Using symmetry-adapted optimized sum-of-products basis functions to calculate vibrational spectra

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Abstract

Vibrational spectra can be computed without storing full-dimensional vectors by using low-rank sum-of-products (SOP) basis functions. We introduce symmetry constraints in the SOP basis functions to make it possible to separately calculate states in different symmetry subgroups. This is done using a power method to compute eigenvalues and an alternating least squares method to optimize basis functions. Owing to the fact that the power method favours the convergence of the lowest states, one must be careful not to exclude basis functions of some symmetries. Exploiting symmetry facilitates making assignments and improves the accuracy. The method is applied to the acetonitrile molecule.

1. Introduction

It is difficult to calculate vibrational spectra of molecules with more than four atoms without making approximations. The most systematic and general method involves computing eigenvalues and eigenvectors of a basis representation of the corresponding Hamiltonian operator. The Hamiltonian matrix is often so large that it is best to use iterative eigensolvers. A direct product (DP) basis is convenient because it facilitates the evaluation of the matrix-vector products required to use an iterative eigensolver [1]. The basis functions are products of functions of a single coordinate. To use an iterative eigensolver, there is no need to store a matrix, but it *is* necessary to store a few vectors. Because the size of the DP basis is n^D, where n is a representative number of 1D basis functions for each coordinate and D the number of coordinates, even storing vectors requires more memory than is available on most computers, if $D > 12$ (i.e. 6 atoms).

The size of the basis, and of the vectors, can be reduced by optimizing 1-D basis functions [2], or by forgoing the advantages of a DP basis and using

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instead contracted basis functions [3] or by pruning a large DP basis [4, 5]. Another strategy is to use sum-of-products (SOP) basis functions which can be represented in a primitive DP basis as a tensor in what is called CP format [6]. The key idea is that a SOP basis function can be written,

$$F(q_1, \ldots, q_D) \simeq \sum_{i_1=0}^{n_1-1} \cdots \sum_{i_D=0}^{n_D-1} F_{i_1 i_2 \ldots i_D} \prod_{k=1}^{D} \theta_{i_k}^k(q_k), \tag{1}$$

where $\theta_{i_k}^k(q_k)$ is a primitive basis function, with

$$F_{i_1 i_2 \ldots i_D} \simeq \sum_{\ell=1}^{R} \prod_{k=1}^{D} f_{i_k}^{(\ell,k)} \ . \tag{2}$$

Storing $F_{i_1 i_2 \ldots i_D}$ requires only storing one-dimensional vectors $\mathbf{f}^{(\ell,k)}$ [7, 8]. The SOP basis functions are not contracted in the usual sense; they are also not selected from a DP basis. All the primitive DP basis functions can contribute to a single SOP basis function. One must choose SOP basis functions that span a space which includes the wavefunctions of interest. This is the main idea of the reduced rank block power method (RRBPM) introduced in Ref. [7]. Its key advantage is that the memory cost of the method scales as $\mathcal{O}(nD)$. This makes it possible to calculate energy levels and wavefunctions of molecules with 20 degrees of freedom with a few GB of memory.

In Ref. [7] symmetry is not used. It is important to take advantage of symmetry for two reasons. (1) Exploiting symmetry makes it possible to assign states one computes to irreducible representations of the symmetry group of the Hamiltonian operator [9, 10]. (2) Exploiting symmetry makes it possible to reduce the CPU and memory cost of computing a spectrum. In the RRBPM case, the CPU cost is reduced because the number of power iterations decreases when computing levels of a single irrep since the effective density of states decreases.

In this letter we introduce the basic ideas required to exploit symmetry. In section 2 we present the theoretical arguments and we explain how to construct efficient symmetry-constrained SOP basis functions. The method is then applied to a realistic 12D Hamiltonian in section 3. We show that reflection in a σ_v plane can be used to improve the calculation of vibrational levels of acetonitrile, without jeopardizing the memory advantage of the RRBPM.

