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# Using an expanding nondirect product harmonic basis with an iterative eigensolver to compute vibrational energy levels with as many as seven atoms

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We demonstrate that it is possible to use a variational method to compute 50 vibrational levels of ethylene oxide (a seven-atom molecule) with convergence errors less than  $0.01 \text{ cm}^{-1}$ . This is done by beginning with a small basis and expanding it to include product basis functions that are deemed to be important. For ethylene oxide a basis with fewer than  $3 \times 10^6$  functions is large enough. Because the resulting basis has no exploitable structure we use a mapping to evaluate the matrix-vector products required to use an iterative eigensolver. The expanded basis is compared to bases obtained from pre-determined pruning condition. Similar calculations are presented for molecules with 3, 4, 5, and 6 atoms. For the 6-atom molecule,  $\text{CH}_3\text{CH}$ , the required expanded basis has about 106 000 functions and is about an order of magnitude smaller than bases made with a pre-determined pruning condition. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4963916>]

## I. INTRODUCTION

It is common to represent the potential energy surface (PES) of a semi-rigid molecule in the vicinity of its equilibrium geometry with a Taylor series.<sup>1,2</sup> The Taylor series is sometimes called a force field. The coefficients are derivatives of the potential and they can be computed with many *ab initio* quantum chemistry packages.<sup>3,4</sup> Some of the packages can also be used to compute vibrational levels from second order perturbation theory.<sup>5</sup> When the PES is a sum of products (SOP) it is now possible to solve the vibrational Schroedinger equation numerically for molecules with about 10 atoms.<sup>6–11</sup> Such calculations, often called variational, fully account for the effects of coupling and anharmonicity. When zeroth-order levels are close (resonances), perturbation theory works poorly. High-lying zeroth-order levels are often close. To calculate energy levels and a vibrational spectrum with a variational method, one represents vibrational wavefunctions in a basis and uses methods of numerical linear algebra to determine the basis function coefficients.<sup>12–15</sup> When a direct product basis is used, for a molecule with  $D$  vibrational coordinates, a wavefunction is

$$\psi(\mathbf{x}) = \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_2} \cdots \sum_{n_D=1}^{N_D} c_{n_1, n_2, \dots, n_D} \times {}^1\theta_{n_1}(x_1) {}^2\theta_{n_2}(x_2) \cdots {}^D\theta_{n_D}(x_D), \quad (1)$$

where  ${}^c\theta(x_c)$  is a 1D basis function for coordinate  $c$ , with maximum indices  $N_1, N_2, \dots, N_D$ . The coefficients  $c_{n_1, n_2, \dots, n_D}$  are components of eigenvectors of a matrix that represents the Hamiltonian operator in the same basis. A direct product basis has the advantage that it enables one to efficiently obtain the eigenvalues and eigenvectors of the Hamiltonian

matrix using an iterative eigensolver, owing to the fact that the matrix-vector products required to use an iterative eigensolver can be performed sequentially, with a cost that scales as  $N^{D+1}$ , where  $N$  is a representative value of  $N_c$ ,  $c = 1, \dots, D$ .<sup>16–19</sup>

Perturbation theory is often the method of first resort because of the memory cost of using a direct product basis. This memory cost of a  $J = 0$  direct-product (iterative) calculation scales as  $N^D$ , with  $D = 3A - 6$ , where  $A$  is the number of atoms. To facilitate such calculations it is therefore important, at least for molecules with more than four atoms, to reduce the size of the basis required to solve the Schroedinger equation.<sup>15</sup> It is, however, also possible to use tensor methods to compute energy levels in a direct product basis without storing  $N^D$  vector components.<sup>6,7,20–22</sup> There are three established ways to reduce the basis size: (1) contract direct product bases for sub-problems by computing eigenfunctions of reduced-dimension Hamiltonians,<sup>14,23–26</sup> (2) prune a direct product basis by discarding some basis functions,<sup>12,27–29</sup> and (3) optimize the 1D functions by using the multi-configuration time-dependent Hartree method.<sup>9</sup> Contraction can be used with a general, i.e., not a SOP, PES. Pruning can be used with a general PES, if it is combined with a nondirect product quadrature or collocation.<sup>30–33</sup> MCTDH can be used with a general PES when a correlated discrete variable representation (DVR) is used, but this requires evaluating the PES many times.<sup>34</sup>

Of the three options, (2) is conceptually the simplest. It is obvious, for example, from perturbation theory, that some of the direct product functions are unnecessary. If a standard direct eigensolver is used, it is clearly best to discard from a direct product basis the functions that are unnecessary. The Schroedinger equation can be solved in a pruned basis by using direct methods that require storing the Hamiltonian matrix, but this is costly. It is the memory cost of such an approach that is most debilitating. If an iterative eigensolver is used, the cost of the calculation depends on the cost of

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matrix-vector products. The cost of matrix-vector products depends on the size of the basis, but also on the structure of the basis. Omitting functions from the direct product basis complicates its structure. Matrix-vector products with a direct product basis are easy and cheap because they can be evaluated by doing sums sequentially. When functions are removed, the basis is pruned and no longer a direct product. Because the pruned basis is not a direct product, it is not obvious that matrix-vector products can be evaluated with sequential summation. It is important to develop ideas for evaluating matrix-vector products in pruned bases.

There are two ways to remove functions from the direct product basis: (1) impose a pre-determined pruning condition; (2) start with a small basis and adaptively add basis functions deemed to be important to obtain convergence. (1) is the most prevalent.<sup>12,27,28,35–40</sup> If the pre-determined pruning condition itself has structure, then it is possible to use sequential summation.<sup>32,39,41</sup> (2) has been used in many recent papers.<sup>11,42–49</sup> It is most straightforward to use a pre-determined pruning condition. If the harmonic frequencies of all the coordinates are similar, then a product harmonic oscillator basis (HOB) can be effectively pruned by retaining only basis functions for which

$$n_1 + n_2 + \cdots + n_D \leq b. \quad (2)$$

This reduces the basis size from  $N^D$  to  $\frac{(D+b)!}{D!b!}$ . This pruning condition was used, for example, in Refs. 30, 39, and 50. In Ref. 50 it is called a polyad truncation. A more general pruning scheme is

$$a_1 n_1 + a_2 n_2 + \cdots + a_D n_D \leq b, \quad (3)$$

where  $a_i$  are integers.<sup>41</sup> We refer to this as F (for frequency) or polyad truncation. Spectroscopists often think of coupling as being most important within polyads.<sup>51,52</sup> Here we include coupling within and between all polyads with polyad number less than or equal to  $b$ . Sequential summation can be used to evaluate matrix-vector products when  $a_i$  in Eq. (3) are integers.<sup>32,41</sup> It is possible to use non-integer  $a_i$  with a direct eigensolver and a powerful computer.<sup>8</sup> A very similar or identical basis can always be made by multiplying Eq. (3) by an integer and using integer coefficients.<sup>53</sup> The MULTIMODE code of Bowman and co-workers also uses a pruned basis, but does not use Eq. (3). Instead they, as is done in electronic structure theory, keep basis functions with single-mode, two-mode, three-mode, etc., excitations.<sup>54</sup> It is also possible to prune by imposing the general condition<sup>33,53,55,56</sup>

$$g^1(n_1) + g^2(n_2) + \cdots + g^D(n_D) \leq b, \quad (4)$$

where  $g^c(n_c)$  are non-decreasing functions.

