

The Utility of Constraining Basis Function Indices When Using the Lanczos Algorithm to Calculate Vibrational Energy Levels[†]

Xiao-Gang Wang and Tucker Carrington, Jr.*

Département de chimie, Université de Montréal, C.P. 6128, succursale Centre-ville,
Montréal (Québec) H3C 3J7, Canada

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Direct product basis sets are frequently used to calculate vibrational energy levels of small polyatomic molecules. They have the important advantage of simplicity. However, they have the important disadvantage that a very large number of direct product functions is necessary to obtain converged energy levels. By using an iterative, rather than an explicit, method to calculate eigenvalues of the Hamiltonian matrix, it is possible to calculate energy levels despite the huge size of the direct product basis. Nonetheless, it is natural to attempt to reduce the size of the direct product basis by excluding functions that do not contribute to the wave functions associated with the energy levels of interest. In this paper we present a variational basis representation (VBR) example and a discrete variable representation (DVR) example demonstrating that it is possible to use the Lanczos method and exclude direct product basis functions by restricting basis function indices while maintaining the favorable n^{f+1} scaling relation for the cost of direct product basis matrix-vector products.

I. Introduction

Several new techniques enable experimentalists to accurately determine high-lying energy levels of small molecules. The development of better *ab initio* methods and the availability of faster computers have permitted *ab initio* quantum chemists to determine potential energy surfaces of useful accuracy close to the minimum. The experimental and *ab initio* advances drive the development of methods for calculating vibrational and rovibrational energy levels of small polyatomic molecules.^{1–4} Almost invariably, energy levels are calculated by computing eigenvalues of a matrix representation of the Hamiltonian operator in a large basis.

The principal impediment to the calculation of energy levels is the number of basis functions required to obtain converged results. The simplest basis functions are direct product functions. To construct a direct product basis one chooses 1-d basis functions, $\phi_{i_k}(q_k)$, $i_k = 1, 2, \dots, n_k$, for each of the vibrational degrees of freedom and makes products:

$$\Phi_{i_1, i_2, \dots, i_f} = \phi_{i_1}(q_1) \phi_{i_2}(q_2) \dots \phi_{i_f}(q_f) \quad (1)$$

The direct product basis includes *all* products of the 1-d basis functions. If, for notational simplicity, we assume $n_k = n$ for $k = 1, 2, \dots, f$ then there are n^f such product basis functions. Many years ago it became clear that the number of basis functions in a direct product basis is too large to permit calculating energy levels and wave functions using an explicit diagonalization method, whose cost scales as N^3 where $N = n^f$ is the size of the Hamiltonian matrix. Large matrices cause trouble for two reasons. First, standard, explicit, diagonalization algorithms modify the matrix and therefore require that it be stored in the core memory of the computer. Second, the cost of explicit diagonalization scales as N^3 , where N is the size of the matrix.⁵

There are two popular strategies for avoiding the problems one confronts when attempting to use an explicit diagonalization

method with a direct product basis: (1) one abandons the direct product basis and chooses instead more complicated but better basis functions (usually obtained from a successive diagonalization/truncation scheme);^{6–9} (2) one abandons the explicit diagonalization method and instead uses an iterative method (i.e., a method that requires only that one evaluate matrix-vector products) and exploits the simple structure of the direct product basis.^{10–18} Both of these strategies are effective, and both are used to calculate spectra.

The simplicity of a direct product basis facilitates evaluating matrix-vector products and therefore makes the calculation of energy levels and wave functions with very large direct product basis sets possible. Using a direct product basis set and the Lanczos algorithm, it is straightforward to calculate vibrational energy levels of most triatomic molecules.¹⁹ Nevertheless, it is somewhat disturbing that so many basis functions are required. For example, we used about 20^3 product PODVR^{20,21} (potential optimized discrete variable representation) basis functions to calculate vibrational energy levels of H₂O,¹⁴ but it is well known^{22,23} that if one uses VBR (variational basis representation) 1-d basis functions and selects from the complete direct product basis only those functions that are strongly coupled, it is possible to compute vibrational levels quite accurately with a much smaller basis. Even for a problem with six vibrational degrees of freedom it is possible to cope with a huge direct product basis,^{14,17,24} but it is natural to wonder if it is possible to improve the basis set without complicating (and rendering less efficient) the calculation of the matrix-vector products required to use the Lanczos algorithm to compute energy levels. It is possible to use successive diagonalization/truncation basis functions with the Lanczos algorithm, but successive diagonalization/truncation matrix-vector products are more complicated and slightly less efficient than their direct-product counterparts.^{16,25,26} Wyatt and co-workers have used product basis functions and applied the Lanczos algorithm to study large molecules for which it is impossible to use the complete direct product basis.^{27,28} Instead, they select functions from the complete basis (using a wave

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* E-mail: Tucker.Carrington@umontreal.ca. Fax: 514-343-7586

operator sorting technique). Unfortunately, their basis of selected functions does not have the simple structure of a complete direct product basis, and therefore a single matrix-vector product in the selected basis is more costly than it would be in a direct product basis (of similar size).

In this article we demonstrate that it is possible to use a basis obtained by selecting functions from a set of direct product basis functions in conjunction with the Lanczos algorithm to calculate energy levels, without sacrificing the favorable n^{f+1} scaling relation^{14,29,30} for the cost of a direct-product matrix-vector product. This is, of course, not possible for arbitrary selection schemes, but it is possible if one selects by constraining the ranges of basis function labels. Assuming selection can be implemented without augmenting the cost of matrix-vector products, it will be useful if there are basis functions in the original direct product basis that do not contribute to the wave functions whose energy levels one wishes to calculate. This is usually the case, but clearly the more carefully one optimizes the 1-d functions from which the direct product basis is built, the less one will gain by excluding some functions from the product basis.