2. Theory

2.1. Reduced-rank block power method (RRBPM)

We assume that the potential energy surface (PES) is known and is in SOP form. We label the coordinates q_k, $k = 1 \ldots D$. There is a primitive basis, $\theta_{i_k}^k(q_k)$, $i_k = 0, \ldots, n_k - 1$, for each coordinate. The SOP basis functions are of

the form of Eq. (1) with $F_{i_1 i_2 \ldots i_D}$ as in Eq. (2). The memory cost is RDn. Each basis function can be written

$$F(q_1, \ldots, q_D) = \sum_{\ell=1}^{R} \prod_{k=1}^{D} \phi^{(\ell,k)}(q_k) = \sum_{\ell=1}^{R} \prod_{k=1}^{D} \left(\sum_{i_k=0}^{n_k-1} f_{i_k}^{(\ell,k)} \theta_{i_k}^{k}(q_k) \right) . \qquad (3)$$

The SOP basis vectors, each of which has the form of Eq. (2), are made using a shifted block power method. This requires applying $(\mathbf{H} - \sigma\mathbf{I})$ to each vector in a block. σ depends on the block size and the largest eigenvalue of $\mathbf{H}$ [7]. Calculations are fast because only one-dimensional matrix-vector products are needed. Each application of $(\mathbf{H} - \sigma\mathbf{I})$ to a vector increases its rank by a factor of $(P+1)$, where P is the number of terms in the Hamiltonian. In the RRBPM, the rank of vectors is reduced, after each step that increases their rank, by using an alternating least square method described in Ref. [11]. To reduce the rank of $\mathbf{F}^{\text{old}}$ from R^{old} to R^{new}, the ALS algorithm uses an iterative process to find vectors ${}^{\text{new}}f_{i_k}^{(\ell,k)}$ to minimize $\| \mathbf{F}^{\text{new}} - \mathbf{F}^{\text{old}} \|$. This is done for each coordinate successively. This gives rise to a succession of systems of R^{new} linear equations to be solved with n_k different right-hand-sides for each coordinate q_k.

The main steps in the algorithm are:

- Apply $(\mathbf{H} - \sigma\mathbf{I})$ in parallel over a block of SOP vectors
- Reduce the rank using alternating least squares.
- Every 10 to 20 iterations, orthogonalize the vectors, make a matrix representing $\hat{H}$ in this SOP basis set.
- Diagonalize the matrix to obtain eigenvalues and eigenvectors .
- Reduce the rank, update the vectors and iterate.

Unless special precautions are taken, an SOP basis, generated as explained above, cannot be ordered so that the corresponding Hamiltonian matrix is block diagonal. Our goal in this letter is to demonstrate that it is possible to make a symmetrized SOP basis and use it to obtain accurate energy levels.

2.2. Symmetric and antisymmetric sum-of-products basis functions

The most common way to take advantage of symmetry when computing a spectrum is to introduce symmetry-adapted basis functions in which the Hamiltonian matrix is block-diagonal. When using an iterative eigensolver this is often not the best approach. The reason is that evaluating matrix-vector products with a matrix obtained by representing the Hamiltonian operator in a symmetry-adapted basis may be costly. The most straightforward approach when using an iterative eigensolver is to do different calculations for start vectors with different symmetries [12, 1] This works because the Hamiltonian is invariant with respect to all symmetry operations and therefore applying the Hamiltonian to a vector does not change its symmetry. In this letter we use

this idea to make symmetry-adapted SOP basis functions from matrix-vector products.

The SOP basis functions we use transform like irreducible representations (irreps) of a sub-group of the full molecular symmetry group. We shall explain the ideas for a sub-group $\{R, E\}$, where E is the identity operation. We assume that all of the coordinates are symmetric or antisymmetric, i.e.,

$$q_k \text{ symmetric } : \quad q_k \stackrel{R}{\rightarrow} q_k, \tag{4}$$

$$q_k \text{ antisymmetric } : \quad q_k \stackrel{R}{\rightarrow} -q_k. \tag{5}$$

The primitive 1-D basis functions are chosen so that some are even and some are odd. We use a harmonic primitive basis so

$$\theta^k_{i_k=even}(q_k) \stackrel{q_k \rightarrow -q_k}{\longrightarrow} \theta^k_{i_k=even}(q_k), \tag{6}$$

$$\theta^k_{i_k=odd}(q_k) \stackrel{q_k \rightarrow -q_k}{\longrightarrow} -\theta^k_{i_k=odd}(q_k). \tag{7}$$

This means that some basis functions change sign (i.e. are symmetric) and others do not (i.e. are antisymmetric) when R is applied. All $\theta^k_{i_k}(q_k)$ of symmetric coordinates are symmetric. $\theta^k_{i_k=even}(q_k)$ of antisymmetric coordinates are symmetric. $\theta^k_{i_k=odd}(q_k)$ of antisymmetric coordinates are antisymmetric. When R is applied to a primitive D-d basis function, $\prod_{k=1}^{D} \theta^k_{i_k}(q_k)$, its sign changes if the number of factors for which i_k is odd is itself odd, otherwise applying R to $\prod_{k=1}^{D} \theta^k_{i_k}(q_k)$ does not change the sign. The D-d basis is therefore split into two parts, one symmetric and one antisymmetric. Throughout the discussion we use e and o to indicate even (symmetric) or odd (antisymmetric) functions (coordinates).

