_1) \varphi_{n_2}(x_2) \cdots \varphi_{n_D}(x_D), \quad (1)$$

where the $\varphi_{n_c}(x_c)$ are some pre-determined basis functions. The coefficients are determined by requiring that the right

hand side (RHS) of Eq. (1), when evaluated at the points, be equal to the *ab initio* energies. This is conceptually simple, but in many dimensions it is expensive or impossible because it requires solving a linear system whose size is the number of basis functions. POTFIT⁹ is a popular and effective alternative. POTFIT also uses a direct product basis, but the 1D functions are “natural potentials” that are generated during the interpolation process. It has three disadvantages: (1) the number of terms in the SOP is often large, (2) POTFIT requires a lot of memory because the points are on a direct product grid and it must be possible to store the potential on the grid in memory, (3) the natural potentials are known only at points. Owing to the second disadvantage, POTFIT is exclusively used to re-fit PESs that are not in SOP form to obtain SOP PESs. Recently, Pelaez and Meyer have developed a related method, multigrid potfit (MGPF), that palliates this memory problem.¹⁰ Very recently, a multilayer version of POTFIT has been proposed.¹⁶ The interpolation method we propose in this paper has the key advantage that it obviates the need to use a direct product basis and grid and therefore requires fewer points, and orders of magnitude fewer when the dimensionality is large. This reduction in the number of points is achieved by taking advantage of the smoothness of the PES. Some PESs are smoother than others. In a nutshell, we combine 1D Lagrange-type interpolants with a Smolyak-based rule^{1,2} and then re-write the resulting function as a linear combination of functions in a pruned product basis. The last step significantly reduces the number of terms in the SOP. The interpolation points are those of a Smolyak grid that includes all the points in a nested set of small direct product grids.¹⁷ The number of small direct product grids is determined by a condition, $g(i_1, i_2, \dots, i_D) \leq H$ that is carefully chosen¹⁸ to reduce the number of terms in the Smolyak SOP PES without affecting the quality of the interpolation. $g(i_1, i_2, \dots, i_D)$ can be chosen to increase the accuracy of the interpolant by taking into account the coupling between the coordinates; this is a way of adapting the definition of the grid to the function being interpolated. The Smolyak interpolation method is applied to an analytic PES of HONO (nitrous acid),^{19,20} without solving a system of linear

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equations whose size is the number of terms in the Smolyak SOP PES. Using the same (damped) 1D fitting bases used in Ref. 19, it is possible to make a SOP PES with the same number of terms (389). This is not trivial because in Ref. 19 many basis constraints are used and the Smolyak procedure (which is advantageous in many dimensions) can only be applied if there is a single basis constraint. The PES of Ref. 19 was damped to cope with holes and therefore it is difficult to interpolate or fit without using damped 1D basis functions. Using damped 1D functions that are not identical to those of Ref. 19, we obtain an excellent fit with 1573 terms. With undamped 1D functions almost 4000 terms are required (but this number can be reduced to 1443 by contracting). Even 4000 is small compared to the $5^5 \times 7$, the number of functions in the direct product basis with which one can exactly represent the PES of Ref. 19.

II. MULTIDIMENSIONAL SMOLYAK INTERPOLATION

The global interpolant we propose is built from 1D Lagrange-type interpolants. Using a direct product of 1D Lagrange-type interpolants, it is easy to make a multi-dimensional interpolant equivalent to the interpolant of Eq. (1), *without* solving a system of linear equations whose size is the number of basis functions. When the number of coordinates, D , becomes large the direct product grid is so large that it is nevertheless not possible to use this approach and it is therefore necessary to use 1D Lagrange interpolants in conjunction with Smolyak ideas. However, we begin by explaining the direct product approach.

Lagrange interpolation in 1D is familiar.²¹ 1D Lagrange-type functions that are not as simple as the classical Lagrange functions, but nonetheless zero or one at each of the interpolation points, can also be used.^{2,22} The Lagrange-type functions we use are (note that n starts at 0 and k starts at one),

$$a_k(x) = \sum_{n=0}^{n^{\max}} B_{k,n} \varphi_n(x), \quad k = 1, 2, \dots, n^{\max} + 1, \quad (2)$$

where the $\varphi_n(x)$ are 1D basis functions and the $B_{k,n}$ coefficients are determined by resolving the system of $n^{\max} + 1$ equations obtained by imposing

$$a_k(x^{k'}) = \delta_{k,k'}, \quad k, k' = 1, 2, \dots, n^{\max} + 1, \quad (3)$$

so that $a_k(x)$ is 1 at the grid point x^k and 0 at the grid points $x^{k'}$, $k' \neq k$. Note that the $\varphi_n(x)$ (and the $a_k(x)$) need not be orthogonal. The interpolant for a 1D function $F(x)$ is

$$\tilde{F}(x) = U^{n^{\max}} F(x) = \sum_{k=1}^{n^{\max}+1} a_k(x) F(x^k), \quad (4)$$

where $U^{n^{\max}}$ is a 1D operator that performs the interpolation.

In D dimensions, one can use a direct product to obtain an analytical representation of a function $F(x_1, x_2, \dots, x_D)$ from

the values of F at a set of N^{grid} points $(x_1^k, x_2^k, \dots, x_D^k)$ with $k = 1, \dots, N^{\text{grid}}$. The direct product interpolant is built from 1D interpolants, $U^{n_c^{\max}}(x_c)$, ($c = 1, 2, \dots, D$), each made from 1D basis functions $\varphi_{n_c}(x_c)$, $n_c = 0, \dots, n_c^{\max}$ and a set of points $x_c^{k_c}$, $k_c = 1, 2, \dots, n_c^{\max} + 1$,

$$\begin{aligned} \tilde{F}(x_1, x_2, \dots, x_D) &= U^{n_1^{\max}} \otimes U^{n_2^{\max}} \otimes \dots \otimes U^{n_D^{\max}} F(x_1, x_2, \dots, x_D) \\ &= \sum_{k_1=1}^{n_1^{\max}+1} \sum_{k_2=1}^{n_2^{\max}+1} \dots \sum_{k_D=1}^{n_D^{\max}+1} a_{k_1}(x_1) a_{k_2}(x_2) \dots a_{k_D}(x_D) \\ &\quad \times F(x_1^{k_1}, x_2^{k_2}, \dots, x_D^{k_D}). \end{aligned} \quad (5)$$

Note that one only needs to solve (for each coordinate) linear systems with $n_c^{\max} + 1$ equations and there is no need to solve a linear system whose size depends on the total number of multi-d Lagrange functions. The simple approach of Eq. (5) is therefore already much less costly than requiring that Eq. (1) be satisfied at a set of points and determining the $C_{n_1, n_2, \dots, n_D}$ by solving a large system of linear equations. Nonetheless, the direct product basis is large if D is larger than about 6. When $D \sim 12$, the grid is so large that it is not possible to store all the function values in memory. This problem affects *all* methods that fit with a direct product. Optimizing the 1D functions helps somewhat, but the direct product structure is the essential problem, since the scaling with the number of dimensions is exponential.