Retaining some basis functions and excluding others has (if the favorable n^{f+1} scaling is maintained) at least two advantages: (1) the cost of a single matrix-vector product is reduced because the total number of basis functions is reduced; (2) the number of matrix-vector products required to obtain converged energy levels is reduced because the spectral range of the Hamiltonian matrix is reduced.¹⁹ The extent to which each of these advantages is important is clearly problem dependent and basis set dependent.

II. Constraining Ranges

To use the Lanczos algorithm to calculate energy levels, one needs to evaluate matrix-vector products of the form (for illustrative purposes the equation is presented for a three degree of freedom problem)

$$\omega_{i'jk} = \sum_{ijk} A_{i'i} B_{jj} C_{k'k} v_{ijk} = \sum_i A_{i'i} \sum_j B_{jj} \sum_k C_{k'k} v_{ijk} \quad (2)$$

where A , B , and C are matrix-representations of operators that depend on a single coordinate and v_{ijk} is a Lanczos vector.

The matrix-vector product is computed sequentially by doing first the sum over k , then the sum over j , and finally the sum over i .^{14,29,30} If one uses a direct product basis set, i , j and k take on all values between i_{\min} , j_{\min} , k_{\min} and i_{\max} , j_{\max} , k_{\max} (respectively). Because the vector v_{ijk} on the right side of the above equation depends on i and j the cost of the sum over k is not increased by allowing k_{\min} and k_{\max} to depend on i and j . This kind of constraint can therefore be introduced without jeopardizing the n^{f+1} scaling rule. For the same reason one can allow j_{\max} and j_{\min} to depend on i while maintaining n^{f+1} scaling. For a problem with f degrees of freedom, successive constraints of this kind are implemented by allowing the index i_1 to take on all possible values, the index i_2 to take on values determined by i_1 , the index i_3 to take on values determined by i_1 and i_2 , etc. (the index i_f takes on values determined by i_1, i_2, \dots, i_{f-1}).

Successive constraints of this type can be imposed in either a VBR or a DVR. In a VBR, the constraints are chosen to exclude weakly coupled basis functions. In a DVR, one can choose constraints so that DVR functions centered about points at which the potential is very large are excluded. In the next two subsections we discuss examples of VBR and DVR constraints.

A. Local Mode Vibrations of Silane. If coupling between VBR basis functions is not large, it is possible to calculate very accurate low-lying energy levels using a VBR basis that does not include functions with large zeroth-order energies (large diagonal matrix elements). One can therefore safely exclude such VBR functions from a direct product basis. It is easiest to exclude basis functions with high zeroth-order energies if all of the 1-d vibrational problems used to define the 1-d functions, from which the product basis is built, are similar or identical. In this case, to exclude VBR functions with large zeroth-order energies one can simply exclude functions for which the sum of the 1-d quantum numbers is larger than some chosen value, i.e., exclude all functions $\Phi_{i_1, i_2, \dots, i_f}$ for which $i_1 + i_2 + \dots + i_f > N_t$, where N_t is a threshold value. This kind of constraint is commonly used when calculating local mode vibrational energy levels.²² By employing this constraint, one is able to calculate energy levels using far fewer VBR basis functions than would be required using a full direct product basis. For a molecule with four local-mode-like degrees of freedom and a direct product basis with $i_k = 0, 1, \dots, N_t$ for all k the ratio of the size of the basis constrained so that $i_1 + i_2 + \dots + i_f \leq N_t$ to the size of the full direct product basis is $\binom{N_t+4}{4} / (N_t + 1)$.⁴ The constraint is particularly effective if the potential is such that it couples only VBR functions with similar zeroth-order energies. This is the case for most local-mode Hamiltonians. If one uses the successive constraint scheme to efficiently apply the $i_1 + i_2 + \dots + i_f \leq N_t$ constraint, reducing the number of VBR basis functions reduces the cost of each matrix-vector product. The cost of a Lanczos calculation is a product of the cost of a single matrix-vector product and the number of iterations required to obtain convergence, which is inversely proportional to the spectral range of the Hamiltonian matrix. Excluding unnecessary functions from a basis accelerates calculating energy levels not only because it reduces the cost of evaluating a single matrix-vector product but also because it decreases the spectral range and hence the number of matrix-vector products required to achieve converged energy levels.

A local-mode Hamiltonian for a tetrahedral hydride molecule with four identical stretching degrees of freedom and a quartic potential is²²

$$H = \frac{1}{2\mu} \sum_{i=1}^4 p_{r_i}^2 - \frac{1}{3M} \sum_{i < j}^4 p_{r_i} p_{r_j} + \frac{1}{2} \sum_{i,j=1}^4 f_{ij} y_i y_j + \frac{1}{6} \sum_{i,j,k=1}^4 f_{ijk} y_i y_j y_k + \frac{1}{24} \sum_{i,j,k,l=1}^4 f_{ijkl} y_i y_j y_k y_l \quad (3)$$

with

$$y_i = 1 - \exp(-a(r_i - r_i^e)) \quad (4)$$

where r_i is the length of bond i , r_i^e is the equilibrium bond length of bond i , $f_{ii} = 2D_e$ and a are Morse oscillator parameters, M is the mass of the central atom, $\mu = (m_H M / m_H + M)$, and m_H is the mass of a hydrogen atom. A basis of products of the Morse functions, denoted by $|i_1 i_2 i_3 i_4\rangle$, is a very good basis for the Hamiltonian of eq 3 with relatively small off-diagonal matrix elements. The D_e and a parameters of the Morse basis functions we use are those of the potential.