Knowing the symmetry properties of the primitive basis functions enables us to choose SOP start vectors that are symmetric or antisymmetric. The symmetry depends on which $\theta^k_{i_k}(q_k)$ in Eq. 3 have nonzero coefficients. An SOP vector is antisymmetric (symmetric) if applying R to the corresponding function changes (does not change) its sign. This makes it possible to separately compute even and odd wavefunctions. To illustrate the ideas, consider an example with three coordinates of which q_1 and q_2 are antisymmetric coordinates and q_3 is a symmetric coordinate. If we consider a single product function whose constituent 1-D vectors ($\mathbf{f}^{(\ell=1,k)} = \mathbf{f}^{(k)}$) are

$$f^{(1)}_{i_1} = \begin{pmatrix} f^{(1)}_0 \\ 0 \\ f^{(1)}_2 \\ 0 \\ f^{(1)}_4 \\ \vdots \end{pmatrix}, \quad f^{(2)}_{i_2} = \begin{pmatrix} f^{(2)}_0 \\ 0 \\ f^{(2)}_2 \\ 0 \\ f^{(2)}_4 \\ \vdots \end{pmatrix} \quad \text{and} \quad f^{(3)}_{i_3} = \begin{pmatrix} f^{(3)}_0 \\ f^{(3)}_1 \\ f^{(3)}_2 \\ f^{(3)}_3 \\ f^{(3)}_4 \\ \vdots \end{pmatrix} \tag{8}$$

then the function represented by $\prod_{k=1}^{3} f^{(k)}_{i_k}$ is necessarily symmetric because $f^{(k)}_{i_k} = 0, k = 1, 2$ if i_k is odd. We denote the function represented by $\prod_{k=1}^{3} f^{(k)}_{i_k}$

as *ee*. Of course, functions made from

$$f^{(1)}_{i_1} = \begin{pmatrix} 0 \\ f^{(1)}_1 \\ 0 \\ f^{(1)}_3 \\ 0 \\ \vdots \end{pmatrix} , \quad f^{(2)}_{i_2} = \begin{pmatrix} 0 \\ f^{(2)}_1 \\ 0 \\ f^{(2)}_3 \\ 0 \\ \vdots \end{pmatrix} \quad \text{and} \quad f^{(3)}_{i_3} = \begin{pmatrix} f^{(3)}_0 \\ f^{(3)}_1 \\ f^{(3)}_2 \\ f^{(3)}_3 \\ f^{(3)}_4 \\ \vdots \end{pmatrix} , \quad (9)$$

are also symmetric. We call this an *oo* function. Similarly, antisymmetric functions can be *eo* or *oe*. We denote these *eo* and *oe* functions. A general antisymmetric function is a sum of functions of both these "types".

If there are M antisymmetric coordinates then a type will be labelled by M letters and there are $T = 2^{M-1}$ different types. In formulae, types will be labelled by an integer t, for example $ee \Leftrightarrow t = 1$ and $oo \Leftrightarrow t = 2$. A general $F_{i_1 i_2 \ldots i_D}$ is a sum of SOP, one for each type,

$$F_{i_1 i_2 \ldots i_D} \simeq \sum_{t=1}^{T} \sum_{\ell_t=1}^{R_t} \prod_{k=1}^{D} f^{(\ell_t,k)}_{i_k} . \quad (10)$$

The number of terms of type t in the SOP is denoted R_t with $\sum_{t=1}^{T} R_t = R$, R being the total rank of $F_{i_1 i_2 \ldots i_D}$.

2.3. Symmetry-adapted RRBPM

As explained at the beginning of the previous subsection, it should be possible to compute states of a given symmetry by using a block of start vectors each of which has the right symmetry. For the example with three coordinates, one can calculate symmetric states by starting with a block of symmetric vectors. The existence of different types, all of which are symmetric, complicates this somewhat. There are symmetric states for which the largest term in an equation like Eq. (3) has a product of an even function of q_1 and an even function of q_2 and other symmetric states for which the largest term in an equation like Eq. (3) has a product of an odd function of q_1 and an odd function of q_2. To favour the convergence of both types of states, we use start vectors that are low-rank SOP with one term of each type. Going back to the 3D example, this choice corresponds to taking a start vector with two terms, one of which is made from the vectors of (8) and the other from the vectors of (9). In this paper the non-zero components are random.

