Parameterized Bases for Calculating Vibrational Spectra Directly from ab Initio Data Using Rectangular Collocation

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ABSTRACT: We compared different parametrized bases for computing anharmonic vibrational spectra using a new version of the rectangular collocation-optimization method of Manzhos and Carrington (*Can. J. Chem.* **2009**, *87*, 864; *Chem. Phys. Lett.* **2011**, *511*, 434). The method enables one to compute a small number of vibrational levels with an ultrasmall basis set without a potential function. To test the ideas, parametrized uncoupled and coupled Gaussian functions as well as direct-product and coupled Hermite basis sets are used to compute four low-lying vibrational energy levels of H_2O on model harmonic and anharmonic uncoupled (polynomial) potential energy surfaces. In addition, we compute levels directly from ab initio points and thereby include all coupling and anharmonicity. We conclude that uncoupled parametrized Gaussian and Hermite functions are a good choice for anharmonic and coupled problems.

1. INTRODUCTION

Vibrational spectroscopy plays an important role in species identification in atmospheric and interstellar media as well as in the condensed phase and at surfaces and interfaces.[1−3] To identify species and also to assign spectra, it is often necessary to be able to compute an accurate vibrational spectrum. In many cases, it is essential that anharmonicity and coupling be included in the calculation. This may be done using perturbation theory[4,5] or collocation,[6,7] VSCF (vibrational self-consistent field),[8,9] and variational methods.[10,11] Perturbation theory is most useful in the absence of resonances and when anharmonicity and coupling are weak. It may, for example, work poorly when bonds are weakened due to interactions with a substrate. The VSCF approximation is severe because it assumes that each wave function is a Hartree product. Collocation and variational approaches are the only systematic and general means of computing spectra that include the effects of coupling and anharmonicity.

Computing spectra of isolated molecules is challenging, but the difficulty is compounded for molecules on a substrate because the configuration space is augmented by the frustrated translational and rotational degrees of freedom. In addition, potential energy surfaces (PES) are nonexistent today for most molecule-surface systems. Available PESs for small molecules are often not very accurate, owing to the difficulty of doing quantum chemistry calculations on surfaces.[12−19] There exist only a handful of calculations of vibrational spectra of adsorbates taking into account anharmonicity and coupling.[20−25] Although calculations show that effects of anharmonicity and coupling are strong enough to influence species assignment,[24−27] theoretical studies of reactions at surfaces rely almost exclusively on the harmonic analysis.[28−31]

In principle, it is possible to use variational and collocation methods, for a molecule on a surface and for an isolated molecule, without a PES, by solving the electronic Schrödinger equation at each collocation or quadrature point. In practice, this is not feasible because the number of points is too large. The number of points is large, in part because the basis used to represent the wave functions is large. Of course, using a large basis also makes the matrix eigenvalue problem costly to solve. One way to decrease the number of required basis functions is to use as basis functions eigenfunctions of reduced[32−34] dimension Hamiltonians.[35−45] Another option is to start with a direct product basis set and discard functions.[46−54] This makes it possible to reduce the number of quadrature or collocation points by orders of magnitude.[55−57] In this paper, we develop a third approach with flexible, parametrized, multivariate basis functions but determine energies by minimizing a residual rather than solving an eigenvalue problem.

Manzhos and Carrington (MC) proposed a collocation-type method using a small, parametrized, flexible basis set.[59−62] By optimizing the basis parameters, it is possible to compute accurate energy levels from a very small basis. However, it is necessary to use more collocation points than basis functions, and one is therefore required to use a rectangular collocation method.[60] However, energies are not solutions of a rectangular eigenvalue problem. Rather, optimization of the energies and basis parameters is intertwined with the solution of the rectangular eigenvalue problem, and the parameters are adjusted until good solutions of the Schrödinger equation are obtained. That is, rather than finding energies E and wave functions $\psi = \sum_{i=1}^{N} c_i \phi_i$ from an eigen-decomposition of a large Hamiltonian matrix $\hat{H}$, wave function coefficients are found by minimizing $\|\hat{H}\vec{\psi} - E\vec{\psi}\|$ at a set of points in configuration space, and the energy and basis are iteratively optimized (see section 2). In ref 59, the method was applied to model problems of different

dimensions (up to six). In ref 61, it was applied to compute the first several vibrational states of the water molecule on a high-quality PES[62] using an exact kinetic energy operator (KEO).[63] For a small number of levels, an accuracy of better than 1 cm^{-1} was achieved with as few as 15 basis functions[61] and with a small number of potential points ($\sim 10^3$). If a similarly small number of points is required for other molecules, it will be possible to compute a spectrum and wave functions directly from ab initio data, bypassing the PES construction, which in itself can be daunting.[13,64-67]

A small basis has many advantages. It obviously facilitates calculation of the spectrum. In addition, if wave functions are linear combinations of only a small number of basis functions, the cost of any calculation which requires integrals of wave functions, e.g., intensities,[68] Franck−Condon factors, rates of nonradiative transitions,[69-72] etc., is reduced.

