A hierarchy of potential energy surfaces constructed from energies and energy derivatives calculated on grids

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In this work we develop and test a methodology for the generation of Born–Oppenheimer potential energy surfaces (PES) for use in vibrational structure calculations. The method relies on the widely used restricted-mode-coupling expansion of the fully coupled potential surface where only up to n or less vibrational coordinates are coupled in the potential. Low-order derivatives of the energy are then used to extrapolate the higher mode-coupling potential terms; derivative information is thus used in a convenient way for the evaluation of higher mode couplings avoiding their explicit calculation on multidimensional grids. The formulation, which is a variant of the popular modified Shepard interpolation, is general for any extrapolation of $(n+p)$-mode-coupling terms from n-mode couplings and can be applied to the energy or any other molecular property surface for which derivative information is available. The method depends only on analytical parameter-free weight functions that satisfy important limiting conditions and control the contribution from each direction of extrapolation. The procedure has been applied on a representative set of 13 molecules, and its accuracy has been tested using only gradients and using both gradients and Hessians. The results provide evidence for the importance of higher mode couplings and illustrate the cost efficiency of the proposed approach. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3092921]

I. INTRODUCTION

The Born–Oppenheimer (BO) approximation is widely used in molecular dynamics studies, since it leads to a conceptually and computationally attractive separation of electronic and nuclear degrees of freedom.[1] The knowledge of the whole molecular potential energy surface (PES) or a part of it is a key ingredient in different fields of research such as reaction dynamics, vibrational and UV spectroscopy, or photoexcitation dynamics. The efficient construction of molecular PESs is thus a central task in theoretical chemistry.

Beyond the harmonic oscillator (HO) model a number of schemes are routinely used to calculate the molecular vibrational spectrum, including recent implementations of perturbation theory with the normal coordinate HO description as Refs. 2 and 3. Our focus is on methods relying on the vibrational self-consistent field (VSCF) approach.[4,5] In the VSCF approach the optimal modals are calculated self-consistently by the application of the variational principle to a single Hartree product wave function. Using the VSCF *ansatz* as a starting point, vibrational Møller–Plesset (VMP),[6–8] vibrational autoadjusting perturbation theory (VAPT),[9] vibrational coupled cluster (VCC),[10,11] and vibrational configuration interaction[12–14] (VCI) methods can be used to include correlation between the modes. All these methods have been

recently formulated in a second quantization approach[15] and implemented[10,11,16,17] in the program MIDASCPP.[18] Other wave function methods are based on quasidegenerate perturbation theory.[19,20] All these methods aim at the solution of the time-independent nuclear Schrödinger equation. A particularly successful approach to the solution of the time-dependent nuclear Schrödinger equation is the multiconfiguration time-dependent Hartree (MCTDH) approach[21] and has been recently applied also to the calculation of vibrational spectra using internal coordinates.[22,23]

In recent years a standard step in the construction of PESs for use in vibrational structure calculations has been the *n*-mode representation, where the full-dimensional PES is approximated as a sum of potential terms of lower dimensionality. Within this approach high-order mode couplings are included in a hierarchical way. Carter *et al.*[24] considered originally up to four-mode couplings forming the basis of their subsequent VCI calculations, while an approach restricted to two-mode couplings was suggested and since then extensively used by Jung and Gerber[7] in their second order VMP calculations. Recently our group introduced a similar open-ended hierarchical approach to the construction of PESs and molecular property surfaces. In our approach the fully coupled potential is similarly written as a sum of potential terms which contain only the simultaneous interaction between a certain number of degrees of freedom (*vide infra*).[25,26] Our implementation provides various options for the evaluation of the PES on a grid and has been interfaced to any of the VSCF, VMP, VAPT, VCI, and VCC vibrational structure methods mentioned above. We note in passing that Yagi *et al.*[27] reported an equivalent formulation for a hierar-

chial construction of the PES. The aim of this paper is to further extend this hierarchial approach by using both potential energy values and low-order derivative information.

We suggest a scheme where computational attractive approaches for estimating higher mode couplings are constructed using derivative information. The explicit calculation of the higher mode-coupling terms is often prohibitive. We note that in this context a number of methods aiming at a efficient calculation of the PES for the generation of vibrational wave functions has been developed including those of Yagi et al.,[27–30] Rauhut,[31] and Benoit.[32,33] These include the selection or prescreening of coupling terms to produce a more sparse PES which includes only the most important mode-coupling terms. Another idea is to use multiresolution approaches, where the higher mode couplings are treated with lower level *ab initio* methods. Such approaches have definitely attractive features. Our scheme offers a quite different approach for addressing the higher mode couplings, that in its pure form considered here avoids explicitly the electronic structure calculations for the highest mode coupling all together. However, our scheme may very well be combined with the aforementioned ideas. Thus one can use our scheme in prescreening procedures as well as in the context of a multiresolution approach.

High-order derivatives have been routinely used in the construction of molecular PES. The most striking example is provided by the widely used quartic force field representation of the PES, where the potential energy/molecular property surface is approximated as a fourth order Taylor expansion centered on the molecular equilibrium configuration. Such an approach, although computationally very attractive, is, however, not appropriate for the accurate description of the PES in regions far from the equilibrium geometry.[34] The modified Shepard interpolation[35] (MSI) scheme may overcome this issue, as the approach relies on not only one, but on several Taylor expansions that span the configurational space of relevance for the vibrational dynamics. In fact, the MSI approach has been extensively used in molecular dynamics; Collins and co-workers[36–39] used the MSI method to interpolate PESs in Cartesian and internal coordinates, by using Taylor series of up to the fourth order, and they have also developed an algorithm to control the weights of the MSI approach based on the confidence volume of each Taylor series. Within the framework of vibrational structure calculations, the MSI approach has also been used by Yagi et al.[28–30] to interpolate PESs in normal coordinates aiming at very few expansion points in conjunction with comparatively high-order Taylor expansions. For an efficient selection of very few expansion points, *a priori* knowledge of the vibrational structure of the molecule is needed. Procedures that do not rely on such prior knowledge would be desirable, but obviously this can be anticipated to go hand in hand with a need for more points. Along the same lines, Evenhuis and Manthe[40] very recently developed a MSI approach based on a Metropolis sampling to generate the candidate points. Such points are afterward accepted if their energy enters in a given range determined by the energy distribution of the molecule based on a harmonic potential. Further selection of the points is done to evenly distribute the points in the surface using the

h-weight[37] and in order to distribute the reference evenly in the relevant regions of the PES by means of the variance criteria.[41] We also note in passing that derivative informations have also been exploited in the fitting of PESs.[42] Furthermore, there has recently been significant progress in the use of the moving least-squares approach for the construction of PESs, including now also derivative information.[43,44]

In the following we propose an approach which uses derivative information for a cost-efficient and accurate construction of potential energy and molecular property surfaces. Our goal is twofold: (i) we aim at a transparent procedure which does not rely on *a priori* knowledge of the vibrational structure of the system, allowing it to be easily implemented as an interface to essentially any electronic structure program, and (ii) we want the scheme to be set in a hierarchial way, so that higher vibrational mode couplings are introduced in a systematic way, depending on the desired accuracy. In doing so we exploit one of the strong facets of modern electronic structure theory, namely, the efficient calculation of energy derivatives, and we define reasonable steps on this ladder in accordance with computational cost considerations such as the scaling with respect to the number of degrees of freedom. As we shall see, the method is mathematically a variant of the MSI but with an alternative motivation and derivation that suggest a particular restrictive way of distributing evaluation points.

The plan of the paper is the following. In Secs. II and III we describe the theoretical background and an implementation of the proposed methodology. The computational details are reported in Sec. IV. Section V reports sample calculations on a representative set of molecules, while conclusion and perspectives are reported in Sec. VI.

II. DESCRIPTION OF THE METHOD

A. Hierarchy on the construction of the PES

For a nonrotating molecular system, assuming the BO approximation, the Hamiltonian in terms of normal coordinates reads according to Watson,[45,46]

$$H = -\frac{1}{2}\sum_k \frac{\partial^2}{\partial q_k^2} + \frac{1}{2}\sum_{\alpha\beta}\pi_\alpha\mu_{\alpha\beta}\pi_\beta - \frac{1}{8}\sum_\alpha\mu_{\alpha\alpha} + V(\mathbf{q}). \quad (1)$$

In Eq. (1), π_α and $\mu_{\alpha\beta}$ are Cartesian components of the vibrational angular momentum and the inverse of the effective moment of inertia, respectively. $V(\mathbf{q})$ is the BO potential energy operator. Often the terms involving the inverse effective moment of inertia are neglected, which leaves us with the following Hamiltonian:

$$H = -\frac{1}{2}\sum_k \frac{\partial^2}{\partial q_k^2} + V(\mathbf{q}). \quad (2)$$