Two different ideas for choosing  $a_i$  will be tested in this paper. Both require knowing only the harmonic frequencies. The first is to choose  $a_i = \lfloor \omega_i / \omega_{\min} + 0.5 \rfloor$  and will be called frequency (F) pruning. The floor function is used to ensure that  $a_i$  is an integer. The second is to choose  $a_i = \lfloor \sqrt{\omega_i / \omega_{\min} + 0.5} \rfloor$ , which was suggested in Ref. 50 (although not rounded to the nearest integer), and will be called S pruning. S pruning gives  $a_i$  intermediate between those of  $a_i = 1$  and F pruning. In this paper we compare Eqs. (2) and (3), two pre-determined pruning conditions,

with each other and with an adaptive approach that builds a pruned basis by adding basis functions judged to be important. A similar basis building approach was used in Ref. 47, where it was applied with phase-space localized (PSL) basis functions. When using PSL functions it is common to use a pre-determined pruning condition based on the energy below which one wishes energy levels. With the basis building approach of Ref. 47, it is possible to obtain converged levels with a smaller PSL basis.

## II. EXPANDING A BASIS OF HOB FUNCTIONS

In this paper, we use bases whose functions are products of HOB functions. We start with a small HOB and add additional HOB functions to it. HOB functions are good for Hamiltonians of the form

$$H = \sum_{i=1}^D \omega_i \left( -\frac{1}{2} \frac{d^2}{dx_i^2} + \frac{1}{2} x_i^2 \right) + \sum_{ijk} f_{ijk} x_i x_j x_k + \sum_{ijkl} f_{ijkl} x_i x_j x_k x_l, \quad (5)$$

when the cubic and quartic force constants are much smaller than the  $\omega$  frequencies. The starting basis includes the functions that satisfy Eq. (2) for  $b = 5$ . In this section, we present a procedure that builds a basis containing the most important HOB functions. It is a black-box, “greedy” method that successively increases the size of the basis by including basis functions that are judged to be important. It might be possible to choose basis functions to add by using information about the cubic and quartic force constants or the spectroscopic  $x_{ij}$  constants.<sup>1</sup> Instead, to make a basis with  $N_{\text{new}}$  functions, we identify important functions in a basis with  $N_{\text{old}} < N_{\text{new}}$  functions by examining eigenvectors of the  $N_{\text{old}} \times N_{\text{old}}$  Hamiltonian matrix and then add their neighbours to the basis with  $N_{\text{old}}$  functions. The basis is then successively enlarged. We hope that this scheme will enable us to calculate the desired energy levels, to a certain accuracy, with the smallest possible number of HOB functions.

To make a basis by adding neighbours, we need (1) a method to assign a measure of importance to each of the  $N_{\text{old}}$  functions and (2) a method to determine which additional functions to add. We have considered two measures of importance. The first is the method of Ref. 47, where it was used with a basis of PSL functions. The importance of basis function  $\mathbf{n}$  (a composite label,  $\mathbf{n} = [n_1, n_2, \dots, n_D]$ ) is assumed to be determined by

$$C_{\mathbf{n}} = \sum_{e=1}^{N_e} |v_{\mathbf{n}e}|, \quad (6)$$

where  $v_{\mathbf{n}e}$  is a component of the matrix of eigenvectors and  $N_e$  is the number of desired vibrational states.

$$\mathbf{H}^{\text{old}} \mathbf{V} = \mathbf{V} \mathbf{E}, \quad (7)$$

$v_{\mathbf{n}e}$  is an element of  $\mathbf{V}$  and  $\mathbf{H}^{\text{old}}$  is the matrix representing the Hamiltonian in the HOB with  $N_{\text{old}}$  functions. The second is

similar. A basis function  $\mathbf{n}$  is deemed important if

$$O_{\mathbf{n}} = \sum_{e=1}^{N_e} v_{\mathbf{n}e}^2 \quad (8)$$

is large. For eigenvector  $e'$ ,  $\sum_{\mathbf{n}} v_{\mathbf{n}e'}^2 = 1$ .  $v_{\mathbf{n}e'}$  is the contribution from basis function  $\mathbf{n}$ . If its contribution is large for the first  $N_e$  states then it is considered to be important. Either  $C_{\mathbf{n}}$  or  $O_{\mathbf{n}}$  may have been used in Ref. 45. In a recent paper, Garnier *et al.* use other ideas to build a basis. They add functions they deem important on the basis of off-diagonal matrix elements.<sup>11</sup> We do not compute matrix elements coupling the  $N_{old}$  functions to functions we consider adding to the basis.

After designating some functions in the basis with  $N^{old}$  functions as the most important, we add their neighbours to the basis. We need to define neighbours. Different authors use different definitions.<sup>11,43–47,49</sup> Because we know that basis functions for which  $\sum_c n_c$  is larger are usually less important, we define the neighbours of  $\mathbf{n} = [n_1, \dots, n_c, \dots, n_D]$  to be the set of  $D$  functions obtained from  $\mathbf{n} = [n_1, \dots, n_c, \dots, n_D]$  by augmenting one of the indices, i.e.,  $[n_1, \dots, n_c + 1, \dots, n_D] \forall c$ . We order the  $N^{old}$  basis functions according to their importance, using Quicksort,<sup>57</sup> and keep track of the corresponding indices in order to refer back to the labels in a list of the basis functions. Neighbours of the most important function are added to the basis. Neighbours of the second most important function are then added to the basis. This process is continued until the size of the basis has been increased by 5%. With the new basis thus formed, we then compute a new set of eigenvalues and eigenvectors, use the eigenvectors to compute new  $C_{\mathbf{n}}$  or  $O_{\mathbf{n}}$ , and repeat the process. When increasing the basis size changes eigenvalues less than our convergence threshold, we stop.

This procedure for increasing the basis size is automatic and in our experience works well. However, if the eigenvectors have structure imposed by symmetry, a blind application of these ideas would not work well. For example, if wavefunctions and basis functions are even or odd in  $x_c$  then some components of the eigenvectors will be zero and it will not work to define neighbours as we have done above. There are obvious ways to adapt to algorithm; the simplest is to apply it within symmetry blocks.