Owing to the advantages of a small basis set, there are many basis optimization approaches. In electronic structure theory, plane wave basis functions can be optimized by varying the definition of the coordinate;[73-76] optimization of the basis also improves the description of electron correlation.[77] Neural networks provide a flexible means of representing orbitals[78] and wave functions.[79,80]

In all previous applications of the MC method,[26,59-61,81] Gaussian functions of the form

$$\phi_i(\vec{Q}) = \prod_{j=1}^{d} \frac{b_{ij}}{\sqrt{\pi}} \exp(-b_{ij}^2(w_{ij} - Q_j)^2) \tag{1}$$

were used. Gaussian basis functions have been used in the study of nuclear dynamics for many years.[82-90] They are easily parametrized and localized, but their most important advantage is simplicity. This is especially important if one uses a variational method and therefore needs to compute matrix elements of the Hamiltonian between two basis functions. There are simple analytic expressions for derivatives of Gaussians (see eq 9). Because it uses a collocation approach, the MC method can be used with other basis functions. In this paper, we apply the MC approach with non-Gaussian basis functions. There is reason to believe that the Gaussian choice is not the best. Each of the Gaussian functions of eq 1 is a product of functions of a single coordinate. They have no information about coupling. In a real sense, Gaussians are less localized in many dimensions than in few. In 1D, about 68% of equally spaced quadrature points are in a region within a standard deviation of the mean. In 6D, it is only about 10%.[91] The purpose of the paper is to present a version of the MC algorithm that works with any user-defined parametrized basis set and to compare the performance of several classes of parametrized functions. To use general basis functions, it is necessary to do finite difference derivatives when applying the kinetic energy operator, but this is easily done. Using only Gaussian functions with the MC method is unnecessarily restrictive. We test two types of basis functions: Gaussians whose argument is not a sum of functions of a single variable and products of harmonic oscillator functions whose arguments are parametrized functions of a single or several coordinates. The Gaussians are nonproduct, i.e., coupled, functions. The harmonic oscillator functions are uncoupled but physically motivated. To the best of our knowledge, there are no previous studies using parametrized basis functions of these types.

The paper is organized as follows: In section 2, the rectangular collocation method is briefly reviewed, and the new ideas required to use general basis functions are introduced. In section 3, we present and discuss the results of computing vibrational frequencies of H_2O on model harmonic and uncoupled anharmonic surfaces and directly from ab initio points. Section 4 concludes.

2. THE MC METHOD: COMPUTING A SPECTRUM VIA OPTIMIZATION AND RECTANGULAR COLLOCATION

In the method of Manzhos and co-workers,[26,59-61,81] vibrational wave functions depending on the d components of $\vec{x}$ are expanded over a set of parametrized functions $\phi_i(\vec{x}|\vec{\lambda}_i)$, where $\vec{\lambda}_i$ is a vector of parameters:

$$\psi(\vec{x}) = \sum_{i=1}^{N} c_i \phi_i(\vec{x}|\vec{\lambda}_i) \tag{2}$$

Implementation of the idea is easier for a simple KEO. In this paper, we use normal coordinates and neglect all cross terms in the KEO

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^{d} \frac{\partial^2}{\partial Q_i^2} \tag{3}$$

In many cases, the cross terms are small.[9,92-94] For isolated molecules, they are typically about as large as rotational constants.[95] When the KEO is simple, implementation is easy regardless of the size of the system. This approach was recently used to compute levels of H_2O on Pt(111).[26] The MC method is well suited for molecule−substrate systems where often only a few levels are probed and a typical experimental accuracy[28,96] of ≥ 1 cm^{-1} is achievable.

In the MC method, a set of wave functions and energies is found that nearly satisfy the Schrödinger equation at a set of points $\{^j\vec{x}\}$, $j = 1, ..., M$, $M > N$:

$$\hat{T}\psi(^j\vec{x}) + V(^j\vec{x})\,\psi(^j\vec{x}) = E\psi(^j\vec{x}) \tag{4}$$

where $\hat{T}$ is the KEO and V is the PES. Upon substituting eq 3 into eq 4, a rectangular collocation matrix equation is obtained:

$$(\hat{M} - E\hat{S})\vec{c} = 0 \tag{5}$$

where

$$S_{ji} = \phi_i(^j\vec{x}|\vec{\lambda}_i)$$
$$M_{ji} = \Gamma_{ji}S_{ji} + V_j S_{ji} \tag{6}$$