For many functions it is better to use a Smolyak-based interpolation.^{1,2,23–27} Smolyak ideas have been used in chemical physics by several groups,^{28–34} although they are usually used to do quadrature.³⁵ A multidimensional Smolyak interpolant is

$$\begin{aligned} I(D, H) &= \sum_{g(i_1, i_2, \dots, i_D) \leq H} \Delta U^{i_1}(x_1) \\ &\quad \otimes \Delta U^{i_2}(x_2) \otimes \dots \otimes \Delta U^{i_D}(x_D) \\ &= \sum_{g(i_1, i_2, \dots, i_D) \leq H} C_{i_1, i_2, \dots, i_D}^{\text{smol}} U^{i_1}(x_1) \\ &\quad \otimes U^{i_2}(x_2) \otimes \dots \otimes U^{i_D}(x_D), \end{aligned} \quad (6)$$

where $U^0(x_c) = 0$ and

$$\Delta U^i(x_c) = U^i(x_c) - U^{i-1}(x_c). \quad (7)$$

The $C_{i_1, i_2, \dots, i_D}^{\text{smol}}$ are determined by inserting Eq. (7) into the first line of Eq. (6). i_c , referred to in this article as a level, labels a member of a family of 1D interpolants for every coordinate, $c = 1, 2, \dots, D$. $m_c(i_c) = n_c^{\max}(i_c) + 1$ is the number of points and basis functions included in the i_c interpolant for coordinate c ; $m_c(i_c) \geq m_c(i_c - 1)$. The 1D interpolations $U^{i_c}(x_c)$ are made using Lagrange-type functions built as explained above (see Eq. (2)), and in terms of the Lagrange-type functions Eq. (6) is

$$\begin{aligned} F(x_1, x_2, \dots, x_D) &\approx \hat{F}(x_1, x_2, \dots, x_D) = I(D, H) F(x_1, x_2, \dots, x_D) = \sum_{g(i_1, i_2, \dots, i_D) \leq H} C_{i_1, i_2, \dots, i_D}^{\text{smol}} \\ &\quad \times \sum_{k_1=1}^{m_1(i_1)} \sum_{k_2=1}^{m_2(i_2)} \dots \sum_{k_D=1}^{m_D(i_D)} F(x_1^{k_1}, x_2^{k_2}, \dots, x_D^{k_D}) a_{k_1}^{i_1}(x_1) a_{k_2}^{i_2}(x_2) \dots a_{k_D}^{i_D}(x_D). \end{aligned} \quad (8)$$

On the right side, an $x_{k_c}^{i_c}$ argument of F is the k_c th point of the i_c 1D interpolant; the superscript indicates the set of points and the subscript indicates the point within the set. To use the Smolyak-based interpolant one must choose 1D basis functions, define 1D interpolation rules, and choose the function $g(i_1, i_2, \dots, i_D)$ which determines which combinations of the 1D rules are included in $I(D, H)$.

First, for every coordinate, one must choose basis functions $\varphi_{n_c}(x_c)$, $n_c = 0, \dots, N_c^{\max}$. We choose $\varphi_{n_c}(x_c)$ that provide a compact representation of the PES we wish to interpolate. They are ordered so that when 1D cut potentials are expanded as linear combinations of $\varphi_{n_c}(x_c)$, the coefficients of $\varphi_{n_c}(x_c)$ are smaller when n_c is larger.

Second, we must choose which $\varphi_{n_c}(x_c)$ functions to use to build each of the $U^{i_c} f(x_c)$ interpolants. We use the first $m_c(i_c)$ functions in the $\varphi_n(x_c)$ $n = 0, \dots, N_c^{\max}$ list. Note that the functions in the i_c family include the functions in the $i_c - 1$ family and $m_c(i_c) - m_c(i_c - 1)$ new functions. Other choices of $m_c(i_c)$ are possible, but in this paper $m_c(i_c) = n_c(i_c) + 1 = i_c$. When $m_c(i_c) = i_c$, $U^1(x_c)$ uses $\varphi_0(x_c)$, $U^2(x_c)$ uses $\varphi_0(x_c)$, $\varphi_1(x_c)$, etc. The interpolant $U^{i_c} F(x_c)$ should be a better approximation for $F(x_c)$ than the interpolant $U^{i_c-1} F(x_c)$. This is ensured in part by ordering the $\varphi_{n_c}(x_c)$ as explained in the previous paragraph.

Third, for every coordinate, and for each i_c , one must choose points x_c^k , $k = 1, \dots, m_c(i_c)$. Good points will always have the property that none of the $\varphi_m(x_c^k)$ are very small when evaluated at all the points. If this were the case, the condition number of the matrix in the linear equation one must solve to obtain the Lagrange type functions would be large. Good points must be in the range of the vibrational wavefunctions. The points of each level should also be linked to the functions in the same level. Most mathematicians use Smolyak interpolation with piecewise linear basis functions.³⁶ With piecewise linear basis functions, it is easy to link basis functions and points because the basis functions are localized and peaked at a single point. Unfortunately, piecewise linear functions are poor basis functions if one wishes to accurately interpolate smooth functions in a large region. Spectral basis functions are much better. How should one choose the points when using spectral basis functions? Szabados has shown that when using spectral functions to do 1D interpolation, Gauss quadrature points are close to points that minimize the Lebesgue constant and therefore probably good interpolation points.³⁷ Because it greatly facilitates evaluating matrix vector products and, when $H - D + 1 > D$, reduces the number of Smolyak points in high dimensional spaces, we use nested points, for which the points of level $i - 1$ are also in level i . As Gauss points are not nested, we need some other scheme for choosing points linked to spectral basis functions. Pseudo-Gauss points²⁸ are one option. In some cases, (nested) Chebyshev points are nearly as good.