Due to its high dimensionality [$3N-6(5)$ for a system with N atoms] the construction of the potential energy operator $V(\mathbf{q})$ can generally only be accomplished in an approximate fashion. A widely used approach in studies of vibrational dynamics is to approximate the full potential $V(\mathbf{q})$ as a sequence of potential energy terms of lower dimensionality,

$$V^{(1)}, V^{(2)}, \dots, V^{(M)} \tag{3}$$

for a total of M vibrational degrees of freedom. To this aim, a set of potential energy functions (PEFs) are defined which include the coupling among a subset n of the M coordinates,

$$V^{m_1} = V(0, \dots, 0, q_{m_1}, 0, \dots, 0),$$

$$V^{m_1,m_2} = V(0, \dots, 0, q_{m_1}, 0, \dots 0, q_{m_2}, 0, \dots, 0), \tag{4}$$

and so forth up to $V^{m_1,m_2,\dots,m_M}$, the fully coupled potential $V(\mathbf{q})$. In Eq. (4) it is assumed that $m_1 \neq m_2$. For the sake of simplicity the set of modes [referred to as a mode combination (MC) hereafter] defining the particular PEF are collected in an n-dimensional vector $\mathbf{m}_n$, so that a n-dimensional PEF is denoted as $V^{\mathbf{m}_n}$. Note that $V^{\mathbf{m}_n}$ is symmetric with respect to the permutation of mode indices in $\mathbf{m}_n$. One typical way to calculate the PEFs, commonly known as a grid approach, is to compute the potential energy values on a set of grid points and interpolate or fit functions accordingly. The PEFs can be used to define the sequence of potential energy terms [see Eq. (3)] that converges to the fully coupled potential. However, by summing over all MCs overcountings are introduced since each PEF includes all the lower-dimensional PEFs corresponding to the set $\mathbf{m}_{n'} \subset \mathbf{m}_n$. Following the general formalism of Ref. 25 we introduce potentials $\bar{V}^{\mathbf{m}_n}$ defined, such that

$$\bar{V}^{\mathbf{m}_n} = S^{\mathbf{m}_n} \sum_{l=1}^{n} (-1)^{n-l} \binom{n}{l} V^{\mathbf{m}_l}, \tag{5}$$

where $S^{\mathbf{m}_n}$ is an operator that symmetrizes with respect to n and m indices.

An alternative way to avoid overcountings has been introduced by Yagi *et al.*[27] which define the potentials in a recursive form. Both formulations are equivalent and lead to a sequence of potentials which is guaranteed to converge to the exact potential when all couplings are included. Thus the following expression defines one hierarchy of potentials converging to the exact limit, for $n=M$, the total number of vibrational degrees of freedom:

$$V \approx V^{(n)} = \sum_{k=1}^{n} \sum_{\mathbf{m}_k} \bar{V}^{\mathbf{m}_k}. \tag{6}$$

Generally, one may include in the expansion only the MCs that are relevant for the representation of the potential,

$$V \approx \sum_{\mathbf{m} \in \mathrm{MCR}\{V\}} \bar{V}^{\mathbf{m}}, \tag{7}$$

where MCR is a MC range—the set of MCs we want to include in the potential. Consider now a grid-based approach for the construction of the PES where potential energy values are calculated on an appropriate set of points. The inclusion of up to n-mode couplings in the approximate PES for a molecule with M modes requires $\sum_{i=0}^{n} \binom{M}{i}(N_p)^i$ single-point calculations for a grid consisting of N_p points in each normal coordinate direction, for simplicity assumed here to be the same for all modes in all couplings which needs not be the case. The unfavorable scaling $\binom{M}{n}(N_p)^n$ with respect to the

level of mode coupling is the bottleneck of every grid-based approach. Thus, for a real molecule the hierarchical approach to the construction of the potential outlined above is difficult to extend beyond a three or four mode-coupling representation, and for medium-sized molecules the inclusion of three-mode couplings proves already very costly. Having additional levels in the hierarchy would be attractive. The focus of this paper is to demonstrate that the number of single-point calculations needed can be drastically reduced if one can approximate the highest mode couplings from information generated in the lower mode cuts, which imply a computational saving in the number of calculations corresponding to the reduced dimensionality. This may facilitate inclusion of higher mode couplings that otherwise could not be included in a practical calculation. In this work we shall consider the use of the derivative information to construct $V^{\mathbf{m}_{n+p}}$. In particular, we will use the derivatives to construct a set of Taylor polynomials of $V^{\mathbf{m}_{n+p}}_{\mathbf{m}_p}$ in each direction of the p modes missing in $V^{\mathbf{m}_n}$. Then we combine such local Taylor expansions to obtain an approximation to $V^{\mathbf{m}_{n+p}}_{\mathbf{m}_p}$. In order to decide the importance of each Taylor polynomial in $V^{\mathbf{m}_{n+p}}_{\mathbf{m}_p}$, we will use weight functions based on the distance,

$$V^{\mathbf{m}_{n+p}} \approx \sum_{\mathbf{m}_p} V^{\mathbf{m}_{n+p}}_{\mathbf{m}_p} w_{\mathbf{m}_p}. \tag{8}$$

Due to the relation between $V^{\mathbf{m}_{n+p}}$ and $\bar{V}^{\mathbf{m}_{n+p}}$ in Eq. (5), this defines also how to evaluate $\bar{V}^{\mathbf{m}_{n+p}}$. Clearly, with the same $\binom{M}{n}(N_p)^n$ number of points considered, information on higher mode couplings is extracted. Compared to calculations by an explicit grid in $n+p$ dimensions, this offers the possibility to construct alternative approximations, where the number of grid points is greatly reduced, at the cost of using derivative information. We shall denote such approaches as extrapolations since they extrapolate information of a function in a rather restricted domain into a much larger domain. On the other hand it will become clear that our approach is rather similar to some known interpolation procedures, with the key issue being the selection of calculation points. We will return to this issue.

The aspect that makes the above considerations significant is the success of modern electronic structure theory in providing efficient algorithms for calculation of energy derivatives. Thus, it is now known that gradients can be obtained almost for free for variational wave functions and density functional theory (DFT). For nonvariational wave functions there are additional concerns, but generally the gradient should be available at the cost of an energy calculation times a small factor (say 2). Second and third derivatives can also be obtained efficiently; however, one should take into account that now of order M linear equations must be solved for an M mode system. Thus, requesting more information of course increases the cost. On the other hand, inclusion of higher derivatives in the extrapolation increases accuracy. The basic principles of our approach are general and allow such higher orders to be exploited even though in the following we will primarily focus on the n to $n+1$ extrapolation and refer to Appendix for the more general case.
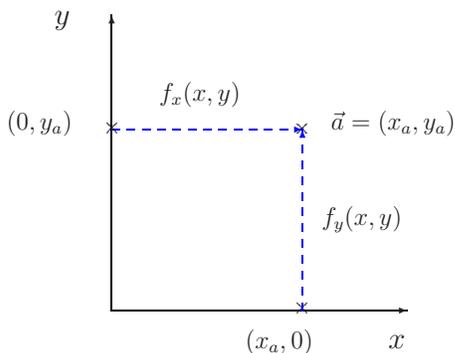
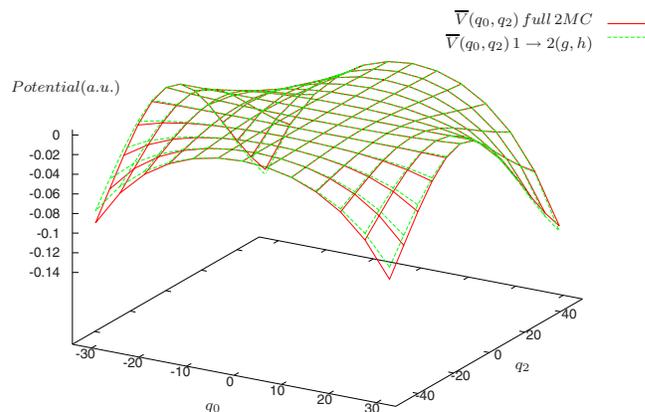FIG. 1. (Color online) Extrapolation from one to two dimensions.

FIG. 2. (Color online) Extrapolation of the symmetric stretching and bending coupling for water molecule using gradient and Hessian derivatives compared against full-2MC PES. For a description of the calculation, see computational details.

The extrapolation method proposed here is used to generate new points at a higher order mode coupling in the hierarchial expansion of the full potential. The initial set of points calculated with an electronic structure program is thus increased through both extrapolation (to higher couplings) and interpolation (at the same level of coupling). The whole set of points is fitted to a polynomial function. The polynomial fit provides a representation of the PES, which consists of a linear combination of products of one-mode functions. As a consequence, the Hamiltonian becomes a sum over T product terms,

$$H = \sum_{t=1}^{T} \prod_{m} h^{m,t}, \tag{9}$$

where $h^{m,t}$ is a single-mode operator, giving a similar structure for integrals involving Hartree-product wave functions. This fact is well known and exploited for high efficiency in time-dependent quantum mechanics[47] and vibrational structure theory.[17]

B. Extrapolation from $\bar{V}^{(1)}$ to $\bar{V}^{(2)}$

As the simplest illustration of the procedure, we approximate (extrapolate) the value of a two-variable function $f(x,y)$ at a point (x_a, y_a) using the value of the function and its low-order partial derivatives at the points $(x_a, 0)$ and $(0, y_a)$. To this aim we will weigh the Taylor series centered at $(x_a, 0)$ in the direction y ($f_y(x,y)$) and the Taylor series centered at $(0, y_a)$ in the direction x ($f_x(x,y)$). Figure 1 illustrates the approach. One choice for the weight function would be the inverse of the distance. However, in order to work with a function with continuous derivatives, we shall take the square of the inverse of the distance. Figure 1 illustrates the approach.