The ALS reduction is a crucial step in the RRBPM. The reduction begins with initial $f^{(\ell_t,k)}_{i_k}$ values, which are optimized to give the best ${}^{\text{new}}f^{(\ell_t,k)}_{i_k}$. When random initial values are used, $\mathbf{F}^{\text{new}}$ does not have symmetry properties, even when $\mathbf{F}^{\text{old}}$ does. It would be possible to obtain an $\mathbf{F}^{\text{new}}$ of a particular symmetry (e.g., for the 3-d example, symmetric) by using initial $f^{(\ell_t,k)}_{i_k}$ chosen so that each term in $\mathbf{F}^{\text{inital}}$ is of one of the types consistent with that symmetry

(e.g., for the 3-d example, ee or oo). However, according to the equations of Ref. [11], when one attempts to reduce a SOP of type t' using an $\mathbf{F}^{\text{inital}}$ that is type t, with $t' \neq t$, one obtains new $f_{i_k}^{(\ell_t,k)}$ that are identically zero. It is therefore better to reduce each term in

$$F_{i_1 i_2 \ldots i_D} = \sum_t F^t_{i_1 i_2 \ldots i_D} = \sum_{t=1}^{T} \sum_{\ell_t=1}^{R_t} \prod_{k=1}^{D} f_{i_k}^{(\ell_t,k)} \tag{11}$$

with initial $f_{i_k}^{(\ell_t,k)}$ chosen so that the initial $F^t_{i_1 i_2 \ldots i_D}$ is of the same type. For the 3-D example in the previous subsection this means that to reduce the ee terms one must use an initial $F^t_{i_1 i_2 \ldots i_D}$ that is ee.

Separately reducing the terms in Eq. (11) also has the advantage that it enables us to ensure that all types are represented in all vectors. If one does not reduce separately, even when each start vector is a sum of terms of different types, the terms of the vectors generated by the RRBPM can be mostly or exclusively vectors of one type. This is due to the fact that the RRBPM drives vectors towards the ground state. To ensure that each RRBPM vector will have contributions from all types we reduce separately and impose R_t^{new} values. This can be done by separating and then reducing and merging:

$$\begin{array}{c}
\sum_{t=1}^{T} \sum_{\ell_t=1}^{R_t^{\text{old}}} \prod_{k=1}^{D} {}^{\text{old}} f_{i_k}^{(\ell_t,k)} \\
\swarrow \quad \downarrow \text{(separation)} \quad \downarrow \quad \searrow \\
\sum_{\ell_1=1}^{R_1^{\text{old}}} \prod_{k=1}^{D} {}^{\text{old}} f_{i_k}^{(\ell_1,k)} \cdots \sum_{\ell_t=1}^{R_t^{\text{old}}} \prod_{k=1}^{D} {}^{\text{old}} f_{i_k}^{(\ell_t,k)} \cdots \sum_{\ell_T=1}^{R_T^{\text{old}}} \prod_{k=1}^{D} {}^{\text{old}} f_{i_k}^{(\ell_T,k)} \\
\downarrow \quad \downarrow \text{ (ALS reductions) } \downarrow \quad \downarrow \\
\sum_{\ell_1=1}^{R_1^{\text{new}}} \prod_{k=1}^{D} {}^{\text{new}} f_{i_k}^{(\ell_1,k)} \cdots \sum_{\ell_t=1}^{R_t^{\text{new}}} \prod_{k=1}^{D} {}^{\text{new}} f_{i_k}^{(\ell_t,k)} \cdots \sum_{\ell_T=1}^{R_T^{\text{new}}} \prod_{k=1}^{D} {}^{\text{new}} f_{i_k}^{(\ell_T,k)} \\
\searrow \quad \downarrow \text{ (merging) } \downarrow \quad \swarrow \\
\sum_{t=1}^{T} \sum_{\ell_t=1}^{R_t^{\text{new}}} \prod_{k=1}^{D} {}^{\text{new}} f_{i_k}^{(\ell_t,k)}
\end{array} \tag{12}$$

$R^{\text{new}} = \sum_t R_t^{\text{new}}$ is fixed before the calculation is started, but how do we choose R_t^{new}? We have considered three strategies. One option is

$$R_1^{\text{new}} = R_t^{\text{new}} = \cdots = R_T^{\text{new}}. \tag{13}$$

We call this reduction strategy 1. Reduction strategy 1 does not take into account that we should minimize errors introduced by rank reduction. The error introduced by reduction with equal partial ranks will be large for vectors dominated by one type. We therefore also test strategy 2 in which the partial ranks R_t^{new} are adjusted, for each $\mathbf{F}$, before each reduction so that they are proportional to

$$|\langle \mathbf{F}^{\text{old},t} | \mathbf{F}^{\text{old}} \rangle| = |\sum_{\ell_t=1}^{R_t^{\text{old}}} \sum_{t'=1}^{T} \sum_{\ell_{t'}=1}^{R_{t'}^{\text{old}}} \prod_{k=1}^{D} \langle {}^{\text{old}}\mathbf{f}^{(\ell_t,k)} | {}^{\text{old}}\mathbf{f}^{(\ell_{t'},k)} \rangle|. \tag{14}$$