Fourth, one must choose the function $g(i_1, i_2, \dots, i_D)$ which determines which combinations of the 1D rules are included in $I(D, H)$ (Eq. (6)). The importance of a good choice of $g(i_1, i_2, \dots, i_D)$ is more obvious when the interpolant in Eq. (8) is written, specializing to the 6D case, as a sum of products of basis functions,

$$\begin{aligned} \hat{F}(x_1, x_2, x_3, x_4, x_5, x_6) \\ = \sum_{g(n_1+1, n_2+1, n_3+1, n_4+1, n_5+1, n_6+1) \leq H} C_{n_1, n_2, n_3, n_4, n_5, n_6} \\ \times \varphi_{n_1}(x_1) \varphi_{n_2}(x_2) \varphi_{n_3}(x_3) \varphi_{n_4}(x_4) \varphi_{n_5}(x_5) \varphi_{n_6}(x_6). \end{aligned} \quad (9)$$

It is clear that a constraint on $(n_1, n_2, \dots)$ must appear in Eq. (9) when Eq. (2) is substituted into Eq. (8) because the upper limits on the sums over n_c indices depend on the corresponding i_c indices which are themselves constrained. When $m_c(i_c) = i_c$, the constraint on the $(n_1, n_2, \dots, n_D)$ is $g(n_1 + 1, n_2 + 1, n_3 + 1, n_4 + 1, n_5 + 1, n_6 + 1) \leq H$ because the constraint on the i_c indices is $g(i_1, i_2, \dots, i_D) \leq H$ and $n_c = i_c - 1$. In Eq. (9), the interpolated function is written as a sum of functions in a pruned basis. The $C_{n_1, n_2, n_3, n_4, n_5, n_6}$ can be determined from the $F(x_{k_1}^{i_1}, x_{k_2}^{i_2}, \dots, x_{k_D}^{i_D})$, i.e., values of the function on the Smolyak grid. One should choose $g(i_1, i_2, \dots, i_D)$ so that the $C_{n_1, n_2, n_3, n_4, n_5, n_6}$ coefficients of product basis functions excluded by the restriction under the sum in Eq. (9) are smaller than the coefficients of product basis functions included by the restriction under the sum. By far, the most popular choice is

$$g(i_1, i_2, \dots, i_D) = i_1 + i_2 + \dots + i_D. \quad (10)$$

However, to derive maximal advantage from Smolyak's idea for combining product grids, it is important to choose the best possible $g(i_1, i_2, \dots, i_D)$. The size of the pruned basis and Smolyak grid depends on $g(i_1, i_2, \dots, i_D)$. When nested points are used, the Smolyak grid is a subset of the full product grid with $\prod_c (m_c(i_c^{\max}))$ points, where $m_c(i_c^{\max}) = N_c^{\max} + 1$. It is possible to choose $g(i_1, i_2, \dots, i_D)$ so that the Smolyak grid is the full product grid. Griebel and Knappek have a technique for adjusting the size of a Smolyak grid.^{38,39} We use a different idea. We set

$$g(i_1, i_2, \dots, i_D) = g^1(i_1) + g^2(i_2) + \dots + g^D(i_D). \quad (11)$$

There is great flexibility in the choice of the $g^c(i_c)$. We often use step functions, e.g., $g^1(1) = 1.1, g^1(2) = 2.1, g^1(3) = 2.9, \dots$; $g^2(1) = 1.0, g^2(2) = 2, g^2(3) = 3, \dots$; and $g^3(1) = 1.4, g^3(2) = 1.9, g^3(3) = 2.0, \dots$, etc. Using the g s, it is possible to make a SOP PES with significantly fewer terms than would be required with Eq. (10). This is achieved by choosing the g s so that the SOP PES has few terms that couple many coordinates.

The $C_{n_1, n_2, \dots, n_D}$ can be determined without solving a system of linear equations whose size is the number of terms in Eq. (27). This can be done by substituting

$$a_{k_c}^{i_c}(x_c) = \sum_{n_c=0}^{n_c^{\max}(i_c)} B_{k_c, n_c}^{i_c} \varphi_{n_c}(x_c), \quad k_c = 1, \dots, n_c^{\max}(i_c) + 1 \quad (12)$$

into Eq. (8), to obtain

$$\begin{aligned} & \sum_{g(i_1, i_2, \dots, i_D) \leq H} C_{i_1, i_2, \dots, i_D}^{\text{smol}} U^{i_1}(x_1) \otimes U^{i_2}(x_2) \otimes \dots \otimes U^{i_D}(x_D) F(x_1, x_2, \dots, x_D) \\ &= \sum_{g(i_1, i_2, \dots, i_D) \leq H} C_{i_1, i_2, \dots, i_D}^{\text{smol}} \sum_{k_1=1}^{n_1^{\max(i_1)+1}} \sum_{n_1=0}^{n_1^{\max(i_1)}} B_{k_1, n_1}^{i_1} \varphi_{n_1}(x_1) \\ & \quad \times \sum_{k_2=1}^{n_2^{\max(i_2)+1}} \sum_{n_2=0}^{n_2^{\max(i_2)}} B_{k_2, n_2}^{i_2} \varphi_{n_2}(x_2) \dots \sum_{k_D=1}^{n_D^{\max(i_D)+1}} \sum_{n_D=0}^{n_D^{\max(i_D)}} B_{k_D, n_D}^{i_D} \varphi_{n_D}(x_D) F(x_1^{k_1}, x_2^{k_2}, \dots, x_D^{k_D}). \end{aligned} \quad (13)$$

Recall that $m_c(i_c) = n_c^{\max(i_c)} + 1$. Equating the RHS of Eq. (13) and the RHS of Eq. (9), one obtains

$$\begin{aligned} C_{n_1, n_2, \dots, n_D} &= \sum_{g(i_1, i_2, \dots, i_D) \leq H} C_{i_1, i_2, \dots, i_D}^{\text{smol}} \sum_{k_1=1}^{n_1^{\max(i_1)+1}} B_{k_1, n_1}^{i_1} \\ & \quad \times \sum_{k_2=1}^{n_2^{\max(i_2)+1}} B_{k_2, n_2}^{i_2} \dots \\ & \quad \times \sum_{k_D=1}^{n_D^{\max(i_D)+1}} B_{k_D, n_D}^{i_D} F(x_1^{k_1}, x_2^{k_2}, \dots, x_D^{k_D}). \end{aligned} \quad (14)$$

Note that the number of terms in the first sum is limited by the requirement that values of $i_1, i_2, \dots, i_D$ must satisfy $n_c^{\max(i_c)} \geq n_c$. When implementing Eq. (14) it is important to evaluate the sums sequentially.