Here, $V_j = V(^j\vec{x})$ and $\Gamma_{ji} = \hat{T}\,\phi_i(^j\vec{x}|\vec{\lambda}_i)$. Parameterization makes it possible to obtain accurate solutions with small basis sets (small N). However, $M > N$ potential points are required to determine the parameters, and consequently, the matrix (eq 5) is rectangular.[59,60] Parameters $\vec{\lambda}_i$ and energies E_k are adjusted (in this case using the SQP algorithm[97] with 300 steps) until a good fit to the Schrödinger equation is obtained. This is done by minimizing R^2, where

$$R = \frac{1}{L} \sum_{k=1}^{L} \frac{\|(\hat{M} - E_k\hat{S})\vec{c}_k\|}{E_k \|\hat{S}\vec{c}_k\|} \tag{7}$$

and k indexes the vibrational levels of interest. For each $\{\vec{\lambda}_i\}$, E_k, the coefficients $\vec{c}_k$ are elements of the eigen-vector of the matrix $(\hat{M} - E_k\hat{S})^H(\hat{M} - E_k\hat{S})$ corresponding to the smallest eigenvalue.[60,98] Here, the superscript H stands for the Hermitian conjugate. The energy is a fitting parameter which is allowed to

vary in the range $E_{\text{ini}} \pm \Delta E$, where E_{ini} is the initial guess, and which is also forced to converge to self-consistency with the wave function:[79]

$$E_k = \frac{\langle \psi_k | \hat{H} | \psi_k \rangle}{\langle \psi_k | \psi_k \rangle} = \frac{\vec{c}_k^T \hat{S}^T \hat{M} \vec{c}_k}{\vec{c}_k^T \hat{S}^T \hat{S} \vec{c}_k} \tag{8}$$

via a penalty term $\alpha \sum_{k=1}^{L} (E_k^{\text{fitted}} - E_k^{\text{eq8}})^2$ which is added to R^2 during optimization (α is chosen so that the two terms have similar orders of magnitude), see ref 26 for more details. The energies of eq 8 are reported for the calculations below.

In all previous applications of the MC idea,[26,59–61,81] parametrized Gaussian basis functions were used, eq 1. In a Gaussian basis and using the KEO of eq 3, simple analytic expressions for the elements of matrix $\hat{\Gamma}$ in eq 6 are obtained:

$$\Gamma_{ji} = \sum_{n=1}^{d} b_{in}^2 (1 - 2b_{in}^2 ({}^j Q_n - w_{in})^2) \tag{9}$$

If an exact KEO or elaborate basis functions are used, the analytic expressions for the elements of $\hat{\Gamma}$ are intractable. One may also wish to use basis functions which do not have a closed-form expression, and in this case, equations for $\hat{\Gamma}$ are impossible. By using finite difference derivatives to obtain the elements of $\tilde{\Gamma}$, one easily obviates the need for a simple KEO and a Gaussian basis. This opens the door to the use of better basis functions. The Gaussians we have previously used are convenient but not necessarily the best basis functions. In this paper, we use the KEO of eq 3 and the three-point finite difference scheme with a step size of 0.1 au in each component of $\vec{Q}$. We have compared elements of $\hat{\Gamma}$ determined with the finite difference scheme and Gaussian basis functions to those calculated from eq 9 and find that they are accurate. Using finite difference derivatives increases the computational time by about a factor of 4 for the calculations reported below. Nonetheless, it has the advantage that it enables us to use better and therefore fewer basis functions and hence solve more difficult problems.

We test two types of basis functions. The first is coupled Gaussians. When product basis functions are used, coupling must be incorporated via linear combination of the basis functions. It seems natural to think that using basis functions that are themselves not factorizable might be advantageous. We therefore test coupled Gaussian basis functions of the form

$$\phi_i(\vec{Q} | \hat{B}_i, \vec{w}_i) = \exp(-(\vec{w}_i - \vec{Q})^T \hat{B}_i (\vec{w}_i - \vec{Q})) \tag{10}$$

where $\hat{B}_i$ is a parameter matrix of dimension $d \times d$. Basis functions of the second type are products of harmonic oscillator functions. We test two kinds of functions of this type. The first kind is

$$\phi_i(\vec{Q} | \vec{a}_i, \vec{b}_i, \vec{c}_i) = \prod_{m=1}^{d} Hf_{n_{im}}(a_{im} + b_{im}Q_m + c_{im}Q_m^2) \tag{11}$$

where $Hf_n(x) = (2^n n! \sqrt{\pi})^{-1/2} e^{-(x^2/2)} H_n(x)$; H_n is a Hermite polynomial of order n; and $\vec{a}_i$, $\vec{b}_i$, and $\vec{c}_i$ are parameters. Note that different arguments are used for different ϕ_i values. The second kind of harmonic oscillator basis is

$$\phi_i(\vec{Q} | \vec{A}_i, \hat{B}_i, \hat{C}_i) = \prod_{m=1}^{d} Hf_{n_{im}}(\Theta_{im}),$$

$$\vec{\Theta}_i = \vec{A}_i + \hat{B}_i \vec{Q} + \vec{C}_i \, \text{diag}(\vec{Q}\vec{Q}^T) \tag{12}$$

where $\vec{A}_i$, $\hat{B}_i$, and $\hat{C}_i$ are parameters and m now labels one of the components of $\vec{\Theta}$ and not one of the original coordinates. Here $\text{diag}(\vec{Q}\vec{Q}^T)$ is a vector with components $(Q_1^2, Q_2^2, ...Q_d^2)$. For both the Hermite bases, the correspondence between i and n_1, n_2, ..., n_d is given in a lookup table in the next section.