The Taylor series from the expansion point $(x_a, 0)$ in the direction of y calculated at the point (x_a, y_a) reads

$$f_y(x_a, y_a) = f(x_a, 0) + y_a \left. \frac{\partial f(x,y)}{\partial y} \right|_{(x_a,0)}$$
$$+ \frac{1}{2} y_a^2 \left. \frac{\partial^2 f(x,y)}{\partial y^2} \right|_{(x_a,0)} + \cdots, \tag{10}$$

and a similar expression holds for $f_x(x_a, y_a)$.

The extrapolated value for $f(x_a, y_a)$ is therefore obtained as a weighted sum of the two Taylor expansions defined above,

$$\tilde{f}(x_a, y_a) = \frac{\dfrac{f_x(x_a, y_a)}{x_a^2} + \dfrac{f_y(x_a, y_a)}{y_a^2}}{\dfrac{1}{x_a^2} + \dfrac{1}{y_a^2}}$$
$$= \frac{(y_a^2 f_x(x_a, y_a) + x_a^2 f_y(x_a, y_a))}{x_a^2 + y_a^2}. \tag{11}$$

Thus, if we are able to evaluate the function and its low-order partial derivatives on N_p points along each axis, we can obtain an extrapolated value for the function at each point on the bidimensional grid obtained as a direct product of the two monodimensional grids. This procedure requires a number of $2N_p$ values of the function and its partial derivatives up to a selected order as opposed to N_p^2 function values for the same direct product grid. Figure 2 shows the accuracy of the approximation for the 2MC PES of water using gradients and Hessians.

C. Extrapolation from $\bar{V}^{(2)}$ to $\bar{V}^{(3)}$

Let us now extrapolate the value of a three-dimensional function at the point $\vec{r}_a = (x_a, y_a, z_a)$, assuming that function values and partial derivatives are available on the xy, yz, and xz planes. For the sake of clarity we introduce the notation $[\vec{r}_a]_{xy} = (x_a, y_a, 0)$ and for an arbitrary number of dimensions $[\vec{r}_a]_{12} = \mathbf{P}_{12} \vec{r}_a$, where $\mathbf{P}_{n_1 \cdots n_m}$ is the projector matrix on the subspace generated by the coordinates $n_1 \cdots n_m$. It is also useful to define the complement of a vector $[\vec{r}_a]_{12}$ to $\vec{r}_a$ as $\overline{[\vec{r}_a]}_{12} = \vec{r}_a - [\vec{r}_a]_{12}$ (see Ref. 48). With this notation, the Taylor expansion at the point $[\vec{r}_a]_{xy} = \overline{[\vec{r}_a]}_z$ in the z direction reads as follows:

$$f_z(\vec{r}_a) = f(\overline{[\vec{r}_a]}_z) + (\vec{r}_a - \overline{[\vec{r}_a]}_z) \vec{\nabla}_{\vec{x}} f(\vec{x})|_{\overline{[\vec{r}_a]}_z}$$
$$+ \frac{1}{2}(\vec{r}_a - \overline{[\vec{r}_a]}_z) \mathbf{H}(\overline{[\vec{r}_a]}_z)(\vec{r}_a - \overline{[\vec{r}_a]}_z)^{\dagger} + \cdots \tag{12}$$
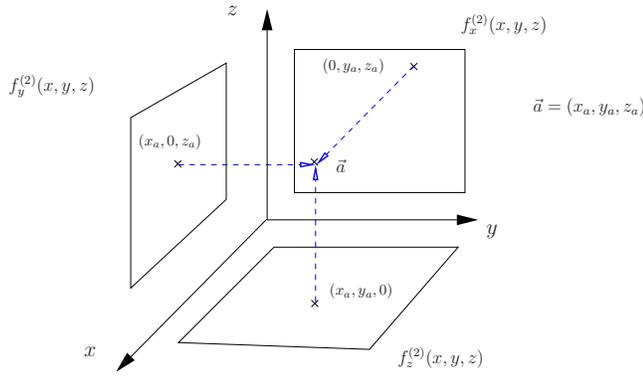
FIG. 3. (Color online) Extrapolation from two to three dimensions.

$$= f([\overrightarrow{r_a}]_z) + [\overrightarrow{r_a}]_z \vec{\nabla}_{\vec{x}} f(\vec{x})|_{[\overrightarrow{r_a}]_z} + \frac{1}{2}[\overrightarrow{r_a}]_z \mathbf{H}([\overrightarrow{r_a}]_z)[\overrightarrow{r_a}]_z^\dagger, \quad (13)$$

where $\mathbf{H}_{ij}(\vec{x}_a) = (\partial^2 f(\vec{r})/\partial r_i \partial r_j)|_{\vec{x}_a}$.

The extrapolated value, $\tilde{f}(\vec{r}_a)$, reads as follows:

$$\tilde{f}(\vec{r}_a) = \frac{x_a^2 y_a^2 f_z(\vec{r}_a) + y_a^2 z_a^2 f_x(\vec{r}_a) + z_a^2 x_a^2 f_y(\vec{r}_a)}{x_a^2 y_a^2 + y_a^2 z_a^2 + z_a^2 x_a^2}. \quad (14)$$

Figure 3 depicts the nature of the approximation for $\tilde{f}(\vec{r}_a)$ when the extrapolation is done from a two-mode coupled PES to a three-mode coupled one. The weight function is a generalization of that used in one- to two-dimension extrapolation. We discuss the weight functions and their properties in Sec. II D.

D. Extrapolation from $\bar{V}^{(n-1)}$ to $\bar{V}^{(n)}$

Let us now generalize the procedure outlined above to an n-dimensional function f at the point $\vec{r} = (r_1, \ldots, r_n)$ extrapolated from n subdomains of dimension $n-1$. To calculate the extrapolated value we need the value of the function and its derivatives at the points $\{[\overrightarrow{r}]_i\}_{i=1,\ldots,n}$,

$$\tilde{f}(\vec{r}) = \sum_i w_i(\vec{r}) f_i(\vec{r}), \quad (15)$$

where the Taylor series of order q reads

$$f_i(\vec{r}) = \sum_{j=0}^{j=q} \left[\frac{1}{j!}(([\overrightarrow{r}]_i) \cdot \vec{\nabla}_{\vec{x}})^j f(\vec{x}) \right]_{[\overrightarrow{r}]_i}, \quad (16)$$

and the weight functions are required to fulfill the following properties:

$$\sum_i w_i(\vec{r}) = 1, \quad (17)$$

$$\lim_{r_i \to 0} w_i(\vec{r}) = 1, \quad (18)$$

$$\lim_{r_j \to 0} w_i(\vec{r}) = 0, \quad \forall j \neq i, \quad (19)$$

$$\lim_{r_i \to \infty} w_i(\vec{r}) = 0, \quad (20)$$

$$w_i([\overrightarrow{a}]_j) = \delta_{ij}, \quad (21)$$

where $\overrightarrow{[a]}_j$ is any of the expansion points from the Taylor series and Eq. (21) is implied by Eqs. (17)–(19).

The following function fulfills these conditions and reduces to the previous special cases,

$$w_i(\vec{r}) = \frac{\frac{1}{r_i^2}}{\sum_j \frac{1}{r_j^2}} = \frac{\prod_{k \neq i} r_k^2}{\sum_j \prod_{k \neq j} r_k^2} = \frac{\|\overrightarrow{[r]}_i\|^{-2}}{\sum_j \|\overrightarrow{[r]}_j\|^{-2}}. \quad (22)$$

The derivates of the weight functions are as follows:

$$\frac{\partial w_i(\vec{r})}{\partial r_j} = \frac{2 w_i(\vec{r})}{r_j}(w_j(\vec{r}) - \delta_{ij}), \quad (23)$$

$$\frac{\partial^2 w_i(\vec{r})}{\partial r_j \partial r_k} = \frac{2}{r_j}\left(\frac{\partial w_i(\vec{r})}{\partial r_k}\right)(w_j(\vec{r}) - \delta_{ij}) - \frac{2\delta_{jk} w_i(\vec{r})}{r_j^2}(w_j(\vec{r})$$
$$- \delta_{ij}) + \frac{2 w_i(\vec{r})}{r_j}\left(\frac{\partial w_j(\vec{r})}{\partial r_k}\right), \quad (24)$$

which gives for the expansion points $\overrightarrow{[a]}_p$,

$$\left.\frac{\partial w_i(\vec{r})}{\partial r_j}\right|_{\overrightarrow{[a]}_p} = \frac{2\delta_{ip}}{a_p}(\delta_{jp} - \delta_{ij}) = 0, \quad (25)$$

$$\left.\frac{\partial^2 w_i(\vec{r})}{\partial r_j \partial r_k}\right|_{\overrightarrow{[a]}_p} = -\frac{2\delta_{jk}\delta_{ip}(\vec{r})}{r_j^2}(\delta_{jp} - \delta_{ij}) = 0. \quad (26)$$