It is crucial that the interpolant of Eq. (6) is *exact* if the function $F(x_1, x_2, \dots, x_D)$ being interpolated satisfies certain conditions. Exact means not that the interpolant, when evaluated at the interpolation points, is equal to the set of values from which it is built. It means that the interpolant is exact everywhere. Barthelmann *et al.* showed¹ that a product of 1D functions,

$$F(x_1, x_2, \dots, x_D) = \varphi_{n_1}(x_1) \varphi_{n_2}(x_2) \dots \varphi_{n_D}(x_D), \quad (15)$$

is exactly interpolated, i.e.,

$$I(D, H) F(x_1, x_2, \dots, x_D) = F(x_1, x_2, \dots, x_D), \quad (16)$$

if one of the products of 1D interpolants

$$U^{i_1}(x_1) U^{i_2}(x_2) \dots U^{i_D}(x_D) \quad (17)$$

in $I(D, H)$, interpolates it exactly. By construction, $U^{i_c}(x_c)$ exactly interpolates $\varphi_{n_c}(x_c)$ if $n_c \leq m(i_c) - 1$. Therefore, if $n_c \leq m_c(i_c) - 1 \forall c$ then $U^{i_1}(x_1) U^{i_2}(x_2) \dots U^{i_D}(x_D)$ will exactly interpolate $\varphi_{n_1}(x_1) \varphi_{n_2}(x_2) \dots \varphi_{n_D}(x_D)$. Knowing when one

product will be exactly interpolated enables one to conclude that a sum of products,

$$\begin{aligned} & F(x_1, x_2, \dots, x_D) \\ &= \sum_{g((n_1+1, n_2+1), \dots, (n_D+1)) \leq L} C_{n_1, n_2, \dots, n_D} \varphi_{n_1}(x_1) \\ & \quad \times \varphi_{n_2}(x_2) \dots \varphi_{n_D}(x_D), \end{aligned} \quad (18)$$

will be exactly interpolated by $I(D, H)$,

$$\begin{aligned} I(D, H) &= \sum_{g(i_1, i_2, \dots, i_D) \leq H} \Delta U^{i_1}(x_1) \\ & \quad \otimes \Delta U^{i_2}(x_2) \otimes \dots \otimes \Delta U^{i_D}(x_D) \end{aligned} \quad (19)$$

if (a) the 1D interpolants are determined from the 1D $\varphi_{n_c}(x_c)$ in Eq. (18), (b) the same g is used in both Eq. (19) and Eq. (18), and (c) H is large enough, i.e., $H \geq L$.

III. TESTING SMOLYAK INTERPOLATION WITH A HONO POTENTIAL

The interpolation method presented in Sec. II allows one to obtain a SOP PES directly from a set of *ab initio* points. This is possible because the number of points required to obtain a good PES is small. Only a small number of fitting points is necessary because the Smolyak interpolation method exploits the smoothness of the potential. To demonstrate that this works we have made a SOP PES for HONO. No *ab initio* calculations are done, instead we re-fit a HONO PES that was also used to test MGPF.^{10,19}

The PES we re-fit is a sum of products of functions of bond coordinates: R_1 for the outer NO bond, R_2 for the inner ON bond, R_3 for the OH bond, θ_1 for the ONO apex angle, θ_2 for the HON apex angle, and τ for the angle between the HON and ONO planes, with $\tau = 0^\circ$ for the cis-form. The authors of Ref. 19 fit the parameters of the function

$$\begin{aligned} V(R_1, R_2, R_3, \theta_1, \theta_2, \tau) &= W(R_1, R_2, R_3, \theta_1, \theta_2) \sum_{n_1, n_2, n_3, n_4, n_5, n_6} C_{n_1, n_2, n_3, n_4, n_5, n_6} (1 - e^{-0.7[R_1 - R_1^{\text{ref}}]})^{n_1} (1 - e^{-0.7[R_2 - R_2^{\text{ref}}]})^{n_2} \\ & \quad \times (1 - e^{-0.7[R_3 - R_3^{\text{ref}}]})^{n_3} (\theta_1 - \theta_1^{\text{ref}})^{n_4} (\theta_2 - \theta_2^{\text{ref}})^{n_5} \cos(n_6[\tau - \tau^{\text{ref}}]) \end{aligned} \quad (20)$$

with

$$W(R_1, R_2, R_3, \theta_1, \theta_2) = e^{-d_1(R_1 - R_1^{\text{ref}})^2} e^{-d_2(R_2 - R_2^{\text{ref}})^2} e^{-d_3(R_3 - R_3^{\text{ref}})^2} e^{-d_4(\theta_1 - \theta_1^{\text{ref}})^2} e^{-d_5(\theta_2 - \theta_2^{\text{ref}})^2} \quad (21)$$

using the restrictions

$$\begin{aligned} n_1 + n_2 + n_3 + n_4 + n_5 &\leq 4, n_6 = 0, 1, 2, \\ n_1 + n_2 + n_3 + n_4 + n_5 &\leq 3, n_6 = 3, \\ n_1 + n_2 + n_3 + n_4 + n_5 &\leq 2, n_6 = 4, \end{aligned} \quad (22)$$

but also include the terms with $(n_1, n_2, n_3, n_4, n_5, n_6) = (0, 0, 6, 0, 0, 0)$, $(0, 0, 5, 0, 0, 0)$, $(0, 0, 6, 0, 0, 1)$, and $(0, 0, 5, 0, 0, 1)$, to 638 *ab initio* points calculated at the CCSD(T)/cc-pVQZ level. The d_c and R_c^{ref} parameters are given in Ref. 19. The number of coefficients in the expansion of Eq. (20) is 389 and this fitted potential allows an accurate determination of the vibrational levels of HONO up to 4000 cm^{-1} above the zero point energy.