If the number of potential terms is not large, it is efficient, when calculating energy levels in the VBR with the Lanczos algorithm, to evaluate matrix-vector products for each term in the Hamiltonian separately. For each term the matrix-vector product has the general form of eq 2. Each of the 1-d matrices

(representing either p_i or y_i) can be computed from closed-form expressions.²² For a quadratic potential term $y_3 y_4$, the constrained matrix-vector products may be computed as follows. The matrix element is

$$\langle i'_1, i'_2, i'_3, i'_4 | y_3 y_4 | i_1, i_2, i_3, i_4 \rangle = \delta_{i'_1 i_1} \delta_{i'_2 i_2} Y_{i'_3 i_3} Y_{i'_4 i_4} \quad (5)$$

with

$$Y_{i'_i} = \langle i' | y | i \rangle \quad (6)$$

After doing the sums over i_1 and i_2 , the nontrivial matrix-vector product for this term is

$$u'_{i'_1 i'_2 i'_3 i'_4} = \sum_{i_3=0}^{i_3^{\max}(i'_1, i'_2)} Y_{i'_3 i_3} \sum_{i_4=0}^{i_4^{\max}(i'_1, i'_2, i_3)} Y_{i'_4 i_4} u_{i_1 i_2 i_3 i_4} \quad (7)$$

It is evaluated in two steps:

$$\begin{aligned} u'_{i'_1 i'_2 i'_3 i'_4} &= \sum_{i_4=0}^{i_4^{\max}(i'_1, i'_2, i_3)} Y_{i'_4 i_4} u_{i_1 i_2 i_3 i_4} \\ u'_{i'_1 i'_2 i'_3 i'_4} &= \sum_{i_3=0}^{i_3^{\max}(i'_1, i'_2)} Y_{i'_3 i_3} u_{i_1 i_2 i_3 i_4}^{(1)} \end{aligned} \quad (8)$$

Underlined indices are subject to the constraint that their sum is less than or equal to N_t .

Clearly, to impose the constraint, $i_1 + i_2 + i_3 + i_4 \leq N_t$, it is necessary to choose

$$i_4^{\max}(i_1, i_2, i_3) = N_t - i_1 - i_2 - i_3 \quad (9)$$

If $i_1 + i_2 + i_3 + i_4 \leq N_t$, then necessarily $i_1 + i_2 + i_3 \leq N_t$, and therefore

$$i_3^{\max}(i_1, i_2) = N_t - i_1 - i_2 \quad (10)$$

Similarly, $i_1 + i_2 \leq N_t$, and

$$i_2^{\max}(i_1) = N_t - i_1 \quad (11)$$

The most efficient way to impose these constraints is to determine and store $i_4^{\max}(i_1, i_2, i_3)$, $i_3^{\max}(i_1, i_2)$, and $i_2^{\max}(i_1)$ before computing the matrix-vector products. The functions $i_4^{\max}(i_1, i_2, i_3)$, $i_3^{\max}(i_1, i_2)$, and $i_2^{\max}(i_1)$ determine the boundary, in a space with Cartesian axes labeled by basis function indices, between the region of included and the region of excluded basis functions. Having determined the region to be included (once), matrix-vector products for all terms with two factors can be computed as explained above for the $y_3 y_4$ term by permuting indices. It would also be possible to impose the constraints using 'IF' statements, but this is about four times much more costly.

Rather than doing matrix-vector products for both $p_{r_i}^2$ and y_i^2 terms, we combine them and exploit the fact that the matrix representation of the sum of the two terms is diagonal. For this term, whose representation matrix is diagonal, the ratio of the cost of the constrained matrix-vector product to the cost of the unconstrained matrix-vector product is simply the ratio of the number of constrained basis functions to the number of direct product basis functions, $((N_t+4)(N_t+3)(N_t+2)/16(N_t+1)^3)$, which is 9.6% for $N_t = 12$. For a term with two factors, both of which are off-diagonal (such as the $y_3 y_4$ term discussed above), the ratio of the cost of the constrained matrix-vector product to that

TABLE 1: A Comparison of the Costs of Constrained ($N_t = 12$) and Unconstrained VBR Calculations of SiH₄ Local Mode Vibrational Levels up to 15 000 cm⁻¹^a

	full basis	constrained basis
basis size ^{b,c}	28561	1820
largest eigenvalue (cm ⁻¹) ^b	92685	29988
no. of iterations ^{b,d}	3281	1261
time (seconds)/1000 iterations ^{b,d}	153	12
total time (seconds) ^{b,d}	501	15
largest eigenvalue (cm ⁻¹) ^c	93429	30254
no. of iterations ^{c,e}	3051	1180
time (seconds)/1000 iterations ^{c,e}	391	122
total time (seconds) ^{c,e}	1194	144

^a For both basis sets we do as many iterations as are required to converge all the energy levels. Computer time is on a single R10000 194 MHz processor of an SGI Origin 2000. ^b With the quadratic potential. ^c With the quartic potential. ^d Evaluating matrix-vector products separately for each term. ^e Using Gauss-Laguerre quadrature to evaluate the potential matrix-vector product.

of the unconstrained matrix-vector product is $((N_t+4)(N_t+3)-(N_t+2)(N_t+5/4)20(N_t+1)^4)$ which is 7.8% for $N_t = 12$. Because this ratio is smaller than the previous one, the ratio of the constrained cost to the unconstrained cost is smaller than the ratio of the constrained basis set size to the unconstrained basis set size. For each term, the approximate cost of the constrained matrix-vector product is obtained by counting the number of loops required to program the two steps of eq 8.