One can easily prove that the extrapolated function takes the values of the derivatives of the full potential at the expansion points,

$$\left.\frac{\partial \tilde{f}(\vec{r})}{\partial r_j}\right|_{\overrightarrow{[a]}_p} = \sum_i w_i(\vec{r}) \left.\frac{\partial f_i(\vec{r})}{\partial r_j}\right|_{\overrightarrow{[a]}_p}$$
$$+ \sum_i f_i(\vec{r}) \left.\frac{\partial w_i(\vec{r})}{\partial r_j}\right|_{\overrightarrow{[a]}_p}$$
$$= \left.\frac{\partial f_p(\vec{r})}{\partial r_j}\right|_{\overrightarrow{[a]}_p} = \left.\frac{\partial f(\vec{r})}{\partial r_j}\right|_{\overrightarrow{[a]}_p}, \quad (27)$$

$$\left.\frac{\partial^2 \tilde{f}(\vec{r})}{\partial r_m \partial r_l}\right|_{\overrightarrow{[a]}_p} = \sum_i w_i(\vec{r}) \left.\frac{\partial^2 f_i(\vec{r})}{\partial r_l \partial r_m}\right|_{\overrightarrow{[a]}_p}$$
$$+ \sum_i f_i(\vec{r}) \left.\frac{\partial^2 w_i(\vec{r})}{\partial r_l \partial r_m}\right|_{\overrightarrow{[a]}_p}$$
$$+ \sum_i \left.\frac{\partial f_i(\vec{r})}{\partial r_m} \frac{\partial w_i(\vec{r})}{\partial r_l}\right|_{\overrightarrow{[a]}_p}$$
$$+ \sum_i \left.\frac{\partial f_i(\vec{r})}{\partial r_l} \frac{\partial w_i(\vec{r})}{\partial r_m}\right|_{\overrightarrow{[a]}_p}$$
$$= \left.\frac{\partial^2 f_p(\vec{r})}{\partial r_m \partial r_l}\right|_{\overrightarrow{[a]}_p} = \left.\frac{\partial^2 f(\vec{r})}{\partial r_m \partial r_l}\right|_{\overrightarrow{[a]}_p}. \quad (28)$$

One can also derive the expressions for the extrapolation from $\bar{V}^{(n-p)}$ to $\bar{V}^{(n)}$. In the present work we only apply the formulation for the case $p=1$ and leave the derivation for a general p to the Appendix.

E. Analysis of the error in the PES due to extrapolation

In this section we briefly discuss the direct error done in the PES by means of the proposed extrapolation scheme. In the following discussion we assume that $\bar{V}^{(n)}$ is an analytical function, i.e., an n-variate polynomial of arbitrary order. In order to simplify the demonstration we also assume that the extrapolation is done from a given hierarchial level $n-1$ to the immediately higher one n. Let us suppose that the Taylor expansions used in the extrapolation include derivatives up to kth order. Therefore, each Taylor expansion extrapolating in the direction of a given coordinate r_i will retrieve all the terms containing powers of r_i up to r_i^k. In addition, terms depending on powers of r_i higher than k are estimated in the extrapolation. Therefore, independently of the weight function used [satisfying Eq. (17)], the resulting extrapolated function will contain *all the terms from the exact polynomial which include powers of the coordinates not higher than k*. Higher order terms will be approximated by a weighted sum of the extrapolated values in each direction of extrapolation. Thus, the current approximation will fail when terms with higher powers are important in the potential, and in the event these terms are poorly approximated by the weighted sum of Taylor expansions.

Let us consider two examples. If we extrapolate $\bar{V}^{(3)}(q_1,q_2,q_3)$ from the $\bar{V}^{(2)}(q_1,q_2)$, $\bar{V}^{(2)}(q_2,q_3)$, and $\bar{V}^{(2)}(q_1,q_3)$ lower mode couplings with the use of gradients and Hessians, the extrapolated function will *exactly* reproduce these terms: $q_1 q_2 q_3$, $q_1^2 q_2 q_3,\ldots$, $q_1^2 q_2^2 q_3^2$, while terms such as $q_1^3 q_2 q_3$, $q_1^2 q_2^3 q_3$, etc., will be only approximated. In general, couplings of three modes with third order or higher powers in the factors for each mode are approximated. Using only gradients the $q_1 q_2 q_3$ term is exact while other terms are approximated. For the simplest case of the extrapolation of a two-mode coupling potential term by using both gradients and Hessians, the $q_1 q_2$, $q_1^2 q_2$, $q_1 q_2^2$, $q_1^2 q_2^2$ terms are exactly reproduced. Using only gradients we see that already the $q_1^2 q_2$, $q_1 q_2^2$, $q_1^2 q_2^2$ terms are approximated, and, in fact, $q_1^2 q_2^2$ will be neglected completely. Thus for the $n=1$ to $n=2$ extrapolation based on only gradients, there may be an improvement relative to the uncoupled case, but since we expect terms such as $q_1^2 q_2^2$ to be important (from standard anharmonic perturbational analysis) the absolute accuracy cannot be expected to be high. However, this does not necessarily imply that higher order extrapolations or extrapolations with gradients in higher order cannot be useful. In the three-mode examples above we found that the extrapolations did include the three mode-coupling terms of highest importance from an order point of view and that the inclusion of second derivatives in the extrapolation prove to be more accurate than a linear extrapolation which in turn should be more accurate than a complete neglect of the mode coupling. This will be confirmed by our numerical results.

In should be noted that our $n \to n+1$ extrapolation step is used with derivative data distributed on a grid of n-dimensions. From the weighted Taylor expansion a set of points is generated in $n+1$ dimensions. This $n+1$ grid is fitted to an analytical representation and used in the calculation of vibrational energies and wave functions. Therefore, how the error in the extrapolation step discussed above propagates in the final results, i.e., vibrational energies, is not completely trivial. However, we do think the above analytical considerations support the fact that a good performance of the current extrapolation scheme can be expected.

F. MSI and the treatment of lower couplings

The similarity between the MSI and the proposed extrapolation scheme is worth mentioning. While the original Shepard interpolation scheme[49] approximates a given function as a sum of weighted values of the function at specific points, the MSI (Ref. [35]) approximates the function through a weighted sum of local Taylor series. Indeed, the comparison between our extrapolation scheme and the MSI reveals that the main difference is that in the former approach the weighted sum of Taylor series is used to generate an approximation for a function in a domain which does not include the reference points, therefore we denote it an extrapolation scheme, whereas the MSI is routinely used for interpolation, i.e., to generate new data points within the range of known function values.

Thus, since the extrapolated points are determined as a direct product of the points for which derivative information is available, this restriction is crucial and is expected to be both the principal source of error and the key to a significant reduction in computational cost. If the mode-coupling expansion, on which all this is based, can be assumed good, we believe that it is also likely that our approach can provide cost-efficient approximations.

Although standard interpolation schemes, such as MSI, are effective in reducing the number of points needed for a satisfactory description of a given n-mode coupled PES, the scaling determined by the number of coupled degrees of freedom is not reduced. In some sense, derivative information in directions other than those of the particular MC term is discarded. It is specifically this information we try to exploit in the extrapolation part of our procedure.

In comparing our work to those of Yagi et al.[28–30] we note that the two approaches have somewhat different starting points. In fact, Yagi et al. aimed at generating a PES by using as few evaluation points as possible. This is accomplished through both a careful selection of the expansion points and the use of high-order Taylor expansions in order to ensure accuracy in a wider region of the PES. Our approach aims at a systematic way to improve the PES by using dense grids of evaluation points for the lower mode couplings, and a Shepard interpolation for the same mode-coupling potential terms does not require the use of high-order Taylor expansions.

Obviously not all the derivative information generated in the calculation of the lower mode-coupling terms is used in the extrapolation, see the discussion above. For the proposed

TABLE I. RMSE values (in cm^{-1}) for the fundamentals and overtone vibrational transition energies of water for (a) interpolation of the fully coupled PES (3MC) with natural splines and MSI for different values of p and (b) extrapolation of the fully coupled PES from the two-mode coupling terms with different values of the weight function parameter p, see Eq. (29).

	Interpolation		Extrapolation
Splines	14.58	$p=1$	2.11
$p=2$	25.88	$p=2$	2.03
$p=4$	1.75	$p=3$	1.96
$p=6$	1.63	$p=4$	2.09
$p=9$	1.65	$p=5$	2.24
$p=12$	1.65	$p=6$	2.34

procedure to be optimal, derivative information not used in the extrapolation step is conveniently used in a MSI as a way to obtain a finer grid of data for that same mode-coupling level.

The MSI will be investigated here as an alternative to other interpolation schemes such as the natural spline interpolation. The MSI scheme uses a weight function of the form

$$w_i(\vec{r}) = \frac{\|[\vec{r}]_i\|^{-2p}}{\sum_j \|[\vec{r}]_j\|^{-2p}}, \qquad (29)$$

where in Eq. (29) p is usually chosen of the order of $3N-6$.[29] The performance of the MSI (for different values of p) is compared with splines interpolation in Table I for the full PES of water (see Sec. IV). Clearly the MSI scheme is superior to natural spline interpolation for values of $p>2$, and a sufficiently high value of p is needed to obtain an accurate interpolation.

Needless to say, the comparison is not fair, since MSI needs derivative information which is not used in the spline interpolation. However, if such derivative information is available, the MSI scheme is superior to spline interpolation. Since this particular aspect has been illustrated several times in the literature, in the following we will exclusively focus on the extrapolation procedure.

One may wonder whether the choice of the exponent p in the definition of the weight function is also critical in the definition of the corresponding weight functions for extrapolation. As reported in Table I for the particular case of extrapolation of the three-mode coupling potential of water from the three two-mode coupling terms, the errors with respect to the full PES are rather insensitive on the actual value of p. For these reasons, we choose to use $p=1$ in the definition of the weight functions for the extrapolation step.

In passing we note that advanced procedures for an effective reduction in the number of evaluation points has been developed by Daves *et al.*[43] within the framework of interpolating moving least-squares approach.