To avoid losing one of the types, and therefore part of the space spanned by the primitive DP basis, we keep at least one term of each type even if the

weight in Eq. (14) is very small. Adjusted partial ranks minimize reduction error. However, they tend to lock in the character of the vectors. Near the end of the calculation, when the $\mathbf{F}$ are nearly eigenvectors, and changing little when $(\mathbf{H}-\sigma\mathbf{I})$ is applied there is no reason not to lock in the character. At the beginning of the calculation, when the vectors change a lot after application of $(\mathbf{H}-\sigma\mathbf{I})$, it is important to allow the character of the vectors to change and minimizing reduction error is less important. To ensure that the character is not locked in too early in the calculation we also use strategy 3. In strategy 3, the partial ranks are fixed until the number of iterations is large enough that the dominant types of the SOP basis vectors, which are becoming closer and closer to the eigenvectors, and the corresponding eigenvalues are stabilized and then we use partial ranks determined by Eq. (14). Fixing the partial ranks at the beginning of the calculation ensures that some types are not pushed out of the basis.

The memory cost of the symmetry-adapted RRBPM is very similar to that of the original RRBPM. It scales as $\mathcal{O}(nDBPR^{\text{new}})$ where n is a representative number of primitive basis functions for a single coordinate, D is the number of coordinates, B is the block size, P is the number of terms in the Hamiltonian and R^{new} is the total reduction rank. For a subgroup with two irreps, the symmetry-adapted RRBPM makes it possible to reduce B by about a factor of 2. In other words twice as many eigenstates can be obtained, with the same amount of memory, with the symmetry-adapted RRBPM as with the original RRBPM. Moreover, half the components of $f_{i_k}^{(\ell_t,k)}$ for antisymmetric coordinates are zero and do not need to be stored in memory.

3. Results and discussion

As an illustrative example we have calculated vibrational eigenstates of the acetonitrile molecule (CH_3CN), a 12D problem. We use a Hamiltonian in normal coordinates,

$$\begin{aligned} H(q_1,\ldots,q_{12}) &= -\frac{1}{2}\sum_{i=1}^{12}\omega_i\frac{\partial^2}{\partial q_i^2}+\frac{1}{2}\sum_{i=1}^{12}\omega_i q_i^2+\frac{1}{6}\sum_{i=1}^{12}\sum_{j=1}^{12}\sum_{k=1}^{12}\phi_{ijk}^{(3)}q_iq_jq_k \\ &\quad+\frac{1}{24}\sum_{i=1}^{12}\sum_{j=1}^{12}\sum_{k=1}^{12}\sum_{\ell=1}^{12}\phi_{ijk\ell}^{(4)}q_iq_jq_kq_\ell. \end{aligned} \tag{15}$$

The SOP PES is deduced from the quartic force field potential of Bégué *et al.* [13] by Avila and Carrington [14]. Coordinates q_1 to q_4 are non degenerate, coordinates q_5 and q_6 are members of a doubly degenerate pair as are q_7 and q_8; q_9 and q_{10}; and q_{11} and q_{12}.

For CH_3CN the symmetry group is C_{3v} with irreducible representations (irreps) A_1, A_2, and E. We use a subgroup and divide the basis into two blocks. The non-degenerate normal coordinates, q_1, q_2, q_3, and q_4 and the degenerate normal coordinates (q_5, q_7, q_9, q_{11}), are all symmetric with respect to

reflection in a σ_v plane, whereas the degenerate normal modes $(q_6, q_8, q_{10}, q_{12})$, are antisymmetric with respect to the same operation [15]. The primitive basis set of products of harmonic oscillator basis functions is split into two subsets, one of which contains functions that change sign when σ_v is applied and the other containing functions that do not change sign when σ_v is applied.