To test the VBR constrained-index basis we have applied it to calculate stretching vibrational energy levels of silane. We use the quadratic fitted potential of ref 31. We choose a maximum value of $N_t = 12$ for the 1-d basis index. To test that this basis set is big enough to compute converged energy levels, we compared levels calculated with $N_t = 12$ to levels computed with $N_t = 14$. Energy levels up to 15 000 cm⁻¹, computed with $N_t = 12$, are within 0.05 cm⁻¹ of energy levels computed with $N_t = 14$.

As explained above, we impose the constraints by evaluating matrix-vector products separately for each term. A cost comparison is given in Table 1. Imposing the constraint reduces the cost of each matrix-vector product by a factor of 13. This agrees with the reduction anticipated on the basis of counting loops. In addition, imposing the constraint reduces the largest eigenvalue from 92 685 cm⁻¹ to 29 988 cm⁻¹. This decreases the number of matrix-vector products required to converge all the levels up to 15 000 cm⁻¹ from 3281 to 1261. By combining the above two factors, imposing the constraint reduces the total cost by a factor of 33 (see Table 1). Energy levels computed with and without the constraint differ by at most 0.10 cm⁻¹.

If the number of terms in the potential is large, it is not efficient to evaluate constrained matrix-vector products for each term. In this case, it is better to use quadrature and to evaluate the potential matrix-vector product as

$$\begin{aligned} u'_{i'_1 i'_2 i'_3 i'_4} &= \sum_{\alpha_1=1}^{N_\alpha} T_{i'_1 \alpha_1} \sum_{\alpha_2=1}^{N_\alpha} T_{i'_2 \alpha_2} \sum_{\alpha_3=1}^{N_\alpha} T_{i'_3 \alpha_3} \sum_{\alpha_4=1}^{N_\alpha} \\ &T_{i'_4 \alpha_4} V(y_1^{\alpha_1}, y_2^{\alpha_2}, y_3^{\alpha_3}, y_4^{\alpha_4}) \sum_{i_1=0}^N T_{i_1 \alpha_1} \sum_{i_2=0}^{i_2^{\max}(i_1)} T_{i_2 \alpha_2} \\ &\sum_{i_3=0}^{i_3^{\max}(i_1, i_2)} T_{i_3 \alpha_3} \sum_{i_4=0}^{i_4^{\max}(i_1, i_2, i_3)} T_{i_4 \alpha_4} u_{i_1 i_2 i_3 i_4} \end{aligned} \quad (12)$$

where $T_{n\alpha_i}$ is an element of the matrix used to evaluate the quadrature.⁴

To test using quadrature with a constrained VBR basis, we have calculated stretching vibrational energy levels of silane using the quartic potential of ref 31, which is obtained by reexpressing the stretch part of the ab initio potential of ref 32 in terms of y_i . We choose a maximum value of $N_i = 12$ for the 1-d basis index. To test that this basis set is big enough to compute converged energy levels we compared levels calculated with $N_i = 12$ to levels computed with $N_i = 14$. Energy levels up to 15 000 cm^{-1} , computed with $N_i = 12$, are within 0.09 cm^{-1} of energy levels computed with $N_i = 14$. Because we use Morse oscillator basis functions we choose

$$T_{n,\alpha_i} = \sqrt{\omega_{\alpha_i}} \tilde{\phi}_n(z_{\alpha_i}) \quad (13)$$

where $z_i = k(1 - y_i)$, $k = \omega/\omega_x$ (ω and ω_x are the Morse frequency and anharmonicity constants), ω_{α} is a Gauss quadrature weight for the associated Laguerre polynomial, $L_n^{k-2N_i-2}$, z_{α} is a corresponding Gauss point

$$\begin{aligned} \tilde{\phi}_n &= \left[\frac{n!(k-2n-1)}{\Gamma(k-n)} \right]^{1/2} z^{N_i-n} L_n^{k-2n-1} \\ &= \frac{1}{\sqrt{a}} e^{z/2} z^{-(k-2N_i-1)/2} \phi_n \end{aligned} \quad (14)$$

and ϕ_n is the Morse eigenfunction. N_{α} is the number of quadrature points. N_i (defined previously) is the largest possible value of basis set index. Setting $N_{\alpha} = N_i + 3$ yields exact integrals for a quartic potential. This can be proved by noting that $\tilde{\phi}_n$ is a polynomial of degree less than or equal to N_i . The constrained sums over i_1, i_2, i_3 , and i_4 are evaluated as explained after eq 7.

The constraint is imposed using eq 12, but because one obtains a diagonal term by combining the y_i^2 and $p_{r_i}^2$ terms, it is advantageous not to include the y_i^2 terms in the potential when calculating potential matrix elements by quadrature. Instead, they are treated separately. Of course, the six quadratic kinetic coupling terms $p_{r_i}p_{r_j}$ are also treated separately. The potential at the 4-d quadrature points is stored, and matrix-vector products (see eq 12) are evaluated in eight steps. Due to the fact that not all of the sums in eq 12 are constrained, the ratio of the cost of a constrained matrix-vector product to the cost of an unconstrained matrix-vector product is no longer close to the ratio of the size of the constrained basis to the size of the unconstrained basis. In addition, N_{α} is slightly larger than N_i . If matrix-vector products were evaluated separately for each term in the potential all sums would be constrained, but because there are 61 potential terms this would be prohibitively expensive.