The use of coupled functions comes at the cost of a larger number of parameters. Table 1 lists the number of parameters

Table 1. The Number of Parameters Per Basis Function for the Basis Sets Considered Here

type of basis	no. of parameters
uncoupled Gaussian	$d + 1$
uncoupled Hermite	$3d$
coupled Gaussian	$d + 1 + [d(d - 1)]/2$
coupled Hermite	$d + 2d^2$

per function for the different basis sets used here. The larger the number of parameters, the more often a rectangular eigenvalue problem must be solved during the fit. The number of parameters, N, and M determine the computational cost. One of the purposes of this study is to compare the cost of calculations with fewer but more flexible basis functions and calculations with more but analytically differentiable basis functions: does the decrease in N compensate for the increased number of parameters per function?

The parameters $\vec{b}_i$ and the diagonal elements of $\hat{B}_i$ are initialized to mimic approximately the (Gaussian) ground state of a harmonic approximation to the potential and are allowed to vary by a factor of 3 from the initial values. Ratios for different coordinates are kept constant during the fit.[26,61] For the Gaussian basis functions of eq 10, $(\hat{B}_i)_{kl} = (\hat{B}_i)_{lk}$. Gaussian positions w are initialized randomly within the limits (vide infra) of $\{^j \vec{Q}\}$ and are forced to stay within those limits. The parameters $\vec{a}_i$, $\vec{b}_i$, $\vec{c}_i$, $\vec{A}_i$, and $\hat{C}_i$ and the off-diagonal elements of $\hat{B}_i$ are given zero initial values and are allowed to vary within empirically determined ranges to ensure the stability of the fit (which is basically to ensure that the arguments of the exponent and of the Hermite function in eqs 10–12 are monotonic functions of $\vec{Q}$ within the relevant coordinate ranges and that the presence of these parameters does not change the nodal structure of the wave function). Energy is initialized randomly within a 20 cm^{-1} window around the values of Table 2. The algorithm was programmed in Matlab.[97]

Table 2. Reference Fundamental Wavenumbers (in cm^{-1}) of Water on the Potential Energy Surfaces Considered Here: Exact for the Harmonic PES, Values Obtained with a Runge–Kutta Solver for the Uncoupled Anharmonic PES, and Values Obtained in the Fit with the Lowest R_{test} for the DFT Point Set

	harmonic PES	uncoupled anharmonic PES	ab initio PES	exptl.[107]
asymmetric stretch	3788.7	3873.6	3597.2	3755.9
symmetric stretch	3630.9	3548.9	3467.4	3657.1
bend	1578.2	1574.9	1522.9	1594.7

3. NUMERICAL TESTS AND DISCUSSION

3.1. Potential Energy Surfaces and Data.
We compared the performance of the basis sets defined in the previous section for three calculations of vibrational levels of H_2O using

two model potential energy surfaces (i and ii) and using a set of ab initio points. Similar potential data were used to test the original MC method in ref 26. PES (i) is harmonic:

$$V_{harm}(\vec{Q}) = \frac{1}{2} \sum_{i=1}^{d} k_i Q_i^2 \tag{13}$$

where force constants k_i are computed from ab initio (GGA DFT) calculations.[99−101] The corresponding normal-mode wavenumbers ω_i are given in Table 2. PES (ii) is anharmonic and uncoupled:

$$V_{anh}(\vec{Q}) = \sum_{i=1}^{d} V_i(Q_i) \tag{14}$$

where $V_i(Q_i)$ are polynomial fits of ab initio points along slices for each Q_i, as described in ref 26. Slices of the harmonic and anharmonic potentials along each normal mode coordinate are shown in Figure 1. Separability is not exploited when computing
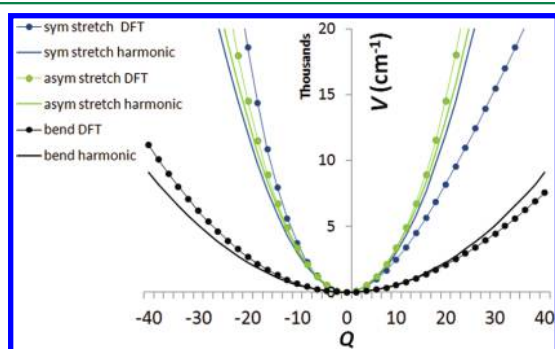

Figure 1. PES slices along normal coordinates of H_2O: obtained by DFT (lines with dots)[26] and in the harmonic approximation (solid lines).

levels on PES (i) and (ii). For the third test, energy levels are computed directly from a set of DFT points (see ref 26). There is no PES, but anharmonicity and coupling are fully accounted for.

