

Using simply contracted basis functions with the Lanczos algorithm to calculate vibrational spectra

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We demonstrate that the combination of simply contracted basis functions and the Lanczos algorithm yields an extremely efficient method for computing vibrational energy levels. In this paper we discuss the ideas, and present some results for CH₄. The basis functions we use are products of eigenfunctions of reduced-dimension Hamiltonians obtained by freezing coordinates at equilibrium.

Nous montrons qu'en combinant une base de fonctions simplement contractées et l'algorithme de Lanczos, on obtient une méthode très efficace pour le calcul des niveaux vibratoires. Dans ce travail, nous présentons cette méthode ainsi que certains résultats pour la molécule de CH₄. Les fonctions de base utilisées sont des produits de fonctions propres de hamiltoniens de dimension réduite obtenus en gelant certaines coordonnées à l'équilibre.

1 Introduction

The development of good methods for calculating vibrational and ro-vibrational spectra of small molecules is a longstanding goal of theoretical chemistry. [1–7]. If one uses a simple product basis the size of the matrix for which one must calculate eigenvalues and eigenvectors is n^f , where n represents the number of basis functions in each degree of freedom and f is the number of degrees of freedom. For a triatomic molecule, with only three vibrational degrees of freedom, it is now straightforward to calculate vibrational levels. For a four-atom molecule the product-basis matrix is so large that it cannot be stored in memory. It is nevertheless possible to calculate vibrational spectra of molecules with four atoms by using one of two established strategies. (1) one uses contracted basis functions obtained by diagonalising reduced dimension Hamiltonians and the usual diagonalization method. [8,4,9]; (2) one use simple product basis functions and an iterative eigensolver (usually the Lanczos[10] or the filter diagonalization method). [11–24]

The two strategies are successful for different reasons. The success of the contracted-direct strategy is due to the small size of the contracted basis used to compute the spectrum. The success of the product-iterative strategy is due to two factors. First it obviates the need to store the Hamiltonian matrix. Second, the product basis makes it possible to evaluate matrix-vector products, and hence to compute eigenvalues, efficiently.

It is enticing to consider the possibility of using contracted basis functions with an iterative eigensolver: it might be possible to exploit *both* the smallness of the contracted basis and the efficiency of the iterative eigensolver.[16,25–27] The basis functions used in most previous attempts to combine a contacted basis and an iterative method are adiabatic contracted functions. [16,25,26] The contracted functions we use, denoted “simply contracted functions” in Ref [16], are eigenfunctions of reduced dimension Hamiltonians obtained by fixing the values of some coordinates. [28]

2 Bend stretch contraction scheme

As vibrational coordinates we use, for an N atom molecule, the lengths of $N - 1$ vectors, $N - 2$ planar angles, and $N - 3$ dihedral angles. [29] The kinetic energy operator (KEO) in these coordinates is surprisingly simple. We use “orthogonal” vectors so that there is no momentum coupling between stretch and bend coordinates.[30–32]

The reduced-dimension Hamiltonian for the bend contraction is,

$$H^{(b)} = T_{ben}(\theta, r_e) + V(\theta, r_e). \quad (1)$$

Its wavefunctions are denoted by

$$X_b(\theta) = \sum_l C_{lb} f_l(\theta) \quad (2)$$

and the energies by E_b . The f_l are primitive FBR (finite basis representation) bend basis functions[33] and the number of retained bend wavefunctions is denoted by n_b . Similarly, the reduced-dimension Hamiltonian for the stretch contraction is,

$$H^{(s)} = T_{str}(r) + V(\theta_e, r). \quad (3)$$

and its wavefunctions are denoted by,

$$Y_s(r) = \sum_{\alpha} D_{\alpha s} g_{\alpha}(r) \quad (4)$$

and the energies by E_s . The g_{α} are primitive DVR (discrete variable representation) [33] stretch basis functions and the number of retained stretch wavefunctions is denoted by n_s . θ_e and r_e represent equilibrium values of all the bend coordinates and all the stretch coordinates.