The PES we re-fit is smooth so we can be certain that Smolyak interpolation will work well. We re-fit using the same bond coordinates as used in Ref. 19. To apply our interpolation method we must choose basis functions and

points and make 1D interpolants $U^{ic}(x_c)$. In Eq. (20) the damping function $W(R_1, R_2, R_3, \theta_1, \theta_2)$ is used to avoid holes in the PES. Because the PES includes $W(R_1, R_2, R_3, \theta_1, \theta_2)$, a SOP PES with a much smaller number of terms can be obtained by incorporating damping into the 1D basis functions. In Subsection III A, we verify that it is possible to reproduce the PES of Eq. (20) using the same damped 1D basis functions used by Richter *et al.*¹⁹ In Subsection III B, we discuss a fit obtained with undamped 1D basis functions, it necessarily has more terms. In Subsection III C, we demonstrate that an excellent SOP PES can be obtained with damped 1D basis functions that are not the same as those used in Subsection III A and Ref. 19.

A. The damped 1D functions of Eq. (20)

The 1D functions of Eq. (20) are a natural choice,

$$\begin{aligned} \varphi_{n_1}(R_1) &= e^{-d_1(R_1-R_1^{ref})^2}(1 - e^{-0.7[R_1-R_1^{ref}]})^{n_1}, & \varphi_{n_2}(R_2) &= e^{-d_2(R_2-R_2^{ref})^2}(1 - e^{-0.7[R_2-R_2^{ref}]})^{n_2}, \\ \varphi_{n_3}(R_3) &= e^{-d_3(R_3-R_3^{ref})^2}(1 - e^{-0.7[R_3-R_3^{ref}]})^{n_3}, & \varphi_{n_4}(\theta_1) &= e^{-d_4(\theta_1-\theta_1^{ref})^2}(\theta_1 - \theta_1^{ref})^{n_4}, \\ \varphi_{n_5}(\theta_2) &= e^{-d_5(\theta_2-\theta_2^{ref})^2}(\theta_2 - \theta_2^{ref})^{n_5}, & \varphi_{n_6}(\tau) &= \cos(n_6\tau). \end{aligned} \quad (23)$$

It is very common when fitting PESs to use powers of the Morse-type variable $(1 - e^{-a[R-R^{ref}]})$ for stretch coordinates, powers of angular displacements for bend coordinates, and trigonometric functions for torsions. The selection of points, and the choice of $m_c(i_c)$ and of $g(i_1, i_2, \dots, i_D)$ are less clear. A good choice of $m_c(i_c)$ and $g(i_1, i_2, \dots, i_D)$ will reduce the number of terms in the Smolyak SOP PES. We choose to use $m_c(i_c) = i_c$ and to select $g(i_1, i_2, \dots, i_D)$ to reduce the number of terms without decreasing the accuracy of the PES. It is not clear that it is possible to choose $g(i_1, i_2, \dots, i_D)$ so that it will be possible to exactly reproduce the PES of Eq. (20).

The simplest choice for $g(i_1, i_2, \dots, i_D)$ is

$$g(i_1, i_2, \dots, i_D) = i_1 + i_2 + \dots + i_D \leq 8 + (D - 1) = 13 \quad (24)$$

(the $D - 1$ is due to the fact that level labels start at 1 and basis function labels start at 0). With this choice the Smolyak interpolation will be exact because each of the terms in $V(R_1, R_2, R_3, \theta_1, \theta_2, \tau)$ in Eq. (20), e.g., $\varphi_{n_1}(R_1)\varphi_{n_2}(R_2)\varphi_{n_3}(R_3)\varphi_{n_4}(\theta_1)\varphi_{n_5}(\theta_2)\varphi_{n_6}(\tau)$, satisfies $n_1 + n_2 + n_3 + n_4 + n_5 + n_6 \leq 7$. The simplest choice has the important disadvantage that the number of terms in the interpolant is $(6 + 7)!(6!7!) = 1716$, more than four times the number of terms in the original PES. This is due to the dissonance between the restrictions of Eq. (22) and the restriction of Eq. (24). The number of terms is much larger than the number of terms in the original potential because although there are only two terms with an n_c as large as 6 in the original PES, $n_1 + n_2 + \dots + n_D \leq 7$ allows *all* of the n_c to be as large as 7. It is better to use

$$g(i_1, i_2, \dots, i_D) = g^1(i_1) + g^2(i_2) + \dots + g^D(i_D) \leq H, \quad (25)$$

and to choose a good value of H and good $g^c(i_c)$. We use $H = 32$. Knowing the conditions that must be fulfilled if a Smolyak interpolant is to be exact, we are able to determine $g^c(i_c)$ that reproduce PES of Eq. (20),

$$\begin{aligned} g^1(1) &= 1, g^1(2) = 7, g^1(3) = 13, g^1(4) = 19, g^1(5) = 25, g^1(i_1) \geq 28 \text{ if } i_1 = 7, 8, 9, \dots, \\ g^2(1) &= 1, g^2(2) = 7, g^2(3) = 13, g^2(4) = 19, g^2(5) = 25, g^2(i_2) \geq 28 \text{ if } i_2 = 7, 8, 9, \dots, \\ g^3(1) &= 1, g^3(2) = 5, g^3(3) = 13, g^3(4) = 19, g^3(5) = 22, g^3(6) \geq 23, \\ g^3(7) &= 25, g^3(i_3) \geq 28 \text{ if } i_3 = 8, 9, 10, \dots, \\ g^4(1) &= 1, g^4(2) = 7, g^4(3) = 13, g^4(4) = 19, g^4(5) = 25, g^4(i_4) \geq 28 \text{ if } i_4 = 7, 8, 9, \dots, \\ g^5(1) &= 1, g^5(2) = 7, g^5(3) = 13, g^5(4) = 19, g^5(5) = 25, g^5(i_5) \geq 28 \text{ if } i_5 = 7, 8, 9, \dots, \\ g^6(1) &= 1, g^6(2) = 3, g^6(3) = 8, g^6(4) = 8, g^6(5) = 15, g^6(i_6) \geq 28 \text{ if } i_6 = 7, 8, 9, \dots \end{aligned} \quad (26)$$

In the previous equation, when i_c is sufficiently large, $g^c(i_c)$ can take any value larger than a given threshold. This is due to the fact that any $g^c(i_c)$ larger than the threshold will exclude

terms from the interpolated PES that are not included in the original PES. The $g^c(i_c)$ of Eq. (26) are chosen so that with the H value we use terms with $n_c > 4$ ($c = 1, 2, 4, 5, 6$) and $n_3 > 6$

do not appear in the interpolated PES. We know they should not appear because they are not in the original PES.