According to section 2, two separate calculations can be done. Symmetric wavefunctions (which correlate with A_1 states and half of the E states) are obtained by using SOP basis functions that are sums of terms each of which is one of 8 possible symmetric types. The 8 types are characterized by whether the 1-d functions of $(q_6, q_8, q_{10}, q_{12})$ are even or odd:

$$\begin{aligned}&(e,e,e,e);\ (o,o,o,o);\ (e,e,o,o);\ (o,o,e,e);\\ &(e,o,o,e);\ (o,e,e,o);\ (e,o,e,o);\ (o,e,o,e).\end{aligned} \tag{16}$$

Conversely, antisymmetric wavefunctions (which correlate with A_2 states and half of the E states) are obtained by using SOP basis functions that are sums of terms each of which is one of 8 possible antisymmetric types. The 8 types are also characterized by whether their 1-d functions of $(q_6, q_8, q_{10}, q_{12})$ are even or odd: (e,e,e,o), (o,o,o,e), etc.

Four calculations are presented: RRBPM without symmetry adaptation and $R^{\text{new}} = 30$; symmetry-adapted RRBPM with fixed partial ranks $R_t^{\text{new}} = 8$ (strategy 1); symmetry-adapted RRBPM with partial ranks chosen according to strategy 2 and a total rank $R^{\text{new}} = 30$; and symmetry-adapted RRBPM with partial ranks chosen according to strategy 3 and fixed at $R_t = 8$ at the beginning of the calculation and a total rank of $R^{\text{new}} = 30$ at the end of the calculation. In all cases the number of power iterations is 6000 and the number of ALS iterations is 10. The even and odd calculations done with symmetry-adapted RRBPM are done with a block size of 60. A block size of 70 is used for the calculations with the original RRBPM. These parameters are chosen so that their CPU costs are nearly equal. Separately reducing a SOP with 8 terms for each of the 8 types, i.e. a total SOP with rank 64 is a little less costly than reducing a symmetry-free SOP with rank 30 but matrix-vector products with rank 64 are more costly. 1000 iterations for a block size of 60 take two days using 30 AMD Opteron(tm) 6386 SE CPUs at 2.8GHz.

The convergence of several eigenvalues is shown in fig. 1. They converge well with reduction strategy 1 (fig. 1 (a)). Looking at the lowest eigenvalues and comparing to Smolyak quadrature results of ref. [14], it seems that using strategy 2 improves the accuracy. For example the error on the first transition frequency close to 361 cm^{-1} is 0.05 cm^{-1} using strategy 2 instead of 0.18 cm^{-1} using strategy 1. However, using strategy 2, we observe that some levels converge slowly and others are missing, even when the number of power iterations is large. The high-lying states of the block are particularly affected, see Fig. 1 (b). This appears to be due to the fact that the partial ranks of some types are too small. The Strategy 3 works better. Levels computed with strategy 3 are given in table 1.

The most important advantage of the symmetry-adapted RRBPM is that it

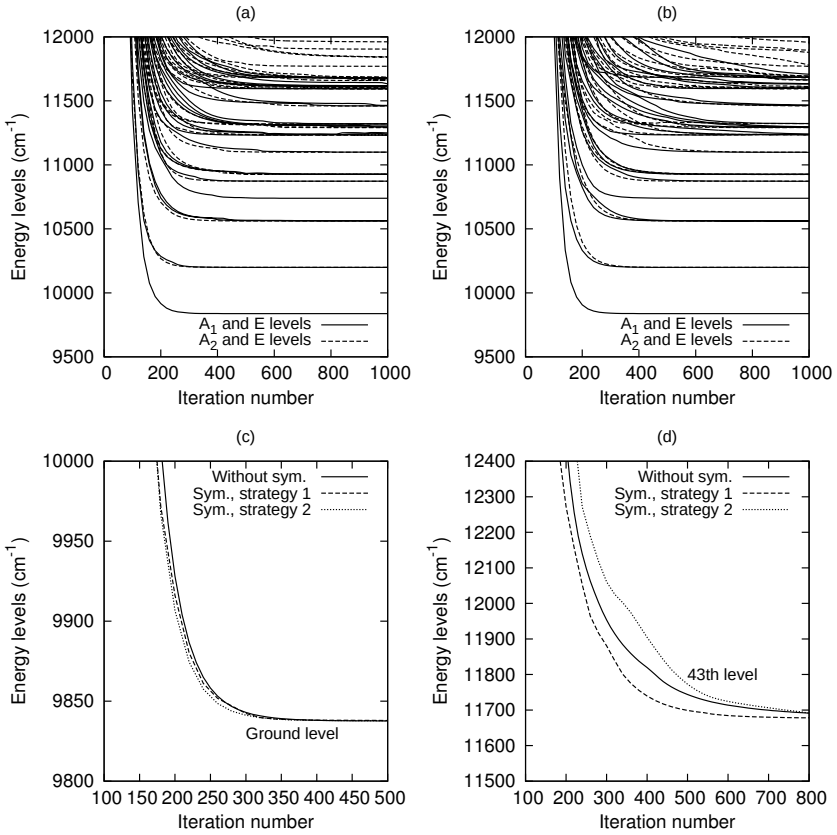

Figure 1: Eigenvalues as a function of the power iteration number, using symmetry-constrained SOP with the rank reduction strategy 1 (a) or strategy 2 (b) and zooms on the first (c) and the 43th eigenvalues (d).