III. IMPLEMENTATION

The first technical issue to address is the conversion from derivatives expressed in terms of Cartesian displacements (such as those obtained from DALTON quantum chemistry package) to derivatives in terms of normal coordinates. The task is easily accomplished through the orthogonal transformation $\mathbf{L}$, $\mathbf{Q}=\mathbf{L}\mathbf{D}^M$, where $\mathbf{D}^M=\mathbf{G}^{-1/2}\mathbf{D}$ is the mass-weighted displacement. $\mathbf{G}$ is a diagonal matrix which contains the inverse of the atomic masses and $\mathbf{D}$ is the $3N$ vector of Cartesian displacements. The $\mathbf{L}$ matrix diagonalizes the mass-weighted Hessian,

$$\mathbf{L}\mathbf{G}^{1/2}\mathbf{F}_D\mathbf{G}^{1/2} = \Lambda\mathbf{L}, \qquad (30)$$

where $F_D = \partial^2 V / \partial D_{P\alpha} \partial D_{Q\beta}$ is the Hessian in Cartesian coordinates.

The derivatives of $\mathbf{V}$ in terms of normal coordinates can be obtained from Cartesian derivatives as follows:

$$\partial_Q\mathbf{V} = (\partial_D\mathbf{V})\mathbf{G}^{1/2}\mathbf{L}^\dagger, \qquad (31)$$

$$\partial_Q^2\mathbf{V} = \mathbf{L}\mathbf{G}^{1/2}(\partial_D^2\mathbf{V})\mathbf{G}^{1/2}\mathbf{L}^\dagger. \qquad (32)$$

An arbitrary potential term, $\bar{V}^{\mathbf{m}_n}$, at $\vec{q}_n$ is expanded around $[\vec{q}_n]_i$ as a Taylor series of up to second order as follows:

$$\bar{V}^{\mathbf{m}_n}(\vec{q}_n) \approx ([\vec{q}_n]_i)^\dagger \cdot \vec{\nabla}\bar{V}^{\mathbf{m}_n}\big|_{\overline{[\vec{q}_n]_i}} + \frac{1}{2}([\vec{q}_n]_i)^\dagger \bar{\mathbf{H}}^{\mathbf{m}_n}(\overline{[\vec{q}_n]_i})$$
$$\times ([\vec{q}_n]_i), \qquad (33)$$

with $(\bar{\mathbf{H}}(\vec{x}_a)^{\mathbf{m}_n})_{ij} = (\partial^2\bar{V}^{\mathbf{m}_n}/\partial q_i \partial q_j)\big|_{\vec{x}_a}$, and where the $\vec{\nabla}\bar{V}^{\mathbf{m}_n}\big|_{\overline{[\vec{q}_n]_i}}$ and $\bar{\mathbf{H}}^{\mathbf{m}_n}(\overline{[\vec{q}_n]_i})$ are calculated from $\vec{\nabla}V\big|_{\overline{[\vec{q}_n]_i}}$ and $\mathbf{H}([\vec{q}_n]_i)$ in accord with Eq. (5).

Any electronic structure program providing first and second order derivatives of the electronic energy, $\partial_D\mathbf{V}$ and $\partial_D^2\mathbf{V}$, can be interfaced in a straightforward manner to MIDASCPP.[18] In this work DFT gradients and Hessians are obtained from the quantum chemistry package DALTON.[50] Once the derivative information is read by the program the above transformation is carried out. Note that a similar transformation can be applied to any molecular property for which derivative information is available. Therefore, the method outlined in the paper can be readily extended to the extrapolation of any molecular property surface using any electronic structure program.

IV. COMPUTATIONAL DETAILS

The method outlined above has been tested on the following set of 13 molecules: F_2O, Cl_2O, FNO, O_3, H_2S, ClNO, H_2O, MgH_2, H_2CO, cis-HNO_2, $SOCl_2$, HFCO, and CCl_2O. For each molecule semiglobal analytical representations of the PES have been generated for different levels of mode couplings. For the triatomic molecules the 3MC PES and PESs including one and two mode couplings have been obtained along with corresponding extrapolated PES; for the tetra-atomic species PESs including up to four-mode couplings have been generated. For a given n-mode coupled PES (n-MC hereafter), the extrapolation to the $(n+1)$-mode coupled PES produces two additional PESs: $n \rightarrow n+1(g)$, which uses the gradient only in the extrapolation step, and $n \rightarrow n+1(g,h)$ using both the gradient and the Hessian. All the electronic calculations have been performed with a local version of DALTON.[50]

TABLE II. H_2O FVCI vibrational transition energies for fundamental and overtone transitions for a selection of approximate PESs (see text). Results in units of cm^{-1} are given with respect to vibrational transition energy values obtained with the fully coupled potential. The last three columns report the RMSEs for fundamentals only, overtones only, and both types of transitions.

Scheme	ν_1	ν_2	ν_3	$2\nu_1$	$2\nu_2$	$2\nu_3$	RMSE(FUND)	RMSE(OVER)	RMSE
3	3704.8	3629.6	1572.1	7360.6	7153.2	3103.2			
$2\rightarrow3(g,h)$	0.7	−0.2	−1.5	1.9	0.9	−4.4	0.9	2.8	2.1
$2\rightarrow3(g)$	5.5	2.8	−2.0	9.1	12.2	−9.3	3.7	10.3	7.7
2	20.1	8.1	1.1	41.9	39.9	−5.1	12.5	33.5	25.3
$1\rightarrow2(g,h)$	−3.1	−0.1	1.0	−1.9	−15.0	−9.3	1.9	10.2	7.4
$1\rightarrow2(g)$	−110.1	−58.0	−68.5	−163.8	−174.8	−149.1	82.0	162.9	129.0
1	−288.6	−86.3	−51.5	−718.8	−198.1	−130.0	176.4	437.0	333.2

The calculations have been carried out in the framework of DFT with the B3LYP functional[51] and the cc-pVTZ (Refs. 52–54) basis set. The analytical representations of the PESs have been obtained using the following procedure. The DFT potential energy values have been evaluated on a coarse grid of points followed by an interpolation onto a finer-mesh grid. The interpolation step uses either MSI or multidimensional cubic splines. The potential energy values on this finer grid are finally fitted to a multivariate polynomial by means of a least-squares procedure.

The grid cutoffs in each of the normal coordinate directions are chosen according to the classical turning point corresponding to $v=8$ for the harmonic motion in that direction. For the triatomic molecules, the grid parameter generators for one-, two-, and three-mode couplings are 64_1, $32_{3/4}$, and $8_{3/4}$, respectively, where the number of points in each direction carries a subscript designating what fraction of the cutoff is to be used.[26] The set of parameters chosen for the tetra-atomic molecules is the following: 32_1, $16_{3/4}$, $8_{3/4}$, $8_{3/4}$, $8_{3/4}$.

For the tetra-atomic species considered in this paper couplings among up to four modes were explicitly calculated with DFT, requiring 26 113 single-point calculations (energy values and first and second order derivatives). All five mode couplings were estimated with the extrapolation procedure outlined above. The calculation of the three-mode coupled PES required a total of 745 and 1857 single-point calculations for the nonlinear triatomic molecules and for the linear

molecule MgH_2, respectively (MgH_2 requires more since the linear MgH_2 has four normal coordinates which also means that the 3MC potential is not the full potential unlike for the nonlinear triatomics). The MSI is used whenever derivative information is available, whereas for the extrapolated surfaces multidimensional natural cubic splines are used as interpolants. The set of finer grids were generated from the corresponding coarse grids by allowing 12, 10, 6, 2, and 2 subdivisions on each interval for the one-, two-, three-, four-, and five-dimensional grids, respectively. The least-squares fitting uses a direct product polynomial basis with a maximum total degree of 12 for the one-, two-, and three-dimensional surfaces. A decreased maximum polynomial degree of $n=8$ is used for the four- and five-dimensional surfaces.

All vibrational structure calculations use a primitive basis set consisting of 11 HO wave functions to expand each VSCF modal, whereas the 6 lowest modals for each mode are retained in the full-VCI (FVCI) calculations.

V. RESULTS AND DISCUSSION

The extrapolation scheme presented in this paper assumes a restricted-mode-coupling expansion for the PES, Eq. (3); derivative information is then used to approximate higher mode coupling in the same sequence. A hierarchial scheme can be constructed as follows. First an approximate PES is constructed by calculating all the potential energy

TABLE III. H_2CO FVCI vibrational transition energies for fundamental and overtones transitions for a selection of approximate PESs (see text). Results in units of cm^{-1} are given with respect to vibrational transition energy values obtained at the full four-mode coupling level. The last three columns report the RMSEs for fundamentals only, overtones only, and both types of transitions.