We now have the ingredients required to build the SOP of Lagrange-type functions in Eq. (8). We can reduce the number of terms by using instead, the form,

$$V^{SOP}(x_1, x_2, x_3, x_4, x_5, x_6) = \sum_{g(n_1+1, n_2+1, n_3+1, n_4+1, n_5+1, n_6+1) \leq H} C_{n_1, n_2, n_3, n_4, n_5, n_6} \times \varphi_{n_1}(x_1) \varphi_{n_2}(x_2) \varphi_{n_3}(x_3) \varphi_{n_4}(x_4) \varphi_{n_5}(x_5) \varphi_{n_6}(x_6). \quad (27)$$

The number of functions in Eq. (27) is equal to the number of points on the Smolyak grid built from nested sets of 1-D points. Eq. (8) has many terms because the Lagrange-type functions depend on both i_c and k_c labels and both these types of indices are summed. Eqs. (8) and (27) are two equivalent representations of the same interpolant. $C_{n_1, n_2, n_3, n_4, n_5, n_6}$ is obtained from Eq. (14). We shall elaborate on ideas for obtaining $C_{n_1, n_2, n_3, n_4, n_5, n_6}$ from $F(x_1^{k_1}, x_2^{k_2}, x_3^{k_3}, x_4^{k_4}, x_5^{k_5}, x_6^{k_6})$ in a forthcoming paper about collocation methods. With the $g^c(i_c)$ defined above and $H = 32$, the Smolyak interpolant of the HONO potential of Eq. (20) is, exactly, built from only 389 interpolation points, and has only 389 terms, i.e., the same than the original PES. If instead one used Eq. (8), then the total number of terms (products of Lagrange functions) would be large (for HONO 3480, with the same $g^c(i_c)$ and H).

For HONO, we have found $g^c(i_c)$ functions that make it possible to use a Smolyak interpolation method to obtain a SOP PES, which after re-expressing it in terms of the $\varphi_{n_c}(R_c)$ functions, has the minimum number of terms. Constraining the Smolyak sum using $g^1(i_1) + g^2(i_2) + \dots + g^D(i_D) \leq H$ rather than $i_1 + i_2 + \dots + i_D \leq H$ greatly reduces the number of terms. The $g^c(i_c)$ can always be adapted to include only the important coupling terms in the PES. This way of constraining is very flexible. Of course, when one is fitting a PES from *ab initio* points it will be necessary to experiment with different definitions of the $g^c(i_c)$, different H , and different $\varphi_{n_c}(x_c)$ to determine the best choices.

B. A basis similar to the basis of Ref. 19 but not damped

As explained previously, because the PES we are interpolating is damped, a SOP fit with fewer terms can be obtained by including damping in the basis. Nonetheless, we have tested the Smolyak procedure with undamped basis functions. We use the same parameters a_i , $i = 1, 2, 3$ in front of $[R_i - R_i^{ref}]$. They can be easily obtained by fitting 1D cuts of the potential. The SOP PES we obtain has many fewer terms than the number of functions ($5^5 \times 7$) in the direct product basis large enough to exactly represent the PES. In this calculation, we use the basis,

$$\begin{aligned} \varphi_{n_1}(R_1) &= (1 - e^{-0.7[R_1 - R_1^{ref}]})^{n_1}, \\ \varphi_{n_2}(R_2) &= (1 - e^{-0.7[R_2 - R_2^{ref}]})^{n_2}, \\ \varphi_{n_3}(R_3) &= (1 - e^{-0.7[R_3 - R_3^{ref}]})^{n_3}, \\ \varphi_{n_4}(\theta_1) &= (\theta_1 - \theta_1^{ref})^{n_4}, \\ \varphi_{n_5}(\theta_2) &= (\theta_2 - \theta_2^{ref})^{n_5}, \\ \varphi_{n_6}(\tau) &= \cos(n_6\tau), \end{aligned} \quad (28)$$

and as interpolation points, Chebyshev-type points for τ , and Chebyshev points for $R_1, R_2, R_3, \theta_1, \theta_2$. All sets of points are nested. We do not use interpolation rules with $m_1 = 1$ and $m_i = 2^i + 1$, for $i > 1$, points. They have too many points. Instead, for every coordinate we create a sequence of sets of interpolation points from a set of M Chebyshev points, by sorting them according to their corresponding potential values (fixing other coordinates at equilibrium) and putting the points with the lowest potential values into the sets for the lowest levels. For τ , $M = 5$ and the Chebyshev points closest to 0 and π are replaced with 0 and π . For the torsional coordinate, U^k , for $k = 1, \dots, 5$ are made from the first k points and $U^k = U^5$, for $k = 6, \dots$. The full set of torsional points is

$$(x_1), (x_1, x_2), (x_1, x_2, x_3), (x_1, x_2, x_3, x_4) \text{ and } (x_1, x_2, x_3, x_4, x_5). \quad (29)$$

For all coordinates, points in the interval $[a, b]$ are obtained from Chebyshev points in the interval $[-1, 1]$ using

$$x_k = \frac{a+b}{2} + \frac{a-b}{2} \cos\left(\frac{2k-1}{2n}\pi\right), \quad k = 1, \dots, M. \quad (30)$$

We begin with a large H value, the simplest pruning condition, $i_1 + i_2 + i_3 + i_4 + i_5 + i_6 \leq H = 5 + 12$, and the $[a, b]$ intervals for the stretch and bend coordinates used in the original fitting of the *ab initio* points. With $H = 17$, one can exactly interpolate terms with factors having n_c as large as 11. It is possible to find $g^c(i_c)$ so that the error in the resulting interpolant is 0.81 cm^{-1} . The error is the mean absolute deviation for a set of 4 227 300 Smolyak points. The number of terms required to achieve this error is 11 452. By optimizing the $[a, b]$ intervals for all coordinates except the torsion, the number of terms can be reduced. We are able to achieve an error of 4.06 cm^{-1} using 3898 terms (1443 terms after contracting the τ coordinate (see Section IV)). Note that the definition of error we use is a stringent measure of the quality of the SOP PES because it does not only measure error at the interpolation points.