The final basis is a product of the retained stretch and bend eigenfunctions

$$|bs\rangle = |X_b\rangle|Y_s\rangle \quad (5)$$

Of course, only the eigenvectors of the reduced-dimension Hamiltonian matrices whose eigenvalues are below a given cutoff energy are retained.

2.1 Matrix-vector products with a simply contracted basis

To facilitate evaluation of matrix-vector products we write the full Hamiltonian

$$H = H^{(b)} + H^{(s)} + \Delta T + \Delta V \quad (6)$$

Matrix-vector products for ΔV are the most difficult. A matrix element of ΔV in the product contracted basis is,

$$\begin{aligned} \langle b' s' | \Delta V(\theta, r) | b s \rangle &= \sum_{l' l} C_{l' b'} C_{l b} D_{\alpha s'} D_{\alpha s} \langle l' \alpha | \Delta V(\theta, r) | l \alpha \rangle \\ &= \sum_{l' l} C_{l' b'} C_{l b} D_{\alpha s'} D_{\alpha s} T_{l' \beta} T_{l \beta} \Delta V_{\beta \alpha}, \end{aligned} \quad (7)$$

where

$$\begin{aligned} T_{l \beta} &= \sqrt{w_{\beta}} f_l(\theta_{\beta}) \\ \Delta V_{\beta \alpha} &= \Delta V(\theta_{\beta}, r_{\alpha}). \end{aligned} \quad (8)$$

$(\theta_{\beta}, w_{\beta})$ are quadrature points and weights for the angles. Note that if there is more than one bend coordinate l and β are composite indices and if there is more than one stretch coordinate α is a composite index. It is sometimes advantageous to rewrite Eq. (7) as

$$\langle b' s' | \Delta V(\theta, r) | b s \rangle = \sum_{\alpha \beta} \tilde{C}_{\beta' b'} \tilde{C}_{\beta b} D_{\alpha s'} D_{\alpha s} \Delta V_{\beta \alpha}, \quad (9)$$

where

$$\tilde{C}_{\beta b} = \sum_l C_{l b} T_{l \beta}. \quad (10)$$

In the standard approach, the ΔV matrix-vector product is evaluated as

$$\begin{aligned} u'_{b' s'} &= \sum_{b s} \langle b' s' | \Delta V(\theta, r) | b s \rangle u_{b s} \\ &= \sum_{\alpha} D_{\alpha s'} \sum_{\beta} \tilde{C}_{\beta b'} \Delta V_{\beta \alpha} \sum_s D_{\alpha s} \sum_b \tilde{C}_{\beta b} u_{b s}. \end{aligned} \quad (11)$$

The matrix-vector product can be done more efficiently by introducing an \mathbf{F} matrix defined by,

$$F_{b' b, \alpha} = \sum_{\beta} \tilde{C}_{\beta b'} \tilde{C}_{\beta b} \Delta V_{\beta \alpha}. \quad (12)$$

in terms of which,

$$\langle b' s' | \Delta V(\theta, r) | b s \rangle = \sum_{\alpha} F_{b' b, \alpha} D_{\alpha s'} D_{\alpha s}. \quad (13)$$

To use our method one calculates and stores all the $F_{b' b, \alpha}$. One then does the ΔV matrix-vector product in three steps. The CPU cost of the matrix-vector product is $n_{\alpha}(n_b^2 +$

$2n_b n_s)$. Assuming $n_b > n_s$ the CPU cost scales as $n_{\alpha} n_b^2$. The cost is much less than the cost of a product-basis matrix-vector product.

Of course this comparison is not really fair, to estimate the total CPU cost of the calculation, one needs to also include the cost of calculating \mathbf{F} . The \mathbf{F} matrix is computed prior to and not during the Lanczos recursion. The calculation of \mathbf{F} can be trivially parallelized as one can allocate the stretch DVR (α) points to different computers or processors and allow each to calculate a block of \mathbf{F} for the allocated α points. Because \mathbf{C} , and $\tilde{\mathbf{C}}$ are discarded before matrix-vector products are evaluated, one can use an extremely large bend basis to converge the contracted bend functions without increasing the memory cost of the calculation (the CPU cost of the calculation of \mathbf{F} does increase moderately). In contrast if one uses the standard approach (Eq. (11)) increasing the size of the bending basis increases both the CPU and the memory cost dramatically.