### III. COMPUTING A SPECTRUM

Knowing the Hamiltonian and having defined a basis (Section II), it remains to compute the spectrum. Although the basis built using the algorithm in Section II is much smaller than a direct product basis, it is large for molecules with more than 5 atoms. For  $\text{CH}_2\text{NH}$  (see Section IV B), the basis is small enough that it would be possible to use a direct eigensolver. For  $\text{CH}_3\text{CN}$  (see Section IV B), the basis has more than  $10^6$  functions and an iterative eigensolver is clearly better. Iterative eigensolvers have been used to compute vibrational spectra for many years.<sup>15,16,18,58–63</sup> It is well known that they make it possible to compute a spectrum without storing the Hamiltonian matrix. This is an important advantage, but iterative eigensolvers are only efficient if there is a good way of evaluating matrix-vector products. When the basis

is a direct product, matrix-vector products can be efficiently evaluated by doing sums sequentially.<sup>16,18</sup> The sequential summation idea exploits the structure of the direct product basis. Some pruned bases do have exploitable structure and can be used with sequential summation.<sup>30,31,33,39,41</sup> A basis built as described in Section II does not have exploitable structure.

In the absence of exploitable structure, one way to efficiently evaluate matrix-vector products is to use a mapping between  $\mathbf{n} = [n_1, \dots, n_c, \dots, n_D]$ , which labels a product basis function, and an index  $p$ , which labels the position of a function in a list of retained basis functions,  $p = 1, 2, \dots, N_k$ , where  $N_k$  is the number of retained basis functions.<sup>64</sup> In Ref. 47, we propose a mapping method that works when the basis has no structure. Here we use a mapping<sup>64</sup> that requires less memory but works only when  ${}^c\theta_{n_c}(x_c)$  functions with consecutive  $n_c$  indices are included in the basis. The method can only be used if the Hamiltonian is a SOP. Matrix-vector products are evaluated term by term and, for each term, factor by factor. We compute eigenvalues of  $\mathbf{H}$ , where  $\mathbf{H} = \sum_{\ell} \mathbf{H}_{\ell}$ . To explain the ideas, we shall focus on a single term. In a direct product basis,

$$\mathbf{H}_{\ell} = {}^1\mathbf{H}^{\ell} \otimes {}^2\mathbf{H}^{\ell} \otimes \dots \otimes {}^D\mathbf{H}^{\ell}. \quad (9)$$

Many of the  ${}^c\mathbf{H}^{\ell}$ ,  $c = 1, 2, \dots, D$  factors are identity matrices. Because the PES is a Taylor series, some of the  ${}^c\mathbf{H}^{\ell}$  are  $\mathbf{x}_c^i$ ,  $i = 1, 2, 3, 4$ ; others are  $\mathbf{p}_c^2$ . We shall drop the superscript  $\ell$  in the rest of this section. To evaluate the matrix-vector product for a single term, we replace the matrix representing the term with a product of matrices (in the pruned multi-dimensional basis) representing its factors. Matrix-vector products for the factors are then done sequentially. For one factor of one term, the required matrix-vector product is

$$v_{n'_1, n'_2, \dots, n'_c, \dots, n'_D} = \sum_{n_c=1}^{N_c} {}^c\mathbf{H}_{n'_c, n_c} z_{n'_1, n'_2, \dots, n'_{c-1}, n_c, n'_{c+1}, \dots, n'_D}, \quad (10)$$

where  $n_c$  is the basis label for coordinate  $c$  and its maximum value is  $N_c$ . Although Eq. (9) is correct only when the full direct product is used, Eq. (10) is correct also when the basis is pruned.

Each  $z$  vector is stored in a 1D array,  $z(p(n'_1, n'_2, \dots, n'_{c-1}, n_c, n'_{c+1}, \dots, n'_D))$ , and the matrix-vector product is

$$v(p' = P_{i',c}) = \sum_{n_c=0}^{U_{p',c}} {}^c\mathbf{H}_{n'_c, n_c} z(p = P_{i'-n'_c+n_c,c}), \quad (11)$$

where  $\mathbf{P}$  is a mapping matrix. The sum must be done for  $i' = 1, 2, \dots, N_k$ . The position  $p'$  of an element of  $v$  is determined from  $i'$  and the mapping matrix  $\mathbf{P}$ . Knowing a value of  $p'$ , one finds values of  $n'_1, n'_2, \dots, n'_c, \dots, n'_D$  from an  $N_k \times D$  table that is denoted as  $A$ . Its  $p$ th row contains the  $D$   $n'_1, n'_2, \dots, n'_c, \dots, n'_D$  labels for the  $p$ th basis function.  $\mathbf{P}$  is constructed so that the  $\mathbf{n}$  that correspond to elements in a column of  $\mathbf{P}$  are in blocks labelled by  $Z_c$ , which is a set of  $D - 1$  indices  $n'_1, n'_2, \dots, n'_{c-1}, n'_{c+1}, \dots, n'_D$  with the  $c$ th index missing.  $i' - n'_c$  in the row index of  $\mathbf{P}$  is the  $i$  value at which a block begins. The blocks are in anti-lexicographic order. For a given element  $p = P_{i',c}$  the corresponding  $\mathbf{n}$  are determined



TABLE I. Table  $A$  for the retained basis functions of the 3D example.

$p$	$n_1$	$n_2$	$n_3$
1	0	0	0
2	1	0	0
3	0	1	0
4	0	0	1
5	1	0	1
6	0	0	2

from the table  $A$ . The elements in a  $P$  column and within a block are ordered so that if  $n_c > n_{c'}$  then  $i > i'$ .  $U_{p',c}$  is the maximum value of  $n_c$  allowed for a given set  $Z_c$ . It is obtained by examining the  $A$  list and determining the maximum  $n_c$  for a set  $Z_c$  and is stored in a matrix  $\mathbf{U}$ .  $U_{pc}$  with different  $p$  but the same  $Z_c$  are identical.  $\mathbf{U}$  is therefore  $N_k \times D$ .

Note that we are not, as is usually done when evaluating matrix-vector products in a pruned basis obtained from a pre-determined pruning condition, separately constraining the transformed and untransformed indices and transforming the input vector into the output vector, index by index sequentially, with  $D + 1$  nested loops.<sup>30,39</sup> Instead, we apply a full-dimensional matrix for each factor. The vector on the LHS of Eq. (11) has only as many elements as there are retained basis functions. This is the strategy of Ref. 64.