As explained in ref 26, points are chosen from a probability density function $pdf(\vec{Q}) = V_{max} - V(\vec{Q})$ (appropriately normalized) to emphasize low-energy parts of the potential.[102] $V_{max} = 20\,000$ cm^{-1}, and values of Q were selected using a pseudo-random Sobol sequence.[103] A total of 3000 points were sampled, of which a random subset of 1500 points was used to fit and the remaining 1500 points were used as a test set to control for overfitting, i.e., to make sure we have good approximate solutions to the Schrödinger equation and not merely functions whose values at the collocation points are nearly equal to those of wavefunctions. The R we report is computed on the test points, $R = R_{test}$ (see eq 7), and was no more than 20% higher than the fitted R_{fit} in all runs, unless stated otherwise. For calculations with PES (i), $V(\vec{Q})$ in the pdf is V_{harm} of eq 13, and $Q_i^{min,max} = \mp 8\hbar/(2\pi\varepsilon_i)^{1/2}$, where ε_i are energies computed from the normal mode wavenumbers given in Table 2, determine the range within which points are chosen. For calculations with PES (ii) and the DFT points, $V(\vec{Q})$ in the pdf is V_{anh} of eq 14, and the range is defined by $V_i(Q_i^{min,max}) = V_{max}$.

In all three cases, we computed four vibrational levels (the ZPE and the three fundamentals) and the R_{test} values and mean absolute differences of the fundamental frequencies from the reference values of Table 2, $\Delta E = \langle |(E_k - ZPE) - (E_k - ZPE)_{ref}| \rangle$. For the uncoupled PES, reference values are determined with a Runge−Kutta program.[104,105] For the ab initio data set, we used

the values of section 3.4 with the lowest R_{test} as a reference, as exact energies are not defined in this case. For the uncoupled potentials, the uncoupled basis functions of eqs 1 and 11 were used, while for the coupled potential, we compared both uncoupled and coupled (eqs 10 and 12) versions of the Gaussian and Hermite bases. For the fits using parametrized Hermite functions of eqs 11 and 12, the orders of Hermite polynomials n_m were chosen from the following lookup table:

function\\m	1	2	3
1	0	0	0
2	0	0	1
3	0	1	0
4	1	0	0
5	0	1	1
6	1	0	1
7	1	1	0
8	1	1	1
9	0	0	2
...			
18	1	1	2
19	1	2	1
...			
27	2	2	2
28	0	0	3
29	0	3	0
30	3	0	0
31	0	1	3
32	0	3	1
...			

i.e., quanta of excitation are progressively added to all modes.

3.2. Fits for the Harmonic Potential. Fitting solutions of the Schrödinger equation with the Hermite basis of eq 11 should be trivial for a harmonic PES, and indeed we find that with four functions, a high-quality fit is quickly obtained: $R_{test} = 2 \times 10^{-4}$ and $\Delta E = 0.03$ cm^{-1}. The fit with the Gaussian basis of eq 1 set is also easy. In Figure 2, errors in wave functions and
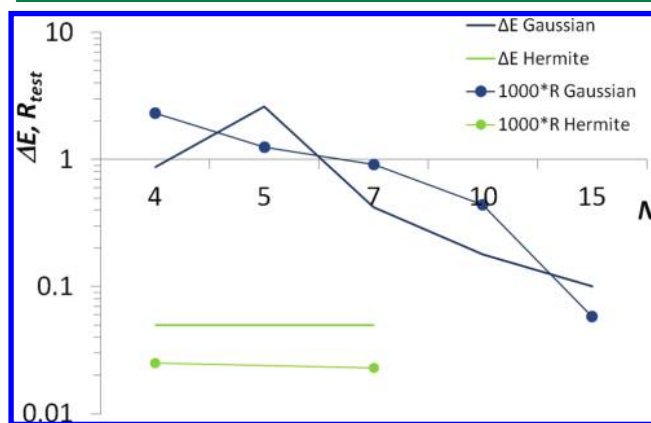

Figure 2. R_{test} (eq 7; thin lines with dots) and difference between computed and reference frequencies in cm^{-1} (thick lines) when solving the Schrödinger equation on the harmonic potential of eq 13. Logarithmic scale.

levels are given for these fits vs N. Only four parametrized Gaussian functions are sufficient to achieve an accuracy for levels on the order of 0.1 cm^{-1} and an R_{test} on the order of 1×10^{-3} for the four levels. This shows the power of parametrization: a high-quality fit is obtained with the same number of basis functions as wave functions.