3 Application to CH₄

For CH₄ the product-iterative method is not feasible. A contracted-iterative calculation is possible.

3.1 Symmetry-adapted basis and Hamiltonian matrix

We use 4+1 Radau vectors[34] and their associated poly-spherical coordinates. The bend KEO is written in terms of angular momentum operators and parity-adapted primitive basis functions are used. We use parity adapted basis functions that are linear combinations of the product functions,

$$|l_1 l_2 m_2 l_3 m_3\rangle = \Theta_{l_1}^{m_1}(\theta_1) Y_{l_2}^{m_2}(\theta_2, \phi_2) Y_{l_3}^{m_3}(\theta_3, \phi_3). \quad (14)$$

Potential matrix elements in the parity-adapted basis are evaluated by Gauss quadrature. [35] We use Legendre weights and points for the polar angles and the trapezoid rule for the azimuthal angles. See Ref. [36]. Although the parity-adapted basis functions are not products of functions of a single variable we have been able to evaluate matrix-vector products efficiently. [36]. As primitive stretch basis functions we use PODVR functions computed from a sinc DVR. [33]

3.2 Results

We use the T8 potential surface of Schwenke described in Ref. [37]. It is an accurate *ab initio* global surface.

The bend energy and wavefunctions are obtained by using a parity-adapted FBR basis with $l_{max} = m_{max} = 25$. We use a potential ceiling value of 20000 cm^{-1} . We retain the bend levels up to $(n_2, n_4) = (4, 1)$, all of which are below 7670 cm^{-1} . There are 133 *A* levels and 113 *B* levels. The bend wavefunctions are compacted with a cut-off energy equal to the potential ceiling value. We have checked to make sure that this compaction cutoff energy is appropriate.

The stretch energies and wavefunctions are obtained from a product of 10 PODVR basis functions for each

stretch coordinate, these in turn are built from a sinc DVR basis in the range $[1.2a_0, 7.0a_0]$. We discard all the PODVR points whose potential energy is above 30000 cm^{-1} . This reduces the stretch basis size from 10000 to 5049. We retain all the stretch levels up to 20000 cm^{-1} . There are 161 A levels and 99 B levels.

The size of the final product basis of bend and stretch wavefunctions is 63960; there are 32600 A symmetry functions and 31360 B symmetry functions. In the final Lanczos calculation a potential ceiling value of 30000 cm^{-1} is used.

Some of our levels are reported in Table I. We show three groups of levels. The first group contains all the levels up to the (00)(30) band where the notation is defined as $(n_1n_3)(n_2n_4)$. The second group contains the $v = n_1 + n_3 = 2$ stretch overtone. The third group contains the highest five levels reported by Schwenke.[37]. Our levels are better converged than those of Schwenke.

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Table 1Vibrational wavenumbers of methane(in cm^{-1}).