Table 1: Transition wavenumbers from the ZPE for CH_3CN in cm^{-1}. The bold values are those differing from more than 5 cm^{-1} from the results of ref. [14]. The braces indicate neighbouring eigenvalues whose corresponding eigenvectors are mixed in linear combinations with different symmetries.

Vib. Assig.	Sym.	Results of ref. [14] (Smolyak quadrature)	RRBPM without symmetry splitting		RRBPM with symmetry splitting	
			Reduction rank=20 Ref. [7]	Reduction rank=30	Fixed rank for each type ($R_t = 8$) until $N_{pow} = 3000$ then adaptive with total reduc. rank $R = 30$	
					subset $A_1 \oplus E$	subset $A_2 \oplus E$
ZPE	A_1	-	9837.63	9837.51	-	-
ω_{11}	E	360.99	361.18, 361.25	361.07, 361.12	361.06	361.13
$2\omega_{11}$	E	723.18	723.37, 724.38	723.27, 723.74	723.68	723.39
$2\omega_{11}$	A_1	723.83	724.96	724.42	724.49	-
ω_4	A_1	900.66	900.97	900.87	900.90	-
ω_9	E	1034.13	1034.50, 1034.55	1034.31, 1034.34	1034.29	1034.81
$3\omega_{11}$	A_2	1086.55	1087.95	1087.41	-	1087.25
$3\omega_{11}$	A_1	1086.55	1088.58	1087.64	1087.33	-
$3\omega_{11}$	E	1087.78	1090.75, 1090.85	1088.81, 1088.92	1088.43	1088.72
$\omega_4 + \omega_{11}$	E	1259.88	1260.89, 1261.12	1260.80, 1260.87	1260.14	1260.55
ω_3	A_1	1388.97	1391.76	1391.03	1390.32	-
$\omega_9 + \omega_{11}$	E	1394.69	1395.74, 1398.24	1396.80, 1398.51	1396.09	1395.46
$\omega_9 + \omega_{11}$	A_2	1394.91	1396.24	**1400.21**,	-	1396.04
$\omega_9 + \omega_{11}$	A_1	1397.69	1401.15	**1402.98**	1401.03	-
$4\omega_{11}$	E	1451.10	1452.92, **1458.62**	1452.09, 1452.26	1452.40	1452.02
$4\omega_{11}$	E	1452.83	1456.24, **1460.80**	1454.22, 1454.96	1454.61	1453.81
$4\omega_{11}$	A_1	1453.40	**1464.40**	1455.37	1455.46	-
ω_7	E	1483.23	1483.52, 1483.51	1483.43, 1483.47	1483.46	1484.22
$\omega_4 + 2\omega_{11}$	E	1620.22	1621.34, 1623.05	1620.98, 1622.06	1621.79	1620.90
⋮	⋮	⋮	⋮	⋮	⋮	⋮
$\omega_9 + 2\omega_{11}$	E	1759.772	**1780.66, 1780.86**	**1771.64, 1781.84**	**1771.25**	**1767.08**
⋮	⋮	⋮	⋮	⋮	⋮	⋮
$5\omega_{11}$	E	1816.80	**1823.34, 1830.31**	1818.29, 1818.57	1818.42	1818.72
$5\omega_{11}$	A_2	1818.95	**1827.34**	1823.01	-	1820.93
$5\omega_{11}$	A_1	1818.95	**1832.19**	**1823.98**	1821.06	-
$5\omega_{11}$	E	1820.03	1823.87, **1828.40**	1821.91, 1823.55	1822.58	1822.27
$\omega_7 + \omega_{11}$	A_2	1844.23	1845.57	1845.89,	-	1845.39
$\omega_7 + \omega_{11}$	E	1844.33	1846.85, **1849.44**	1847.45, 1848.12	1845.95	1847.24
$\omega_7 + \omega_{11}$	A_1	1844.69	1848.14	**1850.66**	1848.07	-
⋮	⋮	⋮	⋮	⋮	⋮	⋮

provides symmetry labels. It also improves the accuracy of some of the levels reported in table 1. Some wavefunctions obtained with the non-symmetrized RRBPM calculation are nearly linear combinations of a few of the essentially exact wavefunctions of [14] with similar energies but different symmetries [7]. These poorly converged states are enclosed in braces in the table. The symmetry-adapted RRBPM calculation does a better job on these states for several reasons. 1) Owing to the symmetry-adapted SOP basis, there is no mixing between symmetric and antisymmetric states. 2) In the symmetry-adapted case the effective density of states is lower and therefore fewer power iterations are required to achieve a given convergence error.