A cost comparison for the quartic potential is also presented in Table 1. Imposing constraints reduces the cost of each matrix-vector product by a factor of 3. Imposing the constraint reduces the largest eigenvalue from 93 429 cm^{-1} to 30 254 cm^{-1} . This decreases the number of matrix-vector products required to converge all of the levels up to 10 500 cm^{-1} from 3051 to 1180. Combining the above two factors, imposing the constraint reduces the total cost by a factor of 8 (See Table 1). Energy levels computed with and without the constraint differ by at most 0.10 cm^{-1} (see Table 2).

One should note that energy levels computed with the quartic potential will be inaccurate because bending degrees of freedom are ignored in this calculation.

In conclusion, using successive constraints enables one to efficiently apply the Lanczos algorithm to calculate energy levels without wastefully including many VBR basis functions that

do not contribute to the wave functions of the desired energy levels, and without jeopardizing the n^{f+1} scaling rule. For the quadratic potential, the cost of computing the energy levels up to 15 000 cm^{-1} is reduced by a factor of 33; for the quartic potential the cost of computing energy levels up to 10 000 cm^{-1} is reduced by a factor of 8.

B. PODVR Calculation of the Vibration of Water. It is natural to consider excluding DVR product basis functions from a direct product DVR basis. The idea is enticing because it is anticipated that it should be possible to exclude many DVR basis functions centered about DVR points at which the potential is larger than the highest energy level one wishes to compute.^{14,33} The utility of throwing away basis functions centered about points at which the potential is high depends, of course, on the regularity of the potential and the quality of the 1-d basis sets from which the product basis functions are built. Other authors have considered different schemes for excluding DVR basis functions.³⁴

In a previous paper, we used a potential optimized DVR (PODVR) direct product basis and an indexing array to exclude PODVR basis functions from the basis to calculate vibrational energy levels of H_2O .¹⁴ We have now used the successive constraint scheme to exclude basis functions more efficiently. We use the same parameters, the same potential, and the same number of PODVR functions (22) in each of the three coordinates as in ref 14. By excluding DVR functions peaked about points at which the potential is larger than 46 000 cm^{-1} , we were able to converge all vibrational energy levels less than about 22 000 cm^{-1} using only 5660 of the 10648 direct product functions. See Table 3. Energy levels computed with the constrained basis were almost as well converged as those with the full basis (the largest error introduced by the constraint is 1.2 cm^{-1} ; see Table 4).

The elements of a DVR matrix representing the Radau coordinate kinetic energy operator (KEO)³⁵ of a triatomic molecule are

$$\begin{aligned} H_{\alpha'_1\alpha'_2\alpha'_3\alpha_1\alpha_2\alpha_3}^{\text{DVR}} &= K_{\alpha'_1\alpha_1}^{(r)} \delta_{\alpha'_2\alpha_2} \delta_{\alpha'_3\alpha_3} + K_{\alpha'_2\alpha_2}^{(r)} \delta_{\alpha'_1\alpha_1} \delta_{\alpha'_3\alpha_3} + \\ &\quad \mu(r_1^{\alpha_1}, r_2^{\alpha_2}) K_{\alpha'_3\alpha_3}^{(\theta)} \delta_{\alpha'_1\alpha_1} \delta_{\alpha'_2\alpha_2} \end{aligned} \quad (15)$$

where the PODVR points in r_1, r_2 , and θ are labeled by α_1, α_2 , and α_3 , and μ is an inverse moment of inertia function. It is best to determine which DVR functions are to be included before doing the constrained matrix-vector products. To determine which DVR functions should be included one could (1) for each pair (α_1, α_2) determine which values of α_3 should be included; or (2) for each pair (α_2, α_3) determine which values of α_1 should be included (because the same DVR is used for r_1 and for r_2 , this is equivalent to determining which values of α_2 should be included for each pair (α_1, α_3)). In scanning scheme (1), one determines $\alpha_3^{\min}(\alpha_1, \alpha_2)$ and $\alpha_3^{\max}(\alpha_1, \alpha_2)$. In scanning scheme (2), one determines $\alpha_1^{\min}(\alpha_2, \alpha_3)$ and $\alpha_1^{\max}(\alpha_2, \alpha_3)$.

If one uses scanning scheme (1), the matrix-vector product for the third term in eq 15 is

$$u'_{\alpha'_1\alpha'_2\alpha'_3} = \mu(r_1^{\alpha'_1}, r_2^{\alpha'_2}) \sum_{\alpha_3=\alpha_3^{\min}(\alpha'_1, \alpha'_2)}^{\alpha_3^{\max}(\alpha'_1, \alpha'_2)} K_{\alpha'_3\alpha_3}^{(\theta)} u_{\alpha'_1\alpha'_2\alpha_3} \quad (16)$$

and the matrix-vector product for the second term in eq 15 is

$$u'_{\alpha'_1\alpha'_2\alpha'_3} = \sum_{\alpha_2} K_{\alpha'_2\alpha_2}^{(r)} u_{\alpha'_1\alpha_2\alpha'_3} \quad (17)$$