3.3. Fits for the Uncoupled Anharmonic Potential. In Figure 3, the parametrized Gaussian (eq 1) and Hermite (eq 11)
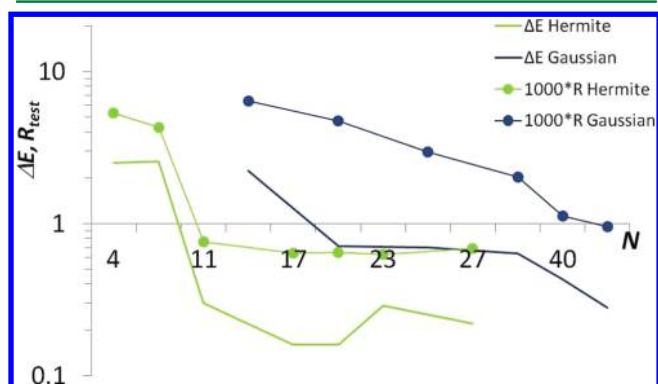

Figure 3. R_{test} (thin lines with dots) and difference between computed and reference frequencies (thick lines) in cm^{-1} when solving the Schrödinger equation on the anharmonic potential of eq 14. The calculation with $N = 50$ Gaussian functions is for $M = 3000$. Logarithmic scale.

bases are compared for solving the anharmonic problem, eq 14. With the parametrized Hermite functions, we achieve an accurate solution ($\Delta E < 0.5$ cm^{-1}, $R_{test} < 1 \times 10^{-3}$) with as few as 11 functions. Even if the number of parameters per basis function is larger for the Hermite than for the Gaussian basis (see Table 1), because fewer basis functions are required, there is an overall reduction in the number of parameters required to achieve a given accuracy.

Reducing the number of required basis functions is important for several reasons. With fewer basis functions, it is easier to find a fit for which R_{test} is almost as small as the R_{fit} computed with the fitting points. For example, it is not possible to find fits with small and similar R_{fit} and R_{test} values when using more than 50 Gaussian and 1500 points. To obtain the points in Figure 3 for $N = 50$, it was necessary to use $M = 3000$ fitting and test points. The need for more data slows the algorithm but, more importantly, is a serious limitation when using ab initio data, where the calculation of a point might require hours or days of CPU time. These tests show the advantages of parametrized physically motivated Hermite basis functions for dealing with anharmonicity and overfitting.

3.4. Fits with the ab Initio Point Set. In Figure 4, results of calculations using uncoupled Gaussians and Hermite bases are shown. When using the uncoupled Gaussian basis, as in the
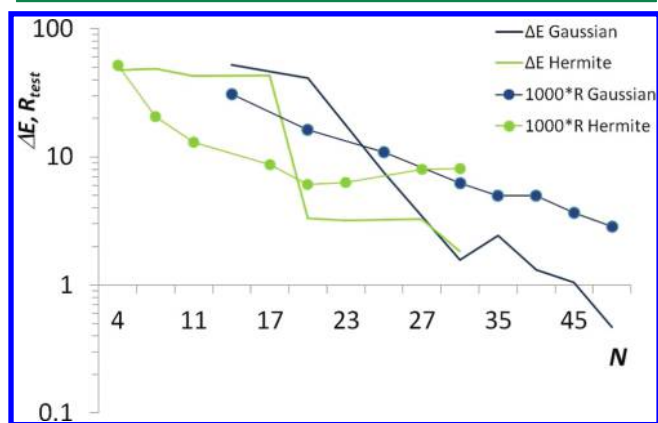

Figure 4. R_{test} (thin lines with dots) and the difference between computed and reference frequencies (thick lines) in cm^{-1} when solving the Schrödinger equation with the ab initio points using uncoupled basis functions, eqs 1 and 11. Logarithmic scale.

previous section, fits with $N < 50$ can be obtained for which R_{test} exceeds R_{fit} by less than 30%. More ab initio data would be required to use $N > 50$ and thereby improve the accuracy. The use of parametrized uncoupled Hermite functions makes it possible to obtain a better accuracy with $N < 30$, without increasing M. There is, however, no reduction in the total number of parameters: to deal with coupling, one requires a large N. In addition, with uncoupled Hermite functions, R_{test} decreases slowly as N increases, and the number of required parameters becomes so large and the optimization so costly that it becomes impossible to get a good fit. In contrast to the case of the Gaussian basis, this is not because of overfitting: R_{fit} and R_{test} are within 15% of each other. Rather, it is an inherent limitation of the uncoupled basis set. For a fixed M, the basis limits the achievable R_{test} and the accuracy of energies (see eq 8). It appears therefore that uncoupled Gaussian functions are better than uncoupled Hermite functions when one wishes to account for coupling.