In order to make it clear how  $\mathbf{A}$  and  $\mathbf{P}$  are used with Eq. (11), consider the 3D example for which the  $\mathbf{A}$  and  $\mathbf{P}$  matrices are given in Tables I and II. In both cases the matrix that is stored is the bottom right corner of the table. For an  ${}^3H$  factor, according to the third column of  $\mathbf{P}$ , the  $i' = 1, i' = 2, \dots, i' = 6$  elements of  $v$  are labelled by  $p' = 1, p' = 4, p' = 6, p' = 2, p' = 5, p' = 3$ . Using Table I, one determines that, for example, for  $p' = 1$ ,  $n'_3 = 0$  and  $Z_3 = (n_1, n_2) = (0, 0)$ . From Table III, one determines that  $U_{p'=1, c=3}$  is 2. This means that the block size is three and  $n_3 = 0, 1, 2$  occur in the sum of Eq. (11). The  $p$  positions, corresponding to functions labelled by  $n_3 = 0, 1, 2$ , in the block  $Z_3 = (n_1, n_2) = (0, 0)$  are elements in the last column of Table II. They are  $p = 1, 4, 6$ . In this example,  $i' - n'_3 + n_3 = 1, 2, 3$ . In Table I, the rows labelled by  $p = 1, 4, 6$  all have equal  $n'_1, n'_2$  and have  $n_3 = 0, 1, 2$ , respectively, as required.

The index range of the sum in Eq. (11) must not have holes: it begins at zero and ends at  $U_{p',c}$ . If holes occurred, an additional mapping would be required.<sup>47</sup> Adding a basis function may introduce a hole, but we check for holes and fill them in. To fill in holes, when we add a basis function

TABLE II. Table  $P$  for the 3D example.

$i$	$P_{i,1}$	$P_{i,2}$	$P_{i,3}$
1	1	1	1
2	2	3	4
3	3	2	6
4	4	4	2
5	5	5	5
6	6	6	3

TABLE III. Table  $U$  for the 3D example.

$p$	$U_{p,1}$	$U_{p,2}$	$U_{p,3}$
1	1	1	2
2	1	0	1
3	0	1	0
4	1	0	2
5	1	0	1
6	0	0	2

$n_1, \dots, n_{c-1}, m_c, n_{c+1}, \dots, n_D$  for dimension  $c$  we check that the basis functions with  $n_1, \dots, n_{c-1}, i, n_{c+1}, \dots, n_D$  where  $i = 0, m_c - 1$  are already included in the basis. If any of these functions are not included in the current basis, they are added when the new functions are added.

$\mathbf{A}$  is in anti-lexicographic order. Building  $\mathbf{P}$  is more costly than building  $\mathbf{A}$ . Each column of  $\mathbf{P}$  is made from  $\mathbf{A}$  by sorting with a radix sort algorithm. To make column  $c$ , we sort the rows of table  $A$  so that the  $Z_c$  indices are in anti-lexicographic order. For the 3D example this means that for  $c = 2$ , the rows occur in the order (0,0,0), (0,1,0); (1, 0, 0); (0, 0, 1); (1, 0, 1); (0, 0, 2). In this list, blocks are separated by a semicolon. Within a block  $n_c$  begins at zero and increases. The corresponding  $p$  values are 1,3,2,4,5,6. These numbers are in the second column of  $\mathbf{P}$ . Three  $N_k \times D$  matrices need to be stored. Tables III and I take less memory as their elements can be stored as 1 byte integers. The elements of  $\mathbf{P}$  may be large enough that a 4 byte integer is required.

As explained previously, the basis is expanded in stages. The eigenvector components we compute to determine the importance of basis functions are labelled by  $p$  and from  $p$ , we readily obtain  $\mathbf{n}$  using  $\mathbf{A}$ . Each important basis function has  $D$  neighbours that might be added to the basis. Before adding neighbours, one must check to see if a neighbour is already in the basis. This could be done by checking all  $N_k$  basis functions listed in  $\mathbf{A}$ . However, this is quite slow when  $N_k$  is large. Instead, we use the  $\mathbf{T}$  mapping method of Ref. 47 (which is similar to the mapping of Ref. 41) to obtain  $p$  for each neighbour. It requires  $D$  operations to obtain  $p$ . Checking is done between applications of the eigensolver and it is therefore not necessary to simultaneously store in memory the  $\mathbf{T}$  matrices required to use the  $\mathbf{T}$  mapping ( $D \times N_c \times N_k$  numbers) and the Arnoldi vectors generated by ARPACK (see Section IV). The mapping matrices  $\mathbf{T}$  are brought into memory from the disk only after  $C_n$  or  $O_n$  have been computed. The memory required for the Arnoldi vectors is about the same as the memory required for the  $\mathbf{T}$  matrices and therefore the total memory cost of the calculation is not increased by using the mapping to check whether a neighbour is already in the basis.

## IV. TEST CALCULATIONS

Calculations demonstrate that it is possible to compute converged energy levels of 15D and 18D Hamiltonians using the expanding basis method of Section II. This is also possible with the bases obtained from the pruning conditions of Eqs. (2) and (3). In this section we present and compare

these results. One set of calculations is done for bilinearly coupled oscillator Hamiltonians with 6D, 12D, and 18D. A second set of calculations is done for molecules with 3, 4, 5, 6, and 7 atoms for which force field PESs are known. For the expanding basis and also for the bases pruned by imposing Eqs. (2) and (3), matrix-vector products are evaluated as explained in Section III. When using Eqs. (2) and (3), it would be possible to avoid the product approximation by using the ideas of Refs. 30, 39, and 41, but we use Eq. (11) because it is simpler to use the same method for all bases. In all cases, except P<sub>2</sub>O, the maximum value of  $n_c$  is 20. For P<sub>2</sub>O, the maximum value of  $n_c$  is 30.

ARPACK with the reverse communication driver `dnaupd` is used to perform all calculations.<sup>65</sup> The number of columns (NCV) is taken to be three times the size of the number of eigenvalues (NEV) calculated, for each Hamiltonian studied. The default stopping criteria of machine precision are used for the calculations.<sup>65</sup> The Lanczos algorithm is not used because the matrix whose eigenvalues we compute is not symmetric. It is not symmetric because of the error introduced by separately applying the factors of a term in the Hamiltonian. This is discussed at the end of Section II of Ref. 64. One could force the matrix to be symmetric by symmetrizing the operator, but this would increase the number of terms in the Hamiltonian. The only important disadvantage of ARPACK is the need to store many vectors. RULE<sup>66</sup> does not require many vectors, but is not as robust as ARPACK. For the bases used in this paper, storing the vectors is not a problem; for the most costly calculation in this paper only  $\approx 5$  GB of memory is required. Storing the Arnoldi vectors requires significantly more memory than storing **P**, **A**, and **U**. The matrix-vector product is parallelized by computing different elements of the output vector, labelled by  $p'$ , on different threads. All calculations were performed on 12 cores with all vectors and the mapping matrices shared between the cores using OpenMP.