TABLE 2: Stretching Vibrational Levels of SiH₄ up to 10 000 cm⁻¹ Calculated Using the Quartic Potential^a

state	c.	c.-u.	state	c.	c.-u.	state	c.	c.-u.
1 0 0 0;A ₁	2198.085	0.000	3 2 0 0;F ₂	10773.097	0.009	3 2 1 0;F ₁	12992.021	0.024
1 0 0 0;F ₂	2208.254	0.000	3 2 0 0;F ₁	10774.008	0.009	3 2 1 0;A ₂	12995.309	0.024
2 0 0 0;A ₁	4342.651	0.000	3 0 1 1;A ₁	10824.350	0.007	3 1 1 1;A ₁	13039.434	0.019
2 0 0 0;F ₂	4344.061	0.000	3 0 1 1;F ₂	10827.603	0.007	3 1 1 1;F ₂	13045.254	0.020
1 1 0 0;A ₁	4402.819	0.000	3 0 1 1;F ₂	10834.174	0.007	0 2 2 2;A ₁	13046.356	0.018
1 1 0 0;F ₂	4412.856	0.000	3 0 1 1;E	10837.057	0.007	0 2 2 2;F ₂	13048.143	0.019
1 1 0 0;E	4417.840	0.000	3 0 1 1;F ₁	10837.139	0.007	2 2 1 1;A ₁	13095.705	0.016
3 0 0 0;A ₁	6414.955	0.000	1 0 2 2;A ₁	10887.724	0.005	2 2 1 1;F ₂	13115.575	0.015
3 0 0 0;F ₂	6415.083	0.000	1 0 2 2;F ₂	10893.780	0.005	2 2 1 1;E	13125.994	0.015
2 1 0 0;A ₁	6538.742	0.000	1 0 2 2;E	10906.316	0.005	7 0 0 0;F ₂	14018.631	0.002
2 1 0 0;F ₂	6544.696	0.000	1 0 2 2;F ₂	10908.028	0.005	7 0 0 0;A ₁	14018.632	0.003
2 1 0 0;E	6549.708	0.000	1 0 2 2;F ₁	10912.295	0.005	6 1 0 0;A ₁	14424.514	0.086
2 1 0 0;F ₂	6555.937	0.000	2 1 1 1;A ₁	10955.918	0.004	6 1 0 0;F ₂	14424.518	0.085
2 1 0 0;F ₁	6560.401	0.000	2 1 1 1;F ₂	10977.682	0.004	6 1 0 0;E	14435.545	0.084
0 1 1 1;A ₁	6613.906	0.000	6 0 0 0;A ₁	12220.548	0.000	6 1 0 0;F ₂	14435.548	0.086
0 1 1 1;F ₂	6623.815	0.000	6 0 0 0;F ₂	12220.548	0.000	6 1 0 0;F ₁	14435.550	0.084
4 0 0 0;A ₁	8418.467	0.000	5 1 0 0;A ₁	12557.078	0.035	5 2 0 0;A ₁	14704.961	0.100
4 0 0 0;F ₂	8418.482	0.000	5 1 0 0;F ₂	12557.104	0.035	5 2 0 0;F ₂	14705.308	0.101
3 1 0 0;A ₁	8615.835	0.002	5 1 0 0;E	12567.570	0.035	5 2 0 0;E	14706.561	0.101
3 1 0 0;F ₂	8617.292	0.002	5 1 0 0;F ₂	12567.579	0.035	5 2 0 0;F ₂	14706.812	0.101
3 1 0 0;E	8625.470	0.002	5 1 0 0;F ₁	12567.602	0.035	5 2 0 0;F ₁	14707.157	0.102
3 1 0 0;F ₂	8626.123	0.002	4 2 0 0;A ₁	12765.906	0.033	5 0 1 1;A ₁	14769.449	0.095
3 1 0 0;F ₁	8627.426	0.002	4 2 0 0;F ₂	12766.766	0.034	5 0 1 1;F ₂	14769.506	0.096
2 2 0 0;A ₁	8691.135	0.001	4 2 0 0;E	12767.388	0.034	5 0 1 1;F ₂	14779.332	0.095
2 2 0 0;F ₂	8692.898	0.001	4 2 0 0;F ₂	12770.486	0.036	5 0 1 1;E	14779.378	0.096
2 2 0 0;E	8693.728	0.001	4 2 0 0;F ₁	12771.343	0.036	5 0 1 1;F ₁	14779.380	0.095
2 0 1 1;A ₁	8743.689	0.001	4 0 1 1;A ₁	12831.988	0.032	4 3 0 0;A ₁	14834.414	0.092
2 0 1 1;F ₂	8751.914	0.001	4 0 1 1;F ₂	12832.481	0.032	4 3 0 0;F ₂	14834.518	0.093
2 0 1 1;F ₂	8762.617	0.001	3 3 0 0;F ₂	12841.160	0.032	4 3 0 0;E	14834.570	0.093
2 0 1 1;E	8769.667	0.001	3 3 0 0;E	12841.179	0.032	4 3 0 0;F ₂	14856.973	0.098
2 0 1 1;F ₁	8769.759	0.001	3 3 0 0;A ₁	12841.380	0.032	4 3 0 0;F ₁	14857.057	0.097
1 1 1 1;A ₁	8831.154	0.000	4 0 1 1;F ₂	12841.961	0.032	4 2 1 0;A ₁	14965.993	0.076
5 0 0 0;A ₁	10353.737	0.000	4 0 1 1;F ₁	12842.016	0.032	4 2 1 0;F ₂	14968.811	0.079
5 0 0 0;F ₂	10353.739	0.000	4 0 1 1;E	12842.332	0.032	4 2 1 0;F ₂	14973.677	0.078
4 1 0 0;A ₁	10621.055	0.010	3 2 1 0;A ₁	12953.026	0.021	4 2 1 0;E	14974.722	0.079
4 1 0 0;F ₂	10621.244	0.010	3 2 1 0;F ₂	12958.119	0.022	4 2 1 0;F ₁	14976.387	0.079
4 1 0 0;E	10631.029	0.010	3 2 1 0;E	12966.663	0.023	4 2 1 0;F ₂	14985.237	0.078
4 1 0 0;F ₂	10631.099	0.010	3 2 1 0;F ₂	12967.988	0.023	4 2 1 0;E	14986.834	0.080
4 1 0 0;F ₁	10631.267	0.010	3 2 1 0;F ₁	12972.382	0.023	4 2 1 0;F ₁	14987.580	0.079
3 2 0 0;A ₁	10755.578	0.008	3 2 1 0;F ₂	12980.480	0.024	4 2 1 0;F ₁	14991.297	0.079
3 2 0 0;F ₂	10756.631	0.008	3 2 1 0;F ₁	12984.338	0.024	4 2 1 0;A ₂	14993.530	0.079
3 2 0 0;E	10757.179	0.008	3 2 1 0;E	12986.459	0.024			