C. A damped basis that is not the basis of Ref. 19

To determine whether it is possible to make a SOP PES with a number of terms close to the ideal number of 389, but without using the ideal basis functions, we applied the Smolyak method using the basis,

$$\begin{aligned} \varphi_{n_1}(R_1) &= e^{-d_1(R_1 - R_1^{ref})^2} [(R_1 - R_1^{ref})/R_1]^{n_1}, \\ \varphi_{n_2}(R_2) &= e^{-d_2(R_2 - R_2^{ref})^2} [(R_2 - R_2^{ref})/R_2]^{n_2}, \\ \varphi_{n_3}(R_3) &= e^{-d_3(R_3 - R_3^{ref})^2} [(R_3 - R_3^{ref})/R_3]^{n_3}, \\ \varphi_{n_4}(\theta_1) &= e^{-d_4(\theta_1 - \theta_1^{ref})^2} (\theta_1 - \theta_1^{ref})^{n_4}, \\ \varphi_{n_5}(\theta_2) &= e^{-d_5(\theta_2 - \theta_2^{ref})^2} (\theta_2 - \theta_2^{ref})^{n_5}, \\ \varphi_{n_6}(\tau) &= \cos(n_6\tau). \end{aligned} \quad (31)$$

Powers of the Morse variable have been replaced with powers of the Simons-Parr-Finlan variable.⁴⁰ The interpolation points are the same as those in Sec. III B. We again make a first interpolation with $i_1 + i_2 + i_3 + i_4 + i_5 + i_6 \leq H = 5 + 12$ and

the same $[a, b]$ intervals for the stretch and bend coordinates. The error is 0.5 cm^{-1} and the number of terms in the SOP is 11 452. Optimizing the $[a, b]$ intervals for the stretch and bend coordinates and the $g^c(i_c)$ functions makes it possible to find an interpolant with 1573 terms (490 terms after τ contraction (see Section IV)) with an error of 1.5 cm^{-1} . Clearly, if damping is incorporated into the basis functions, the Smolyak procedure enables one to obtain an excellent SOP representation of the original PES with a small number of terms, even if the ideal 1D bases are not used.

IV. CONTRACTION

In Secs. II and III, the number of terms in the SOP PES is simply the number of terms in Eq. (27). In Subsection III C, we report that using basis functions that are non optimal, but include damping, the Smolyak interpolant has 1573 terms. Owing to the fact that the PES we are fitting is damped, the Smolyak interpolant built from bases without damping has

$$V^{SOP}(x_1, x_2, x_3, x_4, x_5, x_6) = \sum_{n_1=0}^{n_1^{max}(H)} \varphi_{n_1}(x_1) \sum_{n_2=0}^{n_2^{max}(n_1, H)} \varphi_{n_2}(x_2) \sum_{n_3=0}^{n_3^{max}(n_2, n_1, H)} \varphi_{n_3}(x_3) \sum_{n_4=0}^{n_4^{max}(n_3, n_2, n_1, H)} \varphi_{n_4}(x_4) \\ \times \sum_{n_5=0}^{n_5^{max}(n_4, n_3, n_2, n_1, H)} \varphi_{n_5}(x_5) \sum_{n_6=0}^{n_6^{max}(n_5, n_4, n_3, n_2, n_1, H)} C_{n_1, n_2, n_3, n_4, n_5, n_6} \varphi_{n_6}(x_6), \quad (33)$$

where $n_c^{max}(H, n_1, n_2, \dots, n_{c-1})$ is the maximum value of n_c for fixed values of H and the indices $n_1, n_2, \dots, n_{c-1}$. Eq. (33) can be “contracted” by pre-evaluating the right-most sum,

$$V^{SOP}(x_1, x_2, x_3, x_4, x_5, x_6) = \sum_{n_1=0}^{n_1^{max}(H)} \varphi_{n_1}(x_1) \sum_{n_2=0}^{n_2^{max}(n_1, H)} \varphi_{n_2}(x_2) \\ \times \sum_{n_3=0}^{n_3^{max}(n_2, n_1, H)} \varphi_{n_3}(x_3) \sum_{n_4=0}^{n_4^{max}(n_3, n_2, n_1, H)} \varphi_{n_4}(x_4) \\ \times \sum_{n_5=0}^{n_5^{max}(n_4, n_3, n_2, n_1, H)} \varphi_{n_5}(x_5) \phi^{n_1, n_2, n_3, n_4, n_5}(x_6), \quad (34)$$

where

$$\phi^{n_1, n_2, n_3, n_4, n_5}(x_6) = \sum_{n_6=0}^{n_6^{max}(n_5, n_4, n_3, n_2, n_1, H)} C_{n_1, n_2, n_3, n_4, n_5, n_6} \varphi_{n_6}(x_6). \quad (35)$$

Eq. (34) has five sums instead of six. It is best to choose x_6 to be the coordinate for which the number of terms in the contracted SOP is as small as possible. It is not trivial to determine which coordinate should be selected as x_6 because $n_6^{max}(n_5, n_4, n_3, n_2, n_1, H)$ depends on n_5, n_4, n_3, n_2, n_1 and therefore one must test D options. The reduction in the number of terms is significant. For example, if $n_1 + n_2 + n_3 + n_4 + n_5 + n_6 \leq 12$, the original expansion in Eq. (33) requires (12

more terms, in Subsection III B 3898 terms. The number of terms in our SOP PESs should of course be compared with the number of terms in the PES we are interpolating (389) but it might also be compared with 18 750, which is the number of terms required to obtain a numerically exact SOP PES with POTFIT.¹⁰ However, 18 750 is the number of POTFIT terms *before* “contraction.” With contraction the number of POTFIT terms is 3750. As explained in Refs. 9 and 41, contraction greatly reduces the number of terms. In this section we explain that the same contraction idea can be applied to the Smolyak interpolated SOP PES, despite the fact that it is not made from a direct product.

For a 6D PES, the SOP

$$V^{SOP}(x_1, x_2, x_3, x_4, x_5, x_6) = \sum_{g(n_1+1, n_2+1, n_3+1, n_4+1, n_5+1, n_6+1) \leq H} C_{n_1, n_2, n_3, n_4, n_5, n_6} \\ \times \varphi_{n_1}(x_1) \varphi_{n_2}(x_2) \varphi_{n_3}(x_3) \varphi_{n_4}(x_4) \varphi_{n_5}(x_5) \varphi_{n_6}(x_6) \quad (32)$$

can be written as

$+ 6)/(12!6!) = 18\,564$ products of basis functions and the contracted Eq. (34) requires $(12 + 5)/(12!5!) = 6188$ basis functions. After τ contraction, the SOP PES of Sec. III C has only 490 terms. This is considerably less than the 3750 terms required when using POTFIT.

