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A multimode-like scheme for selecting the centers of Gaussian basis functions when computing vibrational spectra

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ABSTRACT

We compute vibrational energy levels using Gaussian basis functions whose centers are in slabs that include the lower-dimensional hyperplanes on which the Multimode approximation to the potential is based. We use more potential points than basis functions to increase the accuracy. The number of Gaussian basis functions is smaller than the number required using the best existing methods. For formaldehyde, the first 50/100 levels we compute, using 30,000 Gaussians and 120,000 points, in 4D-like slabs, differ from numerically exact levels by 0.3/0.6 cm^{-1} (mean absolute error). With 3D-like slabs, the *mae* for the first 50/100 levels is 0.17/0.47 cm^{-1} with 30,000 basis functions and 0.95/2.06 cm^{-1} with 20,000 basis functions. Although we use a multimode-like idea to select Gaussian centers, we use a single point set and there is no need to write the potential in multimode form and no need to neglect high-order terms.

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1. Introduction

When coupling and anharmonicity are important, it is common to a compute vibrational spectrum by representing vibrational wavefunctions as linear combinations of basis functions and solving a matrix eigenvalue problem [1–5]. Although bases of products of multi-dimensional basis functions have advantages [6–8], it is common to use basis functions that are products of univariate functions. The most popular univariate functions are polynomial based. The multiconfiguration time-dependent Hartree method uses optimized 1D functions [9]. Persistent efforts have been made to find effective ways of using localized 1D Gaussian-type basis functions [10–16]. They have the advantage that it ought to be possible to use only products of 1D Gaussians whose centers are in a small region of configuration (or phase) space. Clearly, it is better not to use a basis whose functions have amplitude in regions of configuration (phase) space in which wavefunctions (their Wigner transforms [17]) are tiny. In this paper, we use Gaussian basis functions, however, they could be replaced with other localized or even non-localized functions [18,19].

To use Gaussian basis methods, one must confront three problems: 1) how to choose which Gaussians to include in the basis; 2) how to compute potential energy surface (PES) matrix elements; 3) how to compute matrix elements of the kinetic energy operator (KEO). In this paper, we present a new solution to 1) and use previously published ideas for 2) and 3) [20]. For multi-dimensional problems, there are two common approaches for choosing which products of 1D Gaussians to use. Some authors use more products centered at points at which the potential is low [16]. This is most easily done by choosing centers from a distribution function peaked at the minimum of the potential. Oher authors begin, at least conceptually, with a regular (often equally spaced) multidimensional grid of multidimensional Gaussians and put only those into the basis whose centers are in or close to the classical region [10,12,14,21]. There are also attempts to numerically minimize a trace to optimize the positions of the Gaussians [15].

We propose a new idea for selecting the multidimensional Gaussian centers. It is well established that if a PES is written as a sum of terms that depend on a single coordinate, terms that depend on two coordinates, terms that depend on three coordinates etc, then terms that depend on more coordinates are less important than terms that depend on fewer coordinates [22]. A PES written in this way is often said to be in multimode (MM) form or a high-dimensional model representation (HDMR). Bowman and co-workers have developed a computer program [23,24] for computing vibrational spectra that exploits the diminishing importance of higher order terms by retaining only basis functions that are coupled by lower order terms [22]. The program uses a *set* of

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low-dimensional grids to evaluate integrals. We exploit the diminishing importance by using it to design a (single) grid that is used to compute matrix elements *and* to choose multidimensional Gaussian centers. It has recently been demonstrated that it is possible to use product basis functions, $\phi_{n1}^{(1)}(x_1)\phi_{n2}^{(2)}(x_2)\ldots\phi_{nD}^{(D)}(x_D)$ and the restriction $\sum_c G^c(n_c) \leqslant H$, where H is a convergence parameter, to construct a Smolyak sparse grid. The functions $G^c(n_c)$ are chosen so that most of the points on the grid are those required to compute matrix elements of the most important terms in the PES [25–27]. However, in these papers, the 1D basis functions are not Gaussians, and the grid is built from 1D grids using the Smolyak recipe, which is not the case here.

Problems 2) and 3) are dealt with using ideas from Ref. [20]. The approach we use can be thought of either as a rectangular collocation method or as a method using a quadrature with constant weights. In this paper, we denote it the space-fixed Gaussian basis (SFGB) method. We need only values of the potential at the collocation/quadrature points. There is no need for a SOP (sum-of-products) PES. There is no need to represent the PES in the MM form and neglect higher order terms. We are exploiting the smallness of higher order terms without neglecting them. We use a space-fixed KEO and thereby obviate the need to derive analytically [28] or compute numerically [29,30] a KEO in terms of the vibrational coordinates on which the basis functions depend. It is possible to operate with a space-fixed (SF) Cartesian KEO on basis functions that are the functions of internal curvilinear coordinates [20].

2. Methods

The new ideas for choosing Gaussian centers and collocation/quadrature points were tested by computing vibrational energy levels of formaldehyde. We used the PES of Ref. [31]. The spectrum computed on it agrees well with the experimental spectrum [20,32]. We used bond coordinates $\boldsymbol{x} = (CO, CH_1, CH_2, \angle OCH_1, \angle OCH_2, \angle H_1COH_2)$, where $\angle H_1COH_2$ stands for the dihedral angle between the OCH planes. The basis functions are functions of these coordinates and the PES is evaluated at a set of points in the bond coordinates.