Scheme	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	$2\nu_1$	$2\nu_2$	$2\nu_3$	$2\nu_4$	$2\nu_5$	$2\nu_6$	RMSE(FUND)	RMSE(OVER)	RMSE
$4\rightarrow5(g,h)$	2686.4	2728.1	1796.0	1500.4	1242.2	1170.1	5468.2	5363.6	3572.9	3000.3	2479.5	2333.7			
$4\rightarrow5(g)$	2686.3	2728.1	1796.0	1500.4	1242.2	1170.1	5468.2	5363.4	3572.8	3000.2	2479.5	2333.6			
4	2687.0	2728.1	1796.0	1500.3	1242.1	1170.1	5468.2	5361.5	3572.8	3000.1	2479.3	2333.5			
$3\rightarrow4(g,h)$	3.8	−0.3	−0.1	−0.0	−0.1	−0.0	−0.4	−5.5	−0.2	−0.0	−0.3	−0.1	1.5	2.2	1.9
$3\rightarrow4(g)$	1.1	−0.9	−0.2	−0.2	−0.2	0.0	−1.7	−4.7	−0.4	−0.5	−0.2	0.4	0.6	2.1	1.5
3	18.6	−0.6	−0.0	0.1	−0.1	0.0	−0.9	−21.9	−0.0	0.1	−1.3	0.5	7.6	9.0	8.3
$2\rightarrow3(g,h)$	18.7	0.8	−0.0	0.4	0.2	0.2	1.1	−16.6	0.1	0.8	−0.9	0.4	7.7	6.8	7.3
$2\rightarrow3(g)$	30.2	7.6	1.1	3.0	3.1	1.0	20.9	11.1	2.1	6.0	3.9	−0.6	12.9	10.1	11.6
2	−21.0	13.5	−0.7	1.4	0.8	2.4	212.4	−79.6	−1.8	4.1	0.2	0.5	10.2	92.6	65.9
$1\rightarrow2(g,h)$	−41.4	8.1	−0.7	0.6	−0.5	1.7	20.2	31.4	−2.0	2.3	−4.5	−3.8	17.2	15.5	16.4
$1\rightarrow2(g)$	−188.8	−75.6	−10.9	−36.4	−43.0	−57.8	−210.1	−205.1	−24.6	−73.0	−91.4	−122.7	89.4	138.8	116.8
1	−316.6	−84.7	−10.3	−36.6	−35.5	−46.7	−612.3	−202.5	−23.5	−74.6	−85.0	−122.7	136.8	271.4	214.9

TABLE IV. RMSEs for the set of molecules considered in the present study. Units are cm^{-1}.

Scheme	Triatomic		Tetra-atomic	
	Fund.	Overt.	Fund.	Overt.
$3 \rightarrow 4(g,h)$			0.7	1.5
$3 \rightarrow 4(g)$			0.4	1.6
3			5.8	12.7
$2 \rightarrow 3(g,h)$	0.4	1.0	8.0	10.5
$2 \rightarrow 3(g)$	1.5	4.2	12.6	30.0
2	4.8	13.0	11.9	53.2
$1 \rightarrow 2(g,h)$	1.6	6.3	11.1	30.5
$1 \rightarrow 2(g)$	36.5	73.2	60.9	107.7
1	73.7	180.6	72.1	151.2

terms corresponding to a preselected MCR, see Eq. (7). Since each potential term in the summation over the MCs is evaluated on a grid of points, this defines a corresponding set of electronic structure calculations, providing energy values and first- and second-order derivatives. If n is the maximum MC level included in the expansion of the potential, the procedure outlined above is then used to approximate all potential energy terms corresponding to the $(n+1)$ MC level. Approximations can be constructed using only gradient data (g) or both gradients and the Hessian data (g,h). Thus the restricted-MC hierarchy of approximations investigated here consists of 1, $1 \rightarrow 2(g)$, $1 \rightarrow 2(g,h)$, 2, $2 \rightarrow 3(g)$, $2 \rightarrow 3(g,h)$, 3 for the three-atomic systems. For the systems with more degrees of freedom we consider a similar hierarchy up to the full four-mode couplings while the five-mode coupling terms of the potential are only approximated by extrapolation. For each of the molecular systems investigated, each PES in the above sequences is then used in a FVCI calculation providing fundamental and overtone transitions. A comparison is then made with vibrational energy levels computed with the more accurate PES obtained at the DFT level, i.e., the three-

mode coupled potential for the three-atomic systems and the four-mode coupled PES for the tetra-atomic species. In doing so one obtains both an estimate of the error made when truncating the restricted-mode-coupling expansion of the PES at a given MC level and a measure of the accuracy of the extrapolation procedure. Results for water and formaldehyde, where the largest variations are seen for the full set of molecules investigated, are reported in Tables II and III, respectively, whereas Table IV and Figs. 4 and 5 summarize the results for the full set of molecules investigated. Data in tabular forms for every molecule investigated are included as Supplementary Material.[55]

We would like to stress the fact that although the DFT/cc-pVTZ methodology is certainly not the method of choice for the construction of PESs of spectroscopic accuracy, this PES is expected to retain the anharmonic character and thus serve to test the performance of the extrapolation scheme. We consider the grids of evaluation points large enough for the tests to exhibit the consequence of the extrapolation which is our main concern. It is another issue whether such large grids are really needed in practical calculations. Moreover, we have chosen to test the proposed methodology on a rather large set of small molecules with the aim of producing a statistical distribution of errors, as opposed to validating the scheme based on a more accurate calculation for a single system.

Table II reports fundamentals and overtone vibrational transition energies of H_2O for the hierarchy of PESs discussed above. In Table II the root mean square errors (RMSEs) for all the vibrational transitions, and separately for fundamentals, and overtones are reported.

Vibrational transition energies obtained by neglecting all mode couplings (labeled as "1") show errors as large as 300 cm^{-1} for some transitions. The well-known limitations of the uncoupled anharmonic oscillator description of the vibrational dynamics are thus clearly seen. The maximum error is reduced to less than 200 cm^{-1} when gradient infor-
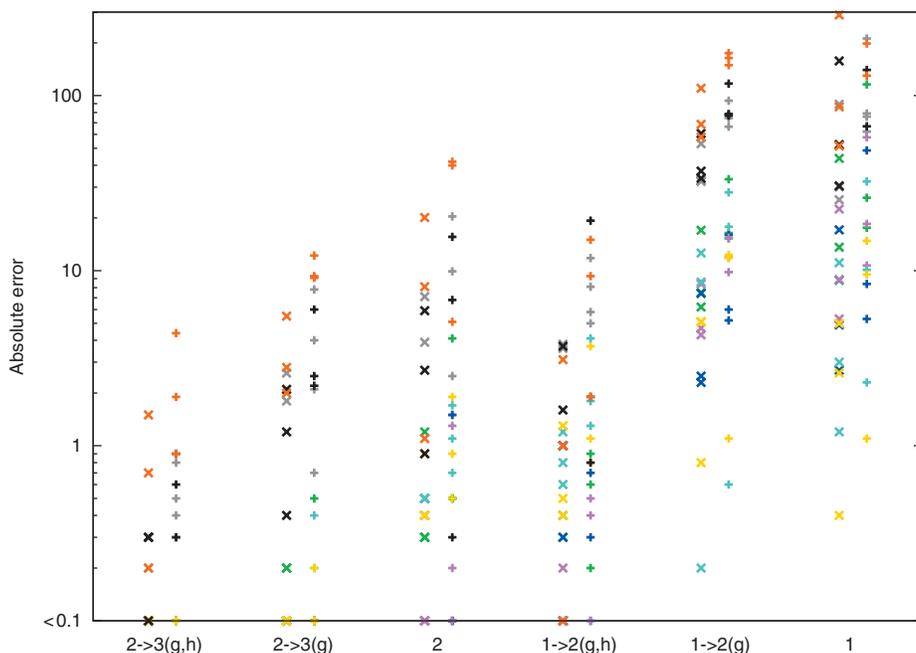

FIG. 4. (Color) Absolute errors for fundamental (x) and overtone (+) vibrations for the triatomic molecules investigated (MgH_2 in gray, O_3 in green, Cl_2O in blue, F_2O in pink, ClNO in cyan, FNO in yellow, H_2S in black, and H_2O in orange) as a function of the approximation used for the representation of the molecular PESs. Units are cm^{-1}.
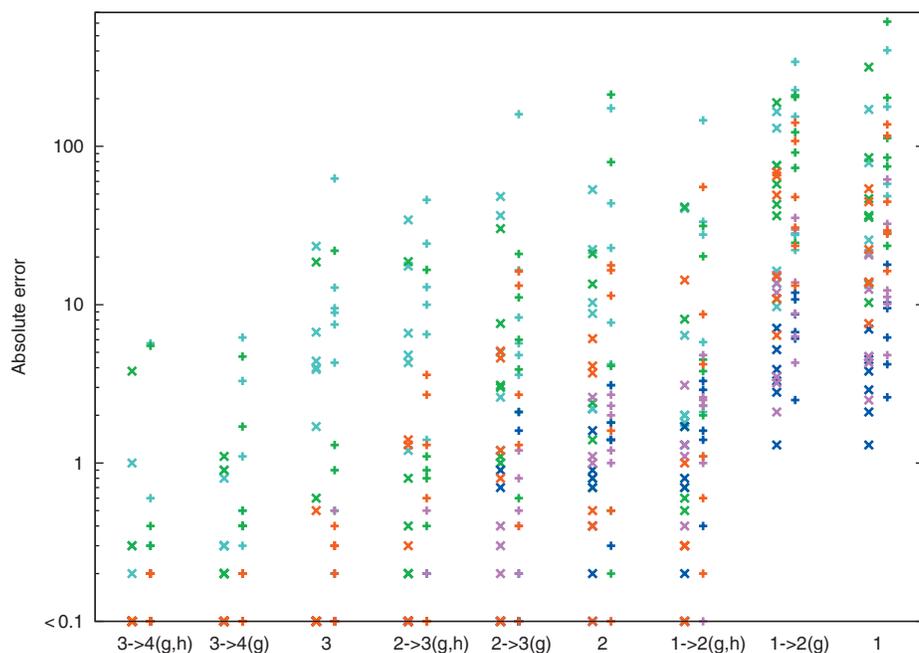
FIG. 5. (Color) Absolute errors for fundamental (x) and overtone (+) vibrations for the tetra-atomic molecules investigated (HNO_2 in cyan, H_2CO in green, CCl_2O in pink, $SOCl_2$ in blue, and HFCO in red) as a function of the approximation used for the representation of the molecular PESs. Units are cm^{-1}.

mation is used to extrapolate the two-mode coupling terms in the potential ($1 \rightarrow 2(g)$). Although the accuracy is improved from the case of uncoupled oscillators, it is still far from being adequate. The errors are instead drastically reduced if the second derivatives are used in the extrapolation: the maximum error is reduced to less than 20 cm^{-1}. It is worth to note that the accuracy obtained by using the ($1 \rightarrow 2(g, h)$) PES is remarkably higher than that corresponding to the PES with full account of the two-mode couplings. This situation is of course fortuitous but, as we shall see, rather typical for the systems studied here.