^a The zero point energy with the constrained and unconstrained basis sets is 4514.575353935 cm⁻¹ and 4514.575353908 cm⁻¹, respectively. Energy levels computed with the constrained basis are in columns marked by c. Differences between energy levels computed with the constrained basis and levels computed with the full basis are in columns marked by c.-u.

TABLE 3: PODVR Calculation of Vibrational Energy Levels of H₂O with V_{max} = 46 000 cm⁻¹^a

	full basis	constrained basis
basis size	10 648	5660
largest eigenvalue (cm ⁻¹)	131 000	117 000
no. of iterations	2324	2063
time (seconds)/1000 iterations	12	7
total time (seconds)	29	15

^a For both basis sets we do as many iterations as are required to converge all the energy levels up to 22 000 cm⁻¹. Computer time is on a single R10000 194 MHz processor of an SGI Origin 2000.

(The matrix-vector product for the first term in eq 15 is similar.) If instead one uses scanning scheme (2), the matrix-vector product for the second term in eq 15 is

$$u'_{\alpha'_1\alpha'_2\alpha'_3} = \sum_{\alpha_3=\alpha_3^{\min}(\alpha'_1,\alpha'_3)}^{\alpha_3^{\max}(\alpha'_1,\alpha'_3)} K_{\alpha'_2\alpha_2}^{(r)} u_{\alpha'_1\alpha_2\alpha_3} \quad (18)$$

The matrix-vector product for the second term is more efficient with scanning scheme (2) than with scanning scheme (1) because the sum one must evaluate with scanning scheme (2)

is constrained (eq 18), whereas the sum one must evaluate with scanning scheme (1) is not constrained (eq 17). We therefore use scanning scheme (1) for the third term and scanning scheme (2) for the second and (equivalent) first terms. Both schemes are equivalent for the matrix-vector product of the potential. The same scanning scheme is used for the primed and the unprimed indices, e.g., in eq 14 for each pair (α'_1, α'_2) we include values of α'_3 between $\alpha_2^{\min}(\alpha'_1, \alpha'_2)$ and $\alpha_2^{\max}(\alpha'_1, \alpha'_2)$.

Terms with two nondiagonal factors do not occur in the Radau coordinate KEO for a triatomic, but it is worth noting that the cost of evaluating a matrix-vector product for such a term would be same in both scanning schemes. For example, for a term

$$K = f(r_1, r_2, \theta) \frac{\partial}{\partial r_1} \frac{\partial}{\partial \theta} \quad (19)$$

with DVR matrix elements,

$$K_{\alpha'_1\alpha'_2\alpha'_3,\alpha_1\alpha_2\alpha_3}^{\text{DVR}} = f_{\alpha'_1\alpha'_2,\alpha'_3} K_{\alpha'_1\alpha_1}^{(r_1)} \delta_{\alpha'_2\alpha_2} K_{\alpha'_3\alpha_3}^{(\theta)} \quad (20)$$

The matrix-vector products can be done in both scanning schemes:

TABLE 4: Vibrational Levels of H₂O up to 22 000 cm⁻¹ Calculated with Constrained and Unconstrained Basis Sets^a