The vibrational spectrum is computed using the space-fixed Gaussian basis method of Ref. [20]. Wavefunctions are expanded in a basis

$$\psi_k(\boldsymbol{x}) = \sum_{n=1}^{N} c_{nk} g_n(\boldsymbol{x}) \tag{1}$$

where $g_n(\boldsymbol{x})$ is a basis function (in this paper we use Gaussians). If the coefficients were determined so that the Schrödinger equation (SE) is satisfied at a set of points $\{\boldsymbol{x_m}\}, m = 1, \ldots, M$, they, and the energies would be obtained by solving the matrix equation

$$\tilde{\boldsymbol{M}}\boldsymbol{c}'_k = E_k \boldsymbol{S}\boldsymbol{c}'_k \tag{2}$$

In our case, $M > N$, and the $\tilde{\boldsymbol{M}}$ matrix in Eq. (2) is rectangular. In Eq. (2), $S_{mn} = g_n(\boldsymbol{x}_m)$, $\tilde{M}_{mn} = \boldsymbol{T}g_n(\boldsymbol{x}_m) + V(\boldsymbol{x}_m)g_n(\boldsymbol{x}_m)$, and $\boldsymbol{c}'_k$ is a vector of coefficients. $\boldsymbol{T}$ is the KEO. This rectangular matrix equation is solved by multiplying on the left with $\boldsymbol{S}^T$ to obtain the square generalized eigenproblem [33–35]

$$\boldsymbol{S}^T\boldsymbol{M}\boldsymbol{c}_k = E_k\boldsymbol{S}^T\boldsymbol{S}\boldsymbol{c}_k \tag{3}$$

where $\boldsymbol{c}_k \approx \boldsymbol{c}'_k$. This is not equivalent to using quadrature to compute potential matrix elements and exact kinetic matrix elements because the (non-symmetric) kinetic matrix is also obtained by doing quadrature. We use

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

where $D = 6$ is the number of dimensions. $\sigma_d \equiv \sigma_0 \times \kappa(d)$, where $\kappa(d)$ is proportional to the range of coordinate d, and σ_0 is chosen to minimize the difference with the reference (variational) spectrum. The space-fixed KEO

$$\boldsymbol{T}^{SF} = -\sum_{k=1}^{3N_{atoms}} \frac{1}{2m_k}\frac{\partial^2}{\partial X_k^2} \tag{5}$$

where X are spaced-fixed Cartesian coordinates, is applied to $g_n(\boldsymbol{x})$ by using $g_n(\boldsymbol{x}(\boldsymbol{X}))$. The method is implemented in Matlab [36]. See Ref. [20] for details.

To make a set of potential points $\{\boldsymbol{x_m}\}$, we choose points within specific ranges from a pseudo-random six-dimensional Sobol sequence [37] and accept points if

$$\frac{V_{max} - V(\boldsymbol{x}) + \Delta}{V_{max} + \Delta} > rand \tag{6}$$

where *rand* is a (uniformly distributed) random number in [0, 1]. We use $V_{max} = 17{,}000\ \text{cm}^{-1}$ and $\Delta = 500\ \text{cm}^{-1}$. The coordinate ranges are $\boldsymbol{x_{min}} = (1.03, 0.84, 0.84, 83, 83, 105)$, $\boldsymbol{x_{max}} = (1.50, 1.69, 1.69, 162, 162, 255)$, where bond lengths are in Å and angles in degrees. We have shown that this kind of point selection results in accurate vibrational spectra [20]. The constraints of Eq. (6) and coordinate ranges define the full-dimensional, 6D point set.

We also form point sets, denoted MM(d), by starting with a six-dimensional Sobol sequence within the same coordinate ranges as above, and accepting only points in the reference set that satisfy, in addition to Eq. (6), the constraint

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

where $H(x)$ is the Heaviside step function. By imposing Eq. (7), we select only points in "slabs" in the configuration space containing hypersurfaces corresponding to displacements of only $d \leqslant D$ coordinates from equilibrium values. In Eq. (7), s determines the thickness of the slabs. A standard MM calculation uses not one grid but many [22]. The grid that is the union of the individual standard MM grids is similar to the grid obtained, for a particular value of d, by putting $s = 0$. In the standard MM case, it is necessary only to use quadrature in a reduced dimensional space. In the approach of this paper, Eq. (3) is equivalent to computing full-dimensional integrals. For this reason it is necessary to use a non-zero $s << 1$. In summary, we make a set of points that is similar to the union of the individual grids used in the standard MM method. The advantage of MM(d) is that it includes only points in the small region of configuration space necessary for computing integrals of an MM representation of the PES that is truncated at d^{th} order. We use MM(d) even though we do not build an MM approximation to the potential. We are starting from a point set (see Eq. (6)) that is similar to that of Garashchuk and Light and discarding points that are in regions of configuration space we deem unimportant [16].

We computed the lowest 100 vibrational levels. For a given calculation, the widths of all basis functions are the same and chosen as described in Ref. [20]. Different widths are used for different d. SFGB spectra are computed both using a reference point set (Eq. (6)) and using MM(d), $d = 2, \ldots, 5$ point sets extracted from the reference set. For all calculations, the Gaussian centers, $x_d^{0,n}$ in Eq. (4), are the first N points from the point set unless stated otherwise. The reference SFGB calculation uses $M = 120{,}000$ points and $N = 40{,}000$ Gaussian basis functions. The reference points depend on the random numbers in Eq. (6). Ten sets of reference points were

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