V. CONCLUSION

In this paper we propose an interpolation method for making SOP PESs directly from *ab initio* energies. The method uses a Smolyak grid and Lagrange-type functions.² It will be particularly advantageous for molecules with more than about 5 atoms. The PES is *not* represented with a direct product basis. The basis functions can be chosen so that with only a small number of terms the SOP PES has reasonable asymptotic behaviour. By using the $g^c(i_c)$ functions, it will often be possible to minimize the number of terms in the SOP PES and the number of *ab initio* calculations required.

The great advantage of the SOP form is that it obviates the need to store the PES on a large full-dimensional grid.^{5,9} POTFIT is a popular and useful tool that enables one to replace the potential evaluated on the grid used to do the dynamics calculation, $V_{\alpha, \beta, \gamma, \dots}$ with a sum of products of matrices labelled by only two indices. The elements of these matrices are single-particle potentials evaluated at points. The POTFIT potential is a direct product. If m_c is the number of single-particle functions for a single coordinate, then the number of terms in the (contracted) POTFIT SOP PES is $\prod_{c=1}^{D-1} m_c$. POTFIT

uses a clever algorithm, designed by its inventors and later re-discovered by mathematicians, to minimize m_c but it is handicapped by its direct product structure and the exponential scaling of the number of terms in the SOP. Multigrid potfit, a technique that enables one to obtain an approximate POTFIT without storing the PES on the full-dimensional (fine) grid, was introduced to reduce the memory cost of POTFIT and not to decrease the number of terms in the SOP representation.¹⁰ The number of terms may be quite large. The Smolyak interpolation method we present in this paper has advantages compared to POTFIT and MGPF. First, because the PES is not represented as a direct product the Smolyak SOP PES has fewer terms. For example, the exact (contracted) POTFIT HONO potential has 3750 terms whereas a (contracted) Smolyak SOP PES made from damped non-optimal bases has 490 terms. The ratio of the number of Smolyak terms to the number of POTFIT terms will decrease as D is increased. Second, a Smolyak SOP PES can be generated from a small number of points; the required number of fitting points is equal to the number of terms in the SOP PES. Third, the Smolyak SOP PES is known as a function of the coordinates and not only at the points of a direct product grid used to do a dynamics calculation. As a consequence, it is not necessary to re-generate the Smolyak SOP PES if it is to be used with a larger grid. An advantage of POTFIT, compared to the Smolyak interpolation method, is that it will work when it is *not* possible to represent the PES as a sum of a small number of products of basis functions, i.e., when the PES is not smooth.

Several authors have demonstrated that a SOP PES can be obtained using neural networks (NN).^{11–15} Manzhos and Carrington used a standard NN with exponential activation functions. Koch and Zhang used a multiplicative neural network. There is some evidence that the number of terms of the SOP is relatively small, but the number of required *ab initio* points may be much larger. In addition, NN PESs may have poor asymptotic behaviour.

Another strategy for obviating the need to store the PES on a full-dimensional grid is to use an expansion with terms depending on a subset of the coordinates. Some of the names used for this idea are: multimode expansion,^{4,42,43} cluster expansion,^{4,44} order-of-coupling expansion,¹⁴ high dimensional model representation,⁴⁵ ANOVA expansion.⁴⁶ The simplest implementation of this idea requires using many lower dimensional grids to fit.^{47,48} As the number of lower dimensional grids increases combinatorically with D , this can make fitting very costly. In a recent paper, a SOP sparse-grid interpolant is used for each of the terms in the expansion, this yields a SOP PES.⁴⁹ The number of terms is the sum of the numbers of terms in the SOPs for each of the terms in the order-of-coupling expansion. For smooth potentials, the number of terms is too large. For example, for formaldehyde (6D) the normal coordinate fit requires 11 461 terms to achieve an accuracy of 0.1 cm^{-1} for the ground state and the fundamentals.⁴⁹ A few hundred terms are certainly sufficient if one uses a single Smolyak interpolant. If no effort is made to choose good $g^c(i_c)$ functions and one uses the simplest choice, $g^c(i_c) = i_c$, then the number of terms in the full-dimensional Smolyak interpolant is $(n^{\max} + D)!/(n^{\max}!D!)$, where $n^{\max} + 1$ is the number of basis functions used for a single coordinate. For $n^{\max} = 4$ and $D = 6$ there are only 210 terms. For $n^{\max} = 4$ and $D = 12$ there are

only 1820 terms. In Ref. 49, 113 877 terms are required for C_2H_4 . In Ref. 50, a C_2H_4 PES deemed accurate to 7800 cm^{-1} above the zero point energy was determined by fitting a SOP with 2236 terms to 82 542 *ab initio* points. As is the case in this article, non-localized basis functions were used. Clearly, the method of Ref. 49 is overkill if the PES is smooth, however, it may be an excellent method for PESs that cannot be written in the form of Eq. (18).

The sparse-grid interpolants of Ref. 49 would have fewer terms if they used basis functions of the type used in Section III, but their basis, and indeed their entire procedure may, like POTFIT, be competitive for potentials that are less smooth. When the potential is smooth the Smolyak SOP PES of this paper requires orders of magnitude fewer *ab initio* points and has orders of magnitude fewer terms in the SOP. Another significant distinction between the approach of Ref. 49 and ours is the way the interpolants are built. The authors of Ref. 49 choose to use many low-dimensional interpolants rather than one full-dimensional interpolant in part because to interpolate they must solve a set of linear equations whose size is the number of basis functions. Using Lagrange-type functions, we avoid the need to invert large matrices.

Several quantum dynamics methods owe their efficiency to the fact that multi-dimensional integrals can be avoided if one uses a product basis and a SOP PES. A routine method for generating SOP PESs *directly* from *ab initio* points will open the door to easy application of methods like multiconfiguration time dependent Hartree.⁵ We propose the Smolyak interpolation method of this paper as a method of first resort. When $\varphi_{n_c}(x_c)$ basis functions and $g^c(i_c)$ functions that define the constraint can be chosen so that the potential may be accurately represented in the form of Eq. (18), then it is possible to find a SOP PES with approximately L terms from approximately L *ab initio* points. The number of terms is certainly less than $\frac{(D+n^{\max})!}{D!(n^{\max})!}$.

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