### A. Bilinearly coupled harmonic oscillator

The bilinearly coupled oscillator Hamiltonian for which we compute levels is<sup>6</sup>

$$H = \sum_{i=1}^D \omega_i \left( -\frac{1}{2} \frac{d^2}{dx_i^2} + \frac{1}{2} x_i^2 \right) + \sum_{i=1}^D \sum_{j=i+1}^D f_{ij} x_i x_j, \quad (12)$$

where  $\omega_i = 1000\sqrt{i}$  and  $f_i = 100$ . Its exact solutions are obtained by transforming to normal coordinates. Calculations have been done with  $D = 6, 12$ , and 18. With these parameters, the eigenvalues are of the same order of magnitude as the vibrational wavenumbers of molecules in  $\text{cm}^{-1}$ . For these Hamiltonians, we increase the basis size until the root mean square error RMSE of the lowest 50 energy levels is less than 0.1.

As presented in Figures 1-3, at all basis sizes, levels computed with either the *C* or the *O* adaptively expanded basis are better than those computed with the basis made with Eq. (2). For the  $D = 18$  Hamiltonian, the superiority of the adaptively expanded bases is more pronounced. At most basis sizes, the *O* basis is better than the *C* basis.

Therefore, when computing levels of molecules, we shall use bases expanded using the *O* importance measure. It is also of interest to compare bases with different pre-determined pruning conditions among themselves.  $a_i = 1$  is not always the best choice. The standard polyad choice, with  $a_i = \lfloor \omega_i / \omega_{\min} + 0.5 \rfloor$ , gives a basis that is about as good as the adaptively expanded bases. The  $a_i = \lfloor \sqrt{\omega_i / \omega_{\min}} + 0.5 \rfloor$  choice also works rather well. For certain basis sizes, these pruning schemes outperform one of the basis expansion methods described in Section II. When coupling is weak, it is clear that an  $a_i = 1$  basis is not as good as a  $a_i = \lfloor \omega_i / \omega_{\min} + 0.5 \rfloor$  basis. This is particularly true when the disparity between the largest and smallest frequencies is also large. This is due to the fact that if  $n_1$  is the label for a high-frequency coordinate and  $n_2$  is the label for a coordinate whose frequency is about a factor of 3 smaller, then coupling between the zeroth-order states  $|n_1 n_2\rangle = |10\rangle$  and  $|03\rangle$  is important because the corresponding zeroth-order energies are close. Although bases obtained by using non-unit  $a_i$  are pretty good, when the basis is large enough that the RMSE is less than 0.1, the *O* adaptively expanded basis is always best. It is possible that the basis expansion method would work better if the Hamiltonian matrix were symmetric. For a non-symmetric matrix, a better measure of importance might be derived from elements of both the right and the left eigenvectors. However, because the matrix is nearly symmetric, the *C* and *O* bases work well. As the basis size is increased, the Hamiltonian matrix becomes closer and closer to being symmetric.

### B. Test calculations: P<sub>2</sub>O, CH<sub>2</sub>O, CH<sub>2</sub>NH, CH<sub>3</sub>CN, and C<sub>2</sub>H<sub>4</sub>O

The expanding basis scheme and the bases made from pre-determined pruning conditions are also compared for molecules with 3, 4, 5, 6, and 7 atoms. All of the vibrational energies are calculated using realistic (but SOP) Hamiltonians: a P<sub>2</sub>O Hamiltonian (with the PES of Pouchan *et al.*<sup>67</sup>), a CH<sub>2</sub>O Hamiltonian (using a refitted potential based on Ref. 68), a CH<sub>2</sub>NH Hamiltonian (with the interpretation of Ref. 69 of the potential of Pouchan and Zaki<sup>70</sup>), a CH<sub>3</sub>CN Hamiltonian (using the interpretation of Ref. 41 of the PES of Ref. 71), and a C<sub>2</sub>H<sub>4</sub>O Hamiltonian (using the potential of Ref. 72, but including force constants not published there). In all cases we compare the largest absolute error (LAE) for the lowest 50 (30 for P<sub>2</sub>O) eigenvalues. Basis sizes are increased until all 50 (30 for P<sub>2</sub>O) levels have an error of less than 0.1  $\text{cm}^{-1}$ . To compute the error, we use as “exact” eigenvalues those obtained with a very large *O* basis and that are converged to 0.001  $\text{cm}^{-1}$ .

Figure 2 shows for P<sub>2</sub>O that the *O* basis expansion method gives the most efficient basis. The  $a_i = 1$  pruning condition performs poorly. The F pruned basis is the best if only poor accuracy is required, but its eigenvalues converge more slowly than those computed with the S pruning. The S pruning is better when the required LAE is less than 2  $\text{cm}^{-1}$ . The  $a_i = 1$  pruned basis is poor because the ratio of the largest to smallest frequency is  $\sim 6$ . One of the 30 eigenvalues has 10 quantum in the lowest frequency mode. The  $a_i = 1$  basis must have