Can one obtain better accuracy by introducing coupling into the basis? With coupled basis functions, is it possible to find a fit for which R_{fit} and R_{test} are similar (i.e., no "over-fitting") in the case of Gaussian functions and to decrease N in the case of Hermite functions? In Figure 5, we show the results of
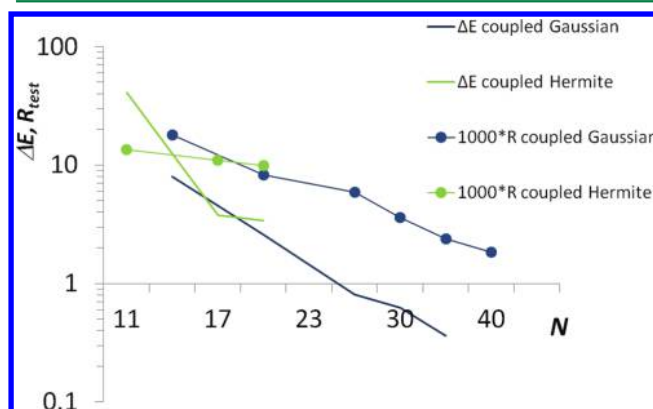

Figure 5. R_{test} (thin lines with dots) and difference between computed and reference frequencies (thick lines) in cm^{-1} when solving the Schrödinger equation with the ab initio points using coupled basis functions, eqs 10 and 12. Logarithmic scale.

calculations using coupled parametrized Gaussian and Hermite functions. The minimum achievable R_{test} is slightly lower with coupled Gaussian functions, but overall no significant advantage was achieved. For a given accuracy, fewer of the coupled (eq 10) than the uncoupled eq 1 Gaussians are required. There is, however, no reduction in the total number of parameters and therefore in the computational expense. The fits with coupled parametrized Hermite functions of eq 12 are very expensive, with 20 functions requiring the optimization of more than 400 nonlinear parameters (Table 1). In the current Matlab implementation of the algorithm, up to 300 parameters can be effectively optimized on a personal computer within a few hours. The balance between flexibility and optimization cost is such that unless more effective schemes for nonlinear optimization are used, such extensively parametrized basis functions are not advantageous. More efficient codes and/or different optimization algorithms (e.g., genetic algorithm or direct search type ideas combined with second-order optimization close to the minimum) are certainly possible, but their exploration is outside of the scope of this work.

3.5. Discussion. Our calculations show that parametrized basis functions of different types allow one to obtain accurate

levels from a small basis. In particular, when using physically motivated Hermite functions, parametrization can result in a significant reduction of the basis set size for anharmonic problems. The advantage of parametrized basis functions is made clear by comparing results for the uncoupled anharmonic potential, computed with $M = 1500$, with uncoupled Hermite bases with fixed and varying parameters. In the fixed case, the basis functions are harmonic oscillator functions with frequencies as in Table 2. A ΔE of $0.31-2.63$ cm^{-1} (depending on the random potential points used) is achieved by using $N = 300$ fixed Hermite functions. Corresponding values of R_{fit} were around $(1.5-1.7) \times 10^{-3}$, and those of R_{test} around $(1.9-2.7) \times 10^{-3}$ (cf. Figure 3). In contrast, calculations using varying parameters have $\Delta E < 0.5$ cm^{-1} on *different* sets of random points with $N \geq 11$. The accuracy of the fixed calculation is actually limited by the density and number (M) of the points, and for the best fits, R_{test} is up to 50% larger than R_{fit} and energies change by several cm^{-1} when the choice of fitting points is varied. For the calculations with the DFT points, $N = 500$ fixed uncoupled harmonic functions gave an R_{fit} of $(0.8-0.9) \times 10^{-3}$ and R_{test} of $(1.9-3.0) \times 10^{-3}$ (cf. Figures 4 and 5) and energies that varied by several cm^{-1} when the different points are used. Allowing the parameters to vary reduces the number of basis functions required to achieve a similar accuracy (see Figure 4). Using coupled basis functions does further reduce the number of basis functions, N, for the fit with the DFT point set. Nevertheless, the total number of parameters required to achieve a given accuracy with coupled and uncoupled bases is similar. For the tests we have done, uncoupled and coupled bases are about equally costly in both the Hermite and the Gaussian cases. However, the coupled basis sets are smaller and that is an important advantage. It is possible that for more strongly coupled or larger problems and with better optimization schemes, coupled bases might also be less costly.

When using parametrized basis functions, the number of required parameters increases when anharmonicity is added and increases again when coupling is added. To achieve $\Delta E \approx 0.5$ cm^{-1}, the numbers of parameters with uncoupled Hermite/Gaussian bases were 36/28 and 99/160 for the harmonic and anharmonic uncoupled PES, respectively. To achieve $\Delta E \approx 1$ cm^{-1} with the DFT points set, the numbers of parameters were around 270 and 180, for uncoupled Hermite and Gaussian bases, respectively.