sym	c	c.-u.	sym	c	c.-u.	sym	c.	c.-u.	sym	c.	c.-u.
A ₁	1594.32	0.00	A ₁	13195.82	0.02	B ₂	16974.73	0.10	A ₁	19724.91	0.13
A ₁	3152.01	0.00	B ₂	13252.53	0.00	A ₁	17054.80	0.14	A ₁	19757.19	0.27
A ₁	3656.49	0.00	A ₁	13453.59	0.02	B ₂	17156.77	0.02	B ₂	19757.28	0.11
B ₂	3755.92	0.00	A ₁	13604.80	0.04	A ₁	17226.37	0.29	A ₁	19883.65	0.14
A ₁	4667.70	0.00	A ₁	13647.80	0.06	A ₁	17312.60	0.23	B ₂	19884.34	0.08
A ₁	5234.29	0.00	B ₂	13658.72	0.00	B ₂	17320.36	0.04	A ₁	20056.41	0.44
B ₂	5332.06	0.00	A ₁	13793.41	0.04	B ₂	17374.80	0.03	B ₂	20126.12	0.04
A ₁	6134.11	0.00	B ₂	13799.24	0.03	A ₁	17435.13	0.30	A ₁	20126.35	0.16
A ₁	6775.03	0.00	A ₁	13829.79	0.08	A ₁	17461.54	0.68	B ₂	20165.69	0.12
B ₂	6873.47	0.00	B ₂	13832.03	0.00	B ₂	17497.06	0.04	A ₁	20377.50	0.45
A ₁	7202.68	0.01	A ₁	13911.77	0.05	A ₁	17542.52	0.11	A ₁	20398.52	0.40
B ₂	7250.93	0.00	B ₂	14075.99	0.01	A ₁	17754.78	0.25	B ₂	20416.14	0.08
A ₁	7444.93	0.00	A ₁	14223.74	0.23	A ₁	17877.95	0.11	A ₁	20429.26	0.99
A ₁	7539.79	0.00	B ₂	14321.49	0.01	B ₂	17903.15	0.03	B ₂	20449.76	0.17
A ₁	8273.25	0.00	A ₁	14541.31	0.01	B ₂	17954.95	0.04	A ₁	20533.41	1.14
B ₂	8375.64	0.00	A ₁	14549.21	0.03	A ₁	18119.73	0.13	B ₂	20542.45	0.25
A ₁	8762.89	0.01	B ₂	14630.26	0.01	A ₁	18171.96	0.04	A ₁	20638.10	0.09
B ₂	8809.59	0.00	A ₁	14778.35	0.10	A ₁	18257.65	0.39	A ₁	20710.29	0.49
A ₁	8863.20	0.00	A ₁	14858.96	0.05	B ₂	18260.93	0.02	B ₂	20722.87	0.12
A ₁	9002.14	0.00	B ₂	14932.73	0.04	A ₁	18272.19	0.23	A ₁	20732.39	0.84
A ₁	9719.76	0.00	A ₁	15109.74	0.08	B ₂	18310.17	0.08	B ₂	20911.05	0.42
B ₂	9832.58	0.00	B ₂	15122.59	0.01	B ₂	18370.98	0.22	A ₁	20914.33	1.19
A ₁	10073.82	0.01	A ₁	15181.28	0.02	A ₁	18404.07	0.12	A ₁	20915.40	0.81
A ₁	10285.76	0.02	A ₁	15350.22	0.06	B ₂	18404.86	0.05	B ₂	20949.31	1.21
B ₂	10332.41	0.00	B ₂	15355.29	0.01	A ₁	18567.25	0.46	A ₁	21020.46	0.27
A ₁	10525.60	0.00	A ₁	15377.15	0.09	A ₁	18665.39	0.35	B ₂	21025.89	0.14
A ₁	10602.81	0.05	B ₂	15545.32	0.04	A ₁	18684.78	0.25	B ₂	21052.24	0.25
B ₂	10615.59	0.00	A ₁	15744.33	0.23	B ₂	18713.17	0.04	A ₁	21205.03	0.28
A ₁	10869.36	0.04	A ₁	15809.26	0.03	B ₂	18764.27	0.07	B ₂	21205.78	0.09
B ₂	11034.09	0.00	B ₂	15839.11	0.02	A ₁	18958.96	0.54	A ₁	21276.65	0.18
A ₁	11082.25	0.00	B ₂	15922.71	0.02	A ₁	18996.24	0.35	A ₁	21284.51	0.28
A ₁	11234.36	0.01	A ₁	16023.82	0.15	B ₂	18996.49	0.09	A ₁	21332.46	0.21
B ₂	11235.21	0.00	A ₁	16057.61	0.03	A ₁	19148.28	0.13	B ₂	21338.53	0.12
A ₁	11766.24	0.02	B ₂	16108.20	0.03	B ₂	19188.85	0.04	A ₁	21378.37	0.57
B ₂	11815.47	0.00	A ₁	16187.12	0.12	A ₁	19250.98	0.28	B ₂	21498.90	0.12
A ₁	12011.51	0.01	A ₁	16525.50	0.09	A ₁	19376.61	0.25	A ₁	21545.68	0.79
A ₁	12144.51	0.05	B ₂	16541.18	0.02	B ₂	19449.39	0.14	B ₂	21566.43	0.17
B ₂	12156.53	0.00	A ₁	16654.19	0.02	B ₂	19468.54	0.07	B ₂	21622.88	0.14
A ₁	12340.68	0.00	A ₁	16784.31	0.05	A ₁	19493.49	0.47	A ₁	21652.32	0.46
A ₁	12408.46	0.04	B ₂	16823.85	0.02	A ₁	19665.01	0.25	A ₁	21758.43	0.93
A ₁	12504.09	0.02	A ₁	16826.20	0.17	B ₂	19667.22	0.06	A ₁	21831.88	0.77
B ₂	12567.05	0.01	A ₁	16899.58	0.10	A ₁	19695.72	0.36	A ₁	21843.64	1.09
B ₂	12571.35	0.00	B ₂	16899.60	0.05	B ₂	19698.49	0.57	B ₂	21866.72	0.23

^a The zero point energy for the constrained and unconstrained basis sets is 4630.34667 cm⁻¹ and 4630.34651 cm⁻¹, respectively. Energy levels computed with the constrained basis are in columns marked by c. The difference between energy levels computed with the constrained basis and levels computed with the full basis are in columns marked by c.-u.

$$u'_{\alpha'_1, \alpha'_2, \alpha'_3} = f_{\alpha'_1, \alpha'_2, \alpha'_3} \sum_{\alpha_1} K_{\alpha'_1, \alpha_1}^{(r_1)} \sum_{\alpha_3=\alpha_3^{\min}(\alpha_1, \alpha'_2)}^{\alpha_3^{\max}(\alpha_1, \alpha'_2)} K_{\alpha'_3, \alpha_3}^{(\theta)} u_{\alpha_1, \alpha'_2, \alpha_3} \quad (21)$$

and

$$u'_{\alpha'_1, \alpha'_2, \alpha'_3} = f_{\alpha'_1, \alpha'_2, \alpha'_3} \sum_{\alpha_3} K_{\alpha'_3, \alpha_3}^{(\theta)} \sum_{\alpha_1=\alpha_1^{\min}(\alpha'_2, \alpha_3)}^{\alpha_1^{\max