To explain the rather significant difference in accuracy between the $1 \rightarrow 2(g)$ and $1 \rightarrow 2(g, h)$ approximations to the two-mode coupling terms, we note that the inclusion of second order derivatives usually provides a bounded PES as opposed to physically unbounded situations that are sometimes encountered with a linear extrapolation. In more accurate terms, a quadratic extrapolation is needed for a correct description of important anharmonic terms such as $q_1^2 q_2^2$ (see Sec. II E).

By comparing the results for the $2 \rightarrow 3(g)$ and $2 \rightarrow 3(g, h)$ approximations with the results obtained at the two-mode coupling level, we note also an increased accuracy for the vibrational transition energy considered: the RMSE is reduced by several factors for both the fundamental and the overtone transitions. The extrapolation of the three-mode coupling potential terms from the corresponding two-mode couplings by using both gradient and Hessian data, ($2 \rightarrow 3(g, h)$), leads to a rather accurate PES, whose maximum error for the vibrational transition energies considered amounts to 4.4 cm^{-1}, as compared to a value of 41.9 cm^{-1} found when using a maximum mode-coupling level of two in the expansion of the potential. It is worth to note that already the sole inclusion of the gradient in the extrapolation of the three-mode coupling terms provides a reasonable accuracy. This is rather promising in view of the low computational cost involved in the calculation of energy first derivatives.

Vibrational transition energies for formaldehyde are reported in Table III. Inspection of the data reveals a trend similar to that encountered for water. The RMSE for the vibrational transition energies is reduced at the $1 \rightarrow 2(g)$ level of approximation compared to the uncoupled anharmonic approximation, but the accuracy is clearly not satisfactory. Inclusion of the second order derivatives in the extrapolation of the two-mode coupling terms [$1 \rightarrow 2(g, h)$ entry in the table] greatly improves the accuracy of the results, while the use of derivative information to extrapolate the three-mode coupling terms does not lead to a consistent improvement of the results for fundamental transitions, where the RMSE is only slightly reduced due to better estimation of some transitions but worse estimation of others compared to the results obtained by using the two-mode coupling approximation. The accuracy is, however, significantly improved for the asymmetric CH stretch fundamental and the symmetric CH stretch overtone (ν_1 and $2\nu_2$), which are affected by rather large errors at the two-mode coupling level due to high coupling between these two states. For these two most difficult states, it is found that the wave function is subject to some mixing of configurations due to resonance interaction with nearby combination bands. Clearly, in the case of such resonances differences in the PES can easily alter the resonance interaction and thus explain why such states are particularly sensitive. The $2 \rightarrow 3(g, h)$ approximation to the PES is characterized by a similar accuracy to the PES with the explicit inclusion of three-mode couplings (entry 3 in Table III). The neglect of the higher mode-coupling terms at the 3MC level significantly affects the accuracy of the CH-stretching transitions for fundamentals and overtone levels, while the extrapolation of the four-mode coupling terms is seen to improve the accuracy, the largest errors being within a few cm^{-1} as compared to a full 4MC calculation. The importance of the five mode-coupling terms in the potential is rather small for all fundamental and overtone transitions, the results differing by less than 0.3 cm^{-1} with re-

spect to the results obtained with a maximum mode-coupling level of 4, except for the two most difficult transitions ν_1 and $2\nu_2$ with differences of 0.6 and 2.1 cm^{-1}, respectively.

The distributions of the absolute errors (logarithmic scale) for fundamental and overtone vibrational excitation energies for the three-atomic and four-atomic systems considered are plotted in Figs. 4 and 5, respectively.

In going through the sequence of approximate PESs used for the three-atomic systems (see Fig. 4), one notices a consistent increase in accuracy. Worth to note is the fact that the maximum error is progressively reduced by an order of magnitude or more for both fundamentals and overtones whenever the second derivatives are included in the extrapolation scheme. Vibrational transition energies obtained by using the $2 \rightarrow 3(g,h)$ approximate PES are characterized by absolute errors that are lower than 0.1 cm^{-1} for all three-atomic molecules except for H_2O, MgH_2, and H_2S, for which the maximum absolute error is lower than 10 cm^{-1}. Furthermore, with the exception of water, the maximum error is less than 1 cm^{-1}.

A similar situation is also encountered in the case of tetra-atomic molecules investigated (see Fig. 5) where the reduction in the maximum error is also encountered, although the effects are not so marked as before. Yet in all cases the accuracy of the results is significantly improved in going from a PES with a maximum mode-coupling level of n to the one with extrapolated $(n+1)$ mode couplings. The $3 \rightarrow 4(g,h)$ PES provides vibrational excitation energies with a maximum error of less than 1 cm^{-1} with the exception of three vibrational states for HNO_2 and H_2CO.

Overall the description of the vibrational dynamics is clearly improved by the use of derivative information for the extrapolation of the $(n+1)$-mode couplings with respect to the n-mode coupled PES. The use of only gradients provides a computationally cheap and sometimes reasonably accurate estimation of mode-mode couplings, while a rather high accuracy is obtained with the inclusion of second order derivatives in the extrapolation.

The results obtained suggest that the extrapolated surfaces give in many instances results that are more accurate than those obtained with the explicit calculation of the mode-coupling terms. Although of course this finding is to be regarded to some extent fortuitous, the significance of this fact must not be overlooked. Thus, the results presented here suggest that the explicit calculation of the two-mode coupling terms does not really pay off in terms of higher accuracy compared to the $1 \rightarrow 2(g,h)$ approximation. A similar remark applies to the comparison of the $2 \rightarrow 3(g,h)$ and 3 approximations in the case of the four-atomic systems investigated. Although these remarks may not be of general validity, there are sound indications that the $n \rightarrow n+1(g,h)$ extrapolation scheme is quite competitive. On the negative side, it also makes the outlined hierarchy less hierarchial in terms of accuracy, in the sense that proceeding from $n \rightarrow n+1(g,h)$ to the more expensive full $n+1$ grid method increases the cost but not necessarily the accuracy.

VI. SUMMARY AND OUTLOOK

In this work we have developed and tested an approximate methodology for the generation of BO potential energy and molecular property surfaces. The formulation of the method is general and requires the availability of derivative information in addition to potential energy/molecular property values. The basic ingredients of the methods are (i) a restricted-mode-coupling expansion for the potential energy/molecular property surface, up to a maximum mode-coupling level n, in the potential, and (ii) the availability of derivative information which is used to extrapolate potential energy terms for mode-coupling levels $m > n$.

The formulation, which is a variant of the popular MSI, is general for any extrapolation of $(n+p)$-mode coupling terms from n-mode couplings and can be applied to both the energy and any other molecular property surface for which derivative information is available. The method depends only on analytical parameter-free weight factors that satisfy important limiting conditions and control the contribution from each direction of extrapolation. The proposed method is optimal in the sense that all derivative information not used in the extrapolation step is used in a MSI approach for the interpolation of the n and lower mode couplings.

The procedure has been applied to a representative set of 13 molecules, and its accuracy has been tested for the use of gradient only and both gradient and Hessian data. A first order expansion gives comparatively good results, relative to complete neglect, for the extrapolation of the highest mode coupling, at very low additional cost. A second order Taylor expansion always gives a substantial improvement of the results compared to the linear extrapolation, giving an accuracy comparable to the full calculation. Even though the computation of second derivatives requires additional cost compared to the calculation of only energies and gradients, the full cost of the extrapolation procedure using second derivatives to extrapolate from a mode-coupling level of n to the $n+1$ level represents still a major reduction compared to that required for a full $n+1$-dimensional grid calculation.

The increasing availability of analytical methods for evaluating first and second derivatives of energies with respect to geometrical distortions will have a significant impact on the methodologies for PES construction. This is already apparent in the recent literature and is substantiated in the present study: the use of derivative information to extrapolate the higher mode-coupling terms of the potential is always worth the price. Thus, the procedures can be used to obtain higher accuracy including mode couplings which otherwise would be prohibitive. In a similar spirit, it allows potentially the use of fewer individual points per mode in average and thereby access to larger systems. It is also anticipated that the methodology can be useful in designing efficient calculations for vibrational contributions to molecule properties where one can speculate that only a few one-mode displacements are needed for the property surface.[56,57] This would be important for explicit anharmonic wave function calculations of such corrections to become closer in efficiency to the Bishop–Kirtman perturbative approach[58–60] that requires only low-order Taylor expansions

at the minimum. Although the extrapolation procedure has been validated for the particular case of vibrational structure calculations, one can hope that similar procedures will be useful in other areas of molecular dynamics. However, careful testing is required as more global features of the PES may be important as compared to the vibrational wave function case.