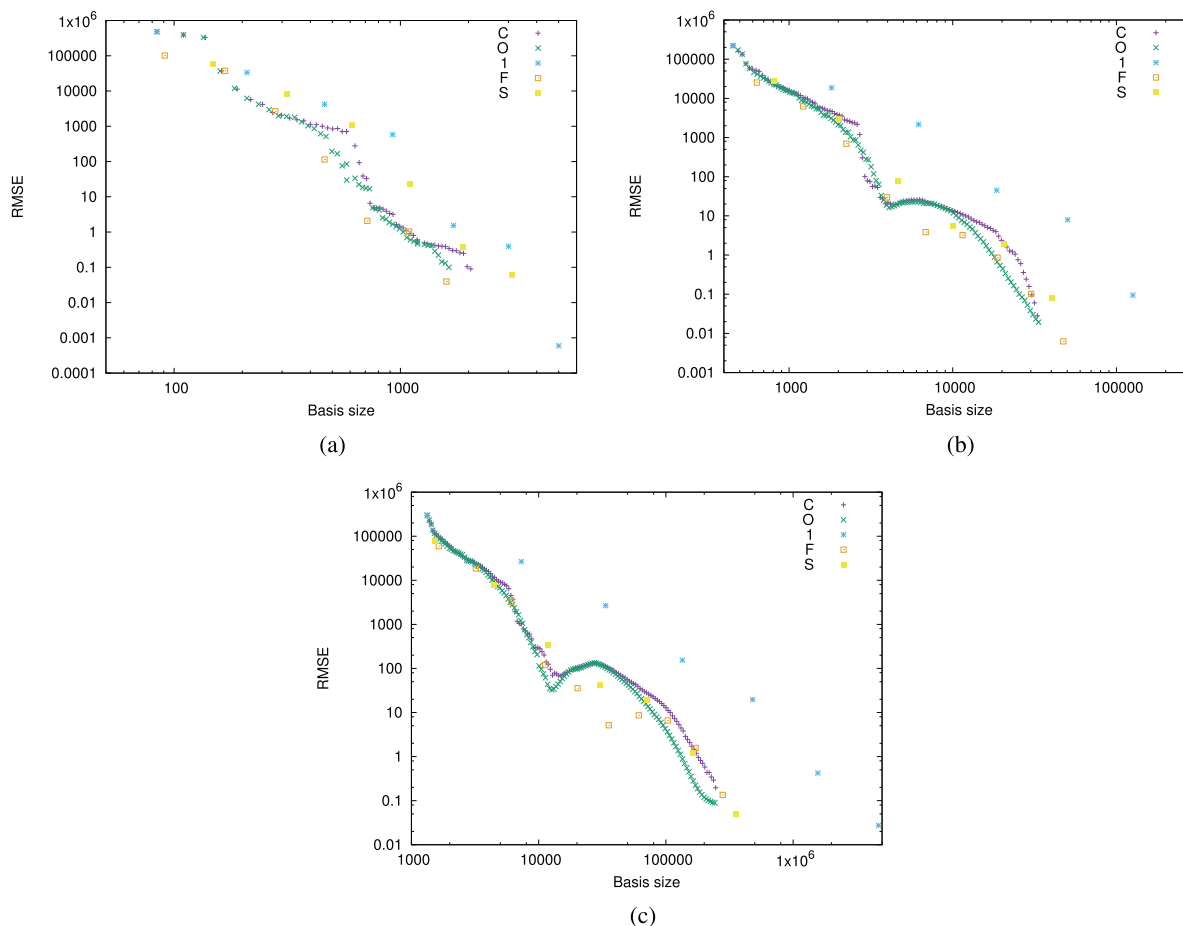


FIG. 1. C and O correspond to the C and O expanded bases, respectively. 1 refers to the  $a_1 = 1$  pruned basis,  $F$  to the  $F$  pruned basis and  $S$  to the  $S$  pruned basis. (a) RMSE of 6D bilinearly coupled eigenproblem. (b) RMSE of 12D bilinearly coupled eigenproblem. (c) RMSE of 18D bilinearly coupled eigenproblem.

at least 286 functions to include one with 10 quantum in the lowest frequency mode. The  $O$  expanded basis with 286 functions is good enough that all 30 levels have convergence errors smaller than  $0.3 \text{ cm}^{-1}$ . Clearly when there is a large difference in harmonic frequencies,  $a_i = 1$  pruning is not best.

For  $\text{CH}_2\text{O}$ ,  $\omega_{\max}/\omega_{\min} \approx 3$ , much smaller than the value for  $\text{P}_2\text{O}$ . Therefore among the lowest 50 eigenvalues, there

are none for which  $n_c > 3$ . As a result, one expects the  $a_i = 1$  basis to be better than for  $\text{P}_2\text{O}$ . As is evident in Fig. 3, the  $O$  expansion scheme is the best and among the pre-determined pruning schemes  $a_i = 1$  is the best. This is consistent with the phase-space analysis of Ref. 8. Halverson and Poirier argue that to achieve high accuracy levels, the  $a_i = 1$  basis is best because the Wigner probability distribution function (PDF) associated with the density operator has the correct

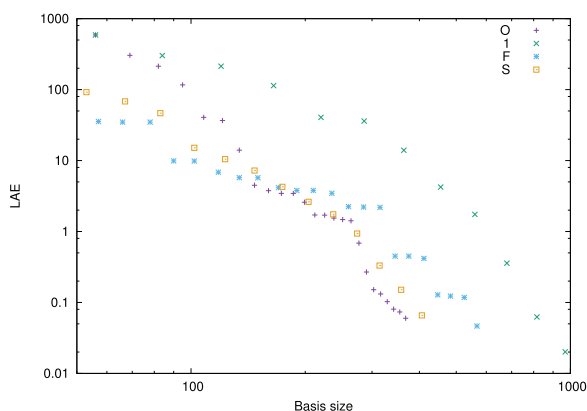


FIG. 2. Largest absolute error of the lowest 30  $\text{P}_2\text{O}$  levels. O corresponds to the O expanded bases, 1 refers to the  $a_1 = 1$  pruned basis,  $F$  to the  $F$  pruned basis, and  $S$  to the  $S$  pruned basis.

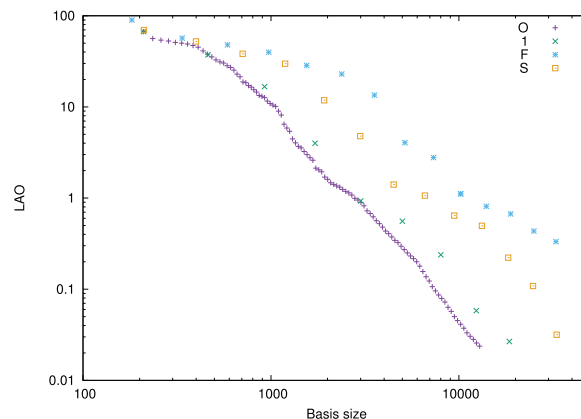


FIG. 3. Largest absolute error of the lowest 50 eigenvalues of  $\text{CH}_2\text{O}$ . O corresponds to the O expanded bases, 1 refers to the  $a_1 = 1$  pruned basis,  $F$  to the  $F$  pruned basis, and  $S$  to the  $S$  pruned basis.

behaviour in the tunnelling region. For a 2D Hamiltonian, the position space projection of PDFs of the density operator for both the basis of Eq. (2) and the exact wavefunctions are approximately circular in the tunnelling region. If a small  $a_i = \lfloor \omega_i/\omega_{min} + 0.5 \rfloor$  basis is sufficient to achieve the desired accuracy, then it is best. However, if the zeroth-order model on which the  $a_i = \lfloor \omega_i/\omega_{min} + 0.5 \rfloor$  basis is predicated is poor, then additional  $a_i = \lfloor \omega_i/\omega_{min} + 0.5 \rfloor$  functions do not go into the important regions of Hilbert space.