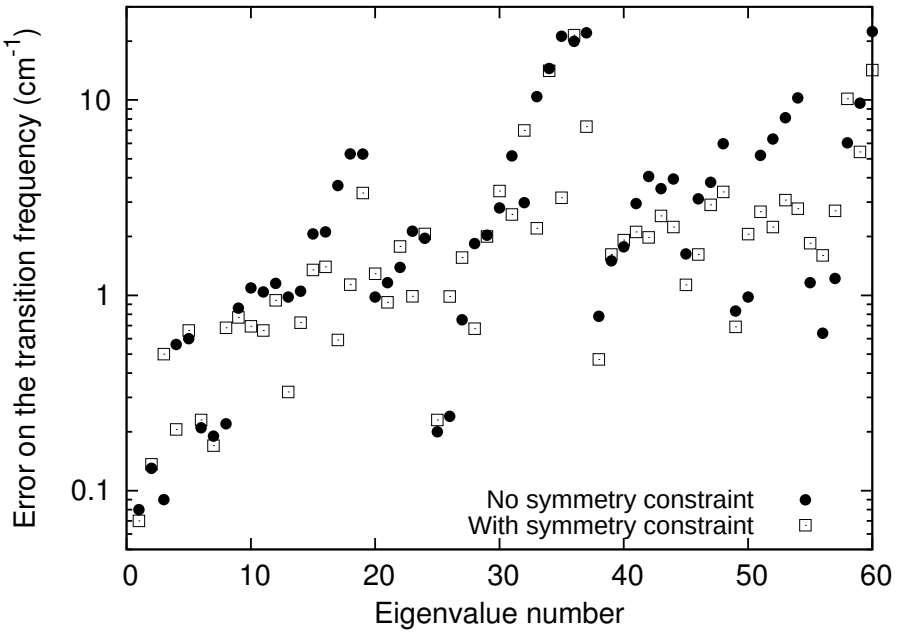

Figure 2: Differences between transition wavenumbers obtained using the RRBPM and the "exact" results of ref. [14], with or without symmetry constraints.

Differences between the levels obtained with Smolyak quadrature [14] and levels obtained with the RRBPM, with and without symmetry adaptation, are reported in fig. 2. For most eigenvalues, both differences are less than 5 cm^{-1}. Some errors are larger. The errors could be reduced by using contracted basis functions [8], larger ranks, and more power iterations. The accuracy of the first several dozen eigenvalues is similar with and without symmetry adaptation. Some of the higher levels are more accurate with symmetry adaptation. The non symmetry-adapted eigenvectors corresponding to these levels are nearly linear combinations of exact eigenvectors of different symmetries. The symmetry-adapted method always has the advantage that it allows one to assign levels.

4. Conclusion

In this letter we introduce a symmetry-adapted version of the RRBPM. The memory cost of the symmetry-adapted version is similar to that of the original RRBPM. It is clear that by using a block of starting vectors of a given symmetry it is possible to compute states of that symmetry. This enables one to obtain states with symmetry labels and accelerates convergence of the power method. Unless one is careful, it is possible to make SOP basis vectors in which some "types" are missing or underrepresented. We have developed several strategies for dealing with this problem and shown that they are effective. Starting vectors of a given symmetry are easily made from $f_{i_k}^{(\ell_t,k)}$ that have appropriate symmetries. Accuracy can be improved by using contractions, increasing the ranks, and increasing the number of power iterations. Better eigensolvers [16, 17] might also be adapted to the SOP format. The key advantage of the RRBPM is its low memory cost: less than 1GB is required for a 12D problem. The memory cost is actually reduced by introducing symmetry adaptation, but the memory cost is so low that the reduction is unimportant. The major advantage of the symmetry-adapted approach is that levels are obtained with symmetry labels. Accuracy is also somewhat improved. Ideas similar to those of this letter could be used with any subgroup for which it is possible to make $\mathbf{F}$ that transform like irreps. It should be possible to use projection operators to generate states of all symmetries from one set of matrix-vector products, as in the symmetry adapted Lanczos algorithm [18, 19], this will obviate the need to use symmetry adapted coordinates, which we exploit in this Letter.

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