In future work we will consider the extension of the procedure to the extrapolation of molecular property surfaces and the application of the proposed scheme for a cost-efficient construction of highly accurate PESs for small- and medium-size systems.

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APPENDIX: DERIVATION OF THE FORMULATION FOR GENERAL EXTRAPOLATION

We consider the general case of an n-dimensional function f at the point $\vec{r}=(r_1,\ldots,r_n)$ extrapolated from $\binom{n}{n-p}$ subdomains of dimension $n-p$ (thus we are extrapolating p coordinates). To calculate the extrapolated value we need the value of the function and its derivatives at the points $\{[\vec{r}]_{i_1\ldots i_p}\}_{i_1<\cdots<i_p=1,\ldots,p}$,

$$\tilde{f}^{(n-p)}(\vec{r}) = \sum_{i_1<\cdots<i_p} w_{i_1\cdots i_p}(\vec{r}) f_{i_1\cdots i_p}(\vec{r}), \tag{A1}$$

where the Taylor series of order q reads

$$f_{i_1\cdots i_p}(\vec{r}) = \sum_{j=0}^{j=q} \left[\frac{1}{j!} (([\vec{r}]_{i_1\cdots i_p}) \cdot \vec{\nabla}_{\vec{x}})^j f(\vec{x}) \right]_{[\vec{r}]_{i_1\cdots i_p}}, \tag{A2}$$

and the weight functions, $\{w_{i_1\cdots i_p}(\vec{r})\}_{i_1<\cdots<i_p}$, are required to fulfill the following properties:

$$\sum_{i_1<\cdots<i_p} w_{i_1\cdots i_p}(\vec{r}) = 1, \tag{A3}$$

$$\lim_{r_{i_1},\ldots,r_{i_p}\to 0} w_{i_1\cdots i_p}(\vec{r}) = 1, \tag{A4}$$

$$\lim_{r_k\to 0} w_{i_1\cdots i_p}(\vec{r}) = 0, \quad \forall\, k \notin \{i_1\cdots i_p\}, \tag{A5}$$

$$\lim_{r_k\to\infty} w_{i_1\ldots i_p}(\vec{r}) = 0, \quad \forall\, k \in \{i_1,\ldots,i_p\}, \tag{A6}$$

other $r_j \,\forall\, j \neq k$ are finite,

$$w_{i_1\cdots i_p}([\vec{a}]_{j_1\cdots j_p}) = \delta_{i_1 j_1}\cdots \delta_{i_p j_p}, \tag{A7}$$

where $[\vec{a}]_{j_1\ldots j_p}$ is any of the points chosen to expand the Taylor Series and Eq. (A7) is implied by Eqs. (A3)–(A5).

The following weight functions fulfill these conditions:

$$w_{i_1\cdots i_p}(\vec{r}) = \frac{\prod_{k=i_1,\ldots,i_p} \frac{1}{r_k^2}}{\sum_{j_1<\cdots<j_p} \prod_{k=j_1,\ldots,j_p} \frac{1}{r_k^2}}$$

$$= \frac{\prod_{k\neq i_1,\ldots,i_p} r_k^2}{\sum_{j_1<\cdots<j_p} \prod_{k\neq j_1,\ldots,j_p} r_k^2}. \tag{A8}$$

The derivatives of the weight functions with respect to r_l are as follows:

$$\frac{\partial w_{i_1\cdots i_p}(\vec{r})}{\partial r_l} = \frac{2 w_{i_1\cdots i_p}(\vec{r})}{r_l}$$
$$\times \left(\sum_{i_1<\cdots<l<\cdots<i_p} w_{i_1\cdots l\cdots i_p}(\vec{r}) - \sum_{q=1}^{p} \delta_{i_q l} \right). \tag{A9}$$

Likewise, the second derivative reads:

$$\frac{\partial^2 w_{i_1\ldots i_p}(\vec{r})}{\partial r_l \partial r_m} = \frac{2}{r_l}\left(\frac{\partial w_{i_1\cdots i_p}(\vec{r})}{\partial r_m} \right)$$
$$\times \left(\sum_{i_1<\cdots<l<\cdots<i_p} w_{i_1\cdots l\cdots i_p}(\vec{r}) - \sum_{q=1}^{p} \delta_{i_q l} \right)$$
$$- \frac{2\delta_{lm} w_{i_1\cdots i_p}(\vec{r})}{r_l^2}\left(\sum_{i_1<\cdots<l<\cdots<i_p} w_{i_1\cdots l\cdots i_p}(\vec{r}) \right.$$
$$\left. - \sum_{q=1}^{p} \delta_{i_q l} \right) + \frac{2 w_{i_1\cdots i_p}(\vec{r})}{r_l}\left(\frac{\partial w_{i_1\cdots l\cdots i_p}(\vec{r})}{\partial r_m} \right), \tag{A10}$$

which for each of the expansion points associated with one of the Taylor series used to approximate f, $[\vec{r}_a]_{j_1\cdots j_p}$, gives

$$\left.\frac{\partial w_{i_1\cdots i_p}(\vec{r})}{\partial r_l}\right|_{[\vec{r}_a]_{j_1\cdots j_p}} = -\frac{2}{a_l}(\delta_{i_1 j_1}\cdots\delta_{i_p j_p})\left(\sum_{i_1<\cdots<l<\cdots<i_p} \delta_{i_1 j_1}\cdots\delta_{l j_k}\cdots\delta_{i_p j_p} - \sum_{q=1}^{p}\delta_{i_q l} \right) = 0, \tag{A11}$$

$$\left.\frac{\partial^2 w_{i_1\cdots i_p}(\vec{r})}{\partial r_l \partial r_m}\right|_{[\vec{r}_a]_{j_1\cdots j_p}} = -\frac{2}{a_l^2}(\delta_{i_1 j_1}\cdots\delta_{i_p j_p})\left(\sum_{i_1<\cdots<l<\cdots<i_p} \delta_{i_1 j_1}\cdots\delta_{l j_k}\cdots\delta_{i_p j_p} - \sum_{q=1}^{p}\delta_{i_q l} \right) = 0. \tag{A12}$$

One may similarly prove that the extrapolated function takes the values of the derivatives of the full potential at the expansion points,

$$\left.\frac{\partial \widetilde{f}(\vec{r})}{\partial r_l}\right|_{[\vec{r}_a]_{j_1\cdots j_p}} = \sum_{i_1<\cdots<i_p} w_{i_1\cdots i_p}(\vec{r})\left.\frac{\partial f_{i_1\cdots i_p}(\vec{r})}{\partial r_l}\right|_{[\vec{r}_a]_{j_1\cdots j_p}} + \sum_{i_1<\cdots<i_p} f_{i_1\cdots i_p}(\vec{r})\left.\frac{\partial w_{i_1\cdots i_p}(\vec{r})}{\partial r_l}\right|_{[\vec{r}_a]_{j_1\cdots j_p}}$$

$$= \left.\frac{\partial f_{j_1\cdots j_p}(\vec{r})}{\partial r_l}\right|_{[\vec{r}_a]_{j_1\cdots j_p}} = \left.\frac{\partial f(\vec{r})}{\partial r_l}\right|_{[\vec{r}_a]_{j_1\cdots j_p}}, \tag{A13}$$

$$\left.\frac{\partial^2 \widetilde{f}(\vec{r})}{\partial r_m\,\partial r_l}\right|_{[\vec{r}_a]_{j_1\cdots j_p}} = \sum_{i_1<\cdots<i_p} w_{i_1\cdots i_p}(\vec{r})\left.\frac{\partial^2 f_{i_1\cdots i_p}(\vec{r})}{\partial r_l\,\partial r_m}\right|_{[\vec{r}_a]_{j_1\cdots j_p}} + \sum_{i_1<\cdots<i_p} f_{i_1\cdots i_p}(\vec{r})\left.\frac{\partial^2 w_{i_1\cdots i_p}(\vec{r})}{\partial r_l\,\partial r_m}\right|_{[\vec{r}_a]_{j_1\cdots j_p}}$$

$$+ \sum_{i_1<\cdots<i_p} \frac{\partial f_{i_1\cdots i_p}(\vec{r})}{\partial r_m}\left.\frac{\partial w_{i_1\cdots i_p}(\vec{r})}{\partial r_l}\right|_{[\vec{r}_a]_{j_1\cdots j_p}} + \sum_{i_1<\cdots<i_p} \frac{\partial f_{i_1\cdots i_p}(\vec{r})}{\partial r_l}\left.\frac{\partial w_{i_1\cdots i_p}(\vec{r})}{\partial r_m}\right|_{[\vec{r}_a]_{j_1\cdots j_p}}$$

$$= \left.\frac{\partial^2 f_{j_1\cdots j_p}(\vec{r})}{\partial r_m\,\partial r_l}\right|_{[\vec{r}_a]_{j_1\cdots j_p}} = \left.\frac{\partial^2 f(\vec{r})}{\partial r_m\,\partial r_l}\right|_{[\vec{r}_a]_{j_1\cdots j_p}}. \tag{A14}$$

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