For  $\text{CH}_2\text{NH}$ ,  $\omega_{max}/\omega_{min} \approx 3.5$ . Once again, among the first 50 states, none have  $n_c > 3$ . When the frequency disparity is large and when coupling is weak, the F pruning may be better than the  $a_i = 1$  pruning, but that is not the case for  $\text{CH}_2\text{NH}$ . In general, the  $a_i = 1$  basis will work better for molecules with more degrees of freedom because they have more coupling terms and more nearly degenerate zeroth-order levels. Among the lowest 50 states, there are none with large  $n_c$  and the  $a_i = 1$  pruning is the best of the bases with a pre-determined pruning condition. However, as was the case for  $\text{CH}_2\text{O}$ , the basis expansion method is better than bases obtained with any of the pre-determined pruning conditions. To achieve a maximum error of  $0.1 \text{ cm}^{-1}$ , one requires 48 620  $a_i = 1$  functions but only 13 326 expanded-basis functions (Fig. 4).

The  $\text{CH}_3\text{CN}$  potential of Ref. 41 has been used numerous times.<sup>6,7,11,22,41,50,73</sup> Also for this molecule, the expanded-basis is best; see Figure 5. However, the advantage of the expanded basis is more pronounced when the basis size is small. For this Hamiltonian,  $\omega_{max}/\omega_{min} \approx 9$ . Coupling is important enough that F pruning is not the best pruning condition. This was recognized in Ref. 41, where spectroscopic constants  $x_{ij}$  were used to determine good  $a_i$  values. According to Figure 5, among the  $a_i$  choices, the  $a_i$  of Ref. 41 (labelled as G) are best, but  $a_i = 1$  is also better than the F and S prunings. A maximum error of  $0.1 \text{ cm}^{-1}$  is achieved using an expanded basis with only 106 209 functions. Using  $a_i = 1$  pruning, one requires 1 352 078 basis functions and with S pruning, one requires over 1 211 394 basis functions. The  $a_i$  of Ref. 41 require 982 335 basis functions. The expanded basis is therefore an order of magnitude smaller than the best basis obtained from a pruning condition. In this case, the S and  $a_i = 1$  pruning

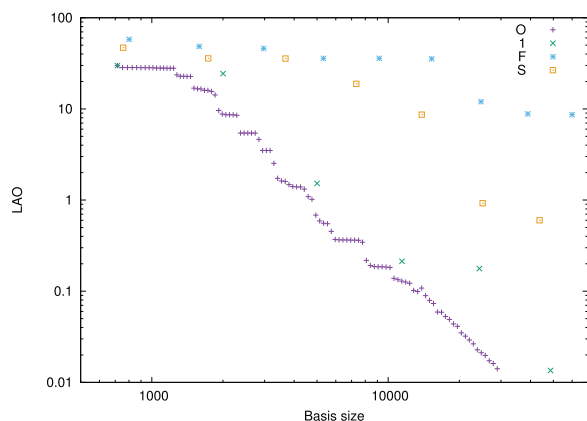


FIG. 4. Largest absolute error of lowest 50 eigenvalues of  $\text{CH}_2\text{NH}$ . O corresponds to the O expanded bases, 1 refers to the  $a_i = 1$  pruned basis, F to the F pruned basis, and S to the S pruned basis.

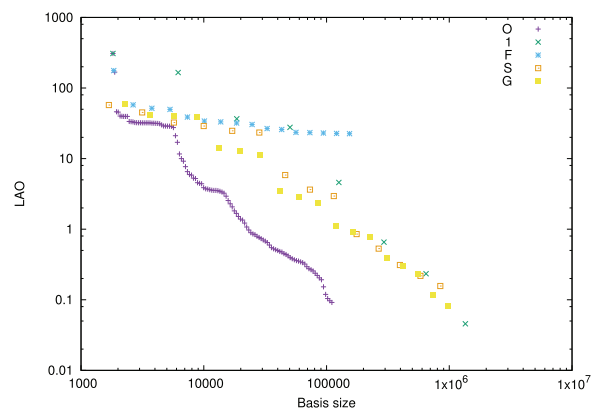


FIG. 5. Largest absolute error of lowest 50 eigenvalues of  $\text{CH}_3\text{CN}$ . O corresponds to the O expanded bases, 1 refers to the  $a_i = 1$  pruned basis, F to the F pruned basis, and S to the S pruned basis, and G to the  $a_i$  used in Ref. 41.

schemes have similar accuracy. S pruning is more accurate than  $a_i = 1$  pruning for small basis sizes, but it converges more slowly and when the basis size is larger than about  $1 \times 10^6$ , the  $a_i = 1$  pruning is better. This agrees with the analysis of Ref. 8, where it is suggested that  $a_i = 1$  pruning is best when the number of required basis functions is much larger than the number of desired eigenstates.

The ethylene oxide calculation is the most difficult of those reported in this paper. Coupling shifts the lowest 50 levels by between  $-178$  and  $-260 \text{ cm}^{-1}$ . We used the same force constants as Thomas and Carrington.<sup>7</sup> Some of the force constants are missing in Ref. 72.<sup>74</sup> We use the mode numbering in the published paper<sup>72</sup> and not the mode numbering the supplementary material of the same paper. The lowest 50 states, converged to within  $0.1 \text{ cm}^{-1}$ , with the O expanded basis and the  $a_i = 1$  pruned basis are shown in Table IV. The same PES has been used in several calculations; Ref. 7 has references. The fundamental frequencies shown in Table IV are all lower than that of the most accurate calculation to date<sup>7</sup> with the largest difference being  $1 \text{ cm}^{-1}$ , for  $\nu_2 = 1$ . Due to the importance of the coupling and the size of the required basis, we expect the  $a_i = 1$  basis to be better than the F and S pruned bases. To assess convergence we compared  $a_i = 1$  and expanded basis eigenvalues. When we stopped increasing the basis sizes, the maximum absolute value of the negative differences  $E_{expanded} - E_{a_i=1}$  was  $0.0066 \text{ cm}^{-1}$  (for state 13) and the maximum of the positive differences  $E_{expanded} - E_{a_i=1}$  was  $0.0058 \text{ cm}^{-1}$  (for state 39). The  $a_i = 1$  basis then had 3 268 760 functions and the expanded basis had 2 955 289 functions. These bases have many more than 90 000 functions, the number of basis functions required to converge the lowest 50 energy levels of the bilinearly coupled oscillator Hamiltonian with the same number of coordinates to the same accuracy. We note that it is difficult to assess convergence of the  $a_i = 1$  calculation by comparing eigenvalues computed with two basis sizes. The 50 lowest eigenvalues computed using  $a_i = 1$  bases with 3 268 760 and 7 726 160 functions differ by at most  $0.001 \text{ cm}^{-1}$ ; however, one of them is more than  $0.006 \text{ cm}^{-1}$  lower using the O expanded basis. Comparing levels computed with two types of pruning schemes is more likely to give a realistic measure



TABLE IV. The lowest 50 vibrational energies of ethylene oxide.

State	Eq. (2)	Eq. (2)	O Expand	State	Eq. (2)	Eq. (2)	O Expand
Basis size	3 268 760	7 726 160	2 955 289	Basis size	3 268 760	7 726 160	2 955 289
1 $v_0$	12 461.468	12 461.467	12 461.467	26	14 400.405	14 400.404	14 400.399
2 $v_{15}$	13 254.110	13 254.110	13 254.107	27	14 404.632	14 404.631	14 404.643
3 $v_{12}$	13 283.378	13 283.378	13 283.383	28	14 422.570	14 422.569	14 422.594
4 $v_5$	13 339.743	13 339.743	13 339.752	29	14 431.328	14 431.328	14 431.360
5 $v_9$	13 478.613	13 478.612	13 478.616	30	14 458.135	14 458.134	14 458.161
6 $v_4$	13 582.642	13 582.642	13 582.646	31	14 459.807	14 459.807	14 459.836
7 $v_{11}$	13 585.094	13 585.094	13 585.099	32	14 481.865	14 481.865	14 481.904
8 $v_{14}$	13 607.192	13 607.191	13 607.200	33	14 484.802	14 484.801	14 484.843
9 $v_7$	13 609.425	13 609.425	13 609.433	34	14 492.473	14 492.473	14 492.479
10 $v_3$	13 732.249	13 732.248	13 732.258	35	14 521.256	14 521.255	14 521.266
11 $v_{10}$	13 928.798	13 928.798	13 928.813	36	14 547.333	14 547.332	14 547.371
12 $v_2$	13 956.633	13 956.632	13 956.643	37	14 588.268	14 588.267	14 588.265
13	14 048.656	14 048.655	14 048.589	38	14 594.673	14 594.672	14 594.674
14	14 072.434	14 072.434	14 072.427	39	14 601.668	14 601.668	14 601.724
15	14 102.406	14 102.406	14 102.417	40	14 612.489	14 612.489	14 612.506
16	14 131.674	14 131.674	14 131.682	41	14 625.692	14 625.692	14 625.722
17	14 156.386	14 156.386	14 156.417	42	14 693.511	14 693.510	14 693.515
18	14 216.133	14 216.133	14 216.183	43	14 700.842	14 700.841	14 700.842
19	14 266.781	14 266.780	14 266.755	44	14 706.759	14 706.758	14 706.764
20	14 293.586	14 293.585	14 293.591	45	14 708.592	14 708.591	14 708.600
21	14 350.357	14 350.357	14 350.380	46	14 724.259	14 724.259	14 724.251
22	14 368.106	14 368.106	14 368.081	47	14 727.186	14 727.185	14 727.209
23	14 370.049	14 370.049	14 370.010	48	14 727.207	14 727.206	14 727.224
24	14 388.558	14 388.557	14 388.543	49	14 734.654	14 734.654	14 734.670
25	14 398.770	14 398.770	14 398.774	50	14 742.820	14 742.820	14 742.791

of convergence than comparing levels computed with two basis sizes and a single pruning scheme.

## V. CONCLUSION

In this paper, we report a pruned-basis calculation of well-converged vibrational levels of a semi-rigid molecule with 7 atoms. It requires about 5 GB of memory and is done on a fairly standard computer (and could be done on many laptops). It is very clear, and has been clear for a long time, that by including only the important functions of a direct product basis in the working basis, one can reduce both the memory and the CPU cost of solving the Schroedinger equation to calculate a vibrational spectrum.<sup>12,30,35,39,41,75</sup> Indeed, Halverson and Poirier have used a pruned basis, to compute many vibrational levels of benzene,<sup>8</sup> although it is hard to know how well converged their levels are.

The advantage of keeping in the basis only the basis functions that actually contribute to the desired wavefunctions is obvious. What is difficult is implementing this strategy. One way to do it is to use powerful parallel computers and direct methods to diagonalize large matrices. When more than about 10 000 eigenvalues are desired this may be the best way.<sup>8,50</sup> It is also possible to use a pruned basis with an iterative eigensolver. This significantly reduces the memory cost. Using an iterative eigensolver in conjunction with a pruned basis is not simple because pruning spoils the direct-product structure of the basis which is key to the efficiency of matrix-vector products.<sup>15,16</sup>

There are two established methods for evaluating matrix-vector products in a pruned basis. The first exploits structure of the pruned basis.<sup>30,39</sup> It cannot be used unless the pruning condition itself has structure. The second uses a mapping and works regardless of the recipe chosen for selecting basis functions to retain.<sup>47,64</sup> Having a method for evaluating matrix-vector products that does not rely on structure of the pruned basis is important if it is possible to find unstructured pruned bases that are smaller than their structured counterparts.

In this paper we present a new method for selecting multidimensional harmonic oscillator functions to include in the basis. We begin with a small basis and add functions in stages. From eigenvectors at stage  $k$ , we determine which functions in the stage  $k$  basis are the most important and we add their “neighbours” to the stage  $k$  basis to make the stage  $k + 1$  basis. Other authors have used similar ideas to expand a basis.<sup>11,43–45,49,76</sup> For model problems and 5 molecules of various sizes, we have demonstrated that the expanded basis is better than bases obtained from several pre-determined pruning conditions. In some cases the expanded basis is significantly better than the best pruned basis. In other cases, structured pruned bases are nearly as good. The  $a_i = 1$  basis works well when (1) a large basis is required to compute the levels of interest to the desired accuracy, (2) the ratio of the largest to the smallest harmonic frequency is not large, and (3) the coupling is important. On the other hand, it is clear that when coupling is unimportant, a basis with  $a_i \approx \omega_i$  must be better than the basis with  $a_i = 1$ . The  $a_i \approx \omega_i$  choice is motivated by a zeroth-order model that is of course poor

when coupling is important. When coupling is very strong, pre-determined pruning conditions of the Eq. (3) form must fail.

It would be possible to improve the method for expanding the basis. When adding neighbours of important basis functions, it might be worthwhile to assess the importance of the functions being added. One could also remove unimportant functions from the basis as it expands. It would be possible to make use of the iterative eigensolver more efficient. One option is to use RULE, a method for computing eigenvalues of a non-symmetric matrix that does not require Arnoldi vectors.<sup>66</sup> Another option is to symmetrize the Hamiltonian operator so that, despite the product approximation used when evaluating matrix-vector products, the matrix whose eigenvalues are computed is symmetric and the standard Lanczos algorithm can be used.<sup>64</sup> The general scheme used in this paper for evaluating matrix-vector products works only if the PES is a SOP. Although there are several methods for making a SOP PES,<sup>77–81</sup> it is obviously important to be able to use pruned basis sets with PESs that are not in SOP form. When the pruned basis has structure, this is possible.<sup>32,33,41</sup>

## ACKNOWLEDGMENTS

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