The calculation time depends on M and N, the kind of basis (number of parameters), and, of course, on the fitting software and hardware used. In our case, using Matlab R2009b, 300 fitting steps, and a standard PC, most fits with uncoupled Gaussian functions took about 1 h of CPU time, calculations with $N = 35$ required about 2 h. Coupled Gaussian functions need somewhat more CPU time: about 2.5 h for $N = 25$ (needed to reach a ΔE of about 1 cm^{-1}). With uncoupled Hermite functions, up to 5.5 h were needed for $N = 30$. Although these calculations are not cheap, one only needs a small number of ab initio points, and there is no need to fit a surface. The coupled Hermite functions of eq 12 did require a lot of CPU time: as much as 20 h for $N = 20$ (420 parameters). They are therefore not recommended. Other types of parametrized basis functions could also be used with the method we propose.

For comparison purposes, we have also solved the square generalized eigenvalue problem $\hat{S}^T \hat{M} \vec{c} = E \hat{S}^T \hat{S} \vec{c}$ with $M > N$ and $\hat{M} \vec{c} = E \hat{S} \vec{c}$ with $N = M$. In both cases, it was not possible to achieve an error of better then $\sim 10^2$ cm^{-1} on levels corresponding to asymmetric and symmetric stretches. It is clear that when using adaptable basis functions, a rectangular collocation approach is advantageous.

A disadvantage of using a fitting method to solve the Schrödinger equation is sensitivity to initial values of the parameters. Here, this includes sensitivity to the initial values of $\vec{b}_i$, $\hat{B}_i$, and E. There is also an element of randomness due to a random initialization of the energy and a random selection of fitting and test points, and initialization of $\vec{w}_i$. When the range for E is more than about 20 cm^{-1}, or initial values of $\vec{b}_i$ and $\hat{B}_i$ are far from the corresponding harmonic values, the convergence becomes slower and fits can get trapped in local minima. The sensitivity to the initial parameter values has to do with limited capabilities of the nonlinear fitting routine used and can be improved as more powerful nonlinear optimizers are implemented. Good initial values of $\vec{b}_i$ and $\hat{B}_i$ are easy to estimate from the harmonic approximation. If good initial energies (such as experimental values) are not available, we have shown that it is possible to start from a potential for which E values are known (e.g., harmonic) and gradually morph it into a target PES.[26,59]

The accuracy of the MC method is also limited by the number and density of the fitting points.[106] By comparing results from several calculations, we estimate, for the calculations with V_{anh} and the DFT point set, an accuracy of about ± 0.5 cm^{-1} and ± 1 cm^{-1} (respectively). This accuracy appears to be limited by the density of the points. In a traditional approach of constructing an analytic PES and then computing levels, the largest error is the fitting error, E_{fit}, incurred when the surface is fitted. The error in levels computed on the surface is some fraction of E_{fit}, and it is this error that should be compared with the error of our algorithm. Our approach is competitive. Here, we consider the accuracy of solving the vibrational Schrödinger equation from data obtained at a given level of electronic structure theory. The accuracy of the underlying electronic structure calculations is of course another matter. The underestimation of the frequencies by about 4% vs experiment in this work is attributed to the errors of GGA DFT.[108,109]

4. CONCLUSION

We have compared different types of parametrized basis functions for solving the vibrational Schrödinger equation with a version of the rectangular collocation-based method of Manzhos and Carrington[59] that uses finite difference derivatives for the KEO. Using finite difference derivatives makes it possible to use any parametrized basis set to compute a small number of vibrational levels directly from a set of potential points. A collocation-based method obviates the need to construct an analytic potential energy surface and therefore simplifies the calculation of vibrational spectra. Any basis functions can be used with the finite difference version, and it therefore makes it possible to choose very flexible functions and thereby to decrease the number of required basis functions.

We tested the performance of uncoupled and coupled Gaussian functions and uncoupled and coupled Hermite functions with a parametrized argument on harmonic and anharmonic uncoupled potentials and on a DFT point set (including anharmonicity and coupling) representing H_2O. Parameterized uncoupled basis sets enable one to drastically reduce the basis size. Using coupled basis functions that are not factorizable enables one to further reduce the basis size, however, at the cost of introducing a larger number of nonlinear fitting parameters. As few as 30 basis functions can be used to compute energy levels of water from a set of DFT points. The estimated error of ~ 1 cm^{-1} is comparable to the error typically incurred when fitting PESs. For H_2O, the cost reduction achieved with coupled basis functions, due to the fact that the coupled basis is smaller, is largely negated by the increase in the cost of the nonlinear fit due to the increase in the number of

parameters. Uncoupled parametrized Gaussian and Hermite basis functions seem therefore to be the best choice.

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Notes
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