| $(n_1n_3)(n_2n_4)$ | sym | This work | Schwenke | Col. 4 – Col. 3 | exp. ^b |
|--------------------|-------|-----------|----------|-----------------|----------------------|
| (00)(00) | 1 A1 | 9688.94 | 9691.56 | 2.62 | |
| (00)(01) | 1 F2 | 1311.39 | 1311.76 | 0.37 | 1310.76 |
| (00)(10) | 1 E | 1532.84 | 1533.26 | 0.42 | 1533.33 |
| (00)(02) | 2 A1 | 2589.11 | 2589.92 | 0.81 | 2587.04 |
| (00)(02) | 2 F2 | 2615.56 | 2616.30 | 0.74 | 2614.26 |
| (00)(02) | 2 E | 2626.61 | 2627.40 | 0.79 | 2624.62 |
| (00)(11) | 3 F2 | 2830.78 | 2831.77 | 0.99 | 2830.32 |
| (00)(11) | 1 F1 | 2846.16 | 2847.04 | 0.88 | 2846.08 |
| (10)(00) | 3 A1 | 2912.95 | 2913.77 | 0.82 | 2916.48 |
| (01)(00) | 4 F2 | 3012.82 | 3014.20 | 1.38 | 3019.49 |
| (00)(20) | 4 A1 | 3062.68 | 3063.74 | 1.06 | 3063.65 |
| (00)(20) | 3 E | 3064.20 | 3065.27 | 1.07 | 3065.14 |
| (00)(03) | 5 F2 | 3873.78 | 3878.34 | 4.56 | 3870.49 |
| (00)(03) | 5 A1 | 3911.30 | 3917.83 | 6.53 | 3909.18 |
| (00)(03) | 2 F1 | 3923.10 | 3929.98 | 6.88 | 3920.50 |
| (00)(03) | 6 F2 | 3934.34 | 3940.95 | 6.61 | 3930.92 |
| (00)(12) | 4 E | 4103.41 | 4109.08 | 5.67 | 4105.15 |
| (00)(12) | 3 F1 | 4130.22 | 4136.63 | 6.41 | 4128.57 |
| (00)(12) | 6 A1 | 4134.71 | 4140.19 | 5.48 | 4132.99 |
| (00)(12) | 7 F2 | 4143.78 | 4150.21 | 6.43 | 4142.86 |
| (00)(12) | 5 E | 4152.66 | 4159.19 | 6.53 | 4151.22 |
| (00)(12) | 1 A2 | 4163.26 | 4169.73 | 6.47 | 4161.87 |
| (10)(01) | 8 F2 | 4220.74 | 4222.23 | 1.49 | 4223.46 |
| (01)(01) | 9 F2 | 4313.10 | 4315.90 | 2.80 | 4319.21 |
| (01)(01) | 6 E | 4316.46 | 4318.93 | 2.47 | 4322.15 |
| (01)(01) | 4 F1 | 4316.71 | 4319.61 | 2.90 | 4322.58 |
| (01)(01) | 7 A1 | 4317.30 | 4320.23 | 2.93 | 4322.72 |
| (00)(21) | 10 F2 | 4348.96 | 4355.27 | 6.31 | 4348.77 |
| (00)(21) | 5 F1 | 4363.59 | 4369.53 | 5.94 | 4363.31 |
| (00)(21) | 11 F2 | 4378.60 | 4384.32 | 5.72 | 4379.10 |
| (10)(10) | 7 E | 4431.10 | 4432.60 | 1.50 | 4446.41 |
| (01)(10) | 6 F1 | 4530.19 | 4538.85 | 8.66 | 4537.57 ^b |
| (01)(10) | 13 F2 | 4536.64 | N/A | | 4543.76 ^b |
| (00)(30) | 8 E | 4591.44 | 4596.10 | 4.66 | 4592.03 |
| (00)(30) | 2 A2 | 4594.46 | 4599.15 | 4.69 | 4595.32 |
| (00)(30) | 8 A1 | 4594.73 | 4599.45 | 4.72 | 4595.56 |
| (20)(00) | 15 A1 | 5780.78 | 5783.20 | 2.42 | 5790.25 |
| (11)(00) | 27 F2 | 5852.46 | 5856.91 | 4.45 | |
| (02)(00) | 18 A1 | 5959.44 | 5962.76 | 3.32 | 5968.09 |
| (02)(00) | 30 F2 | 5991.96 | 5996.29 | 4.33 | 6004.69 |
| (02)(00) | 20 E | 6030.30 | 6034.60 | 4.30 | 6043.87 |
| (00)(05) | 33 F2 | 6401.71 | 6428.34 | 26.63 | |
| (00)(05) | 20 A1 | 6429.52 | 6461.34 | 31.82 | |
| (00)(05) | 34 F2 | 6474.02 | 6778.67 | 304.65 | |
| (00)(05) | 35 F2 | 6529.48 | 6824.36 | 294.88 | |
| (00)(14) | 5 A2 | 6702.66 | 6906.35 | 203.69 | |

^a From Ref. [38]. ^b There are typos in these two levels in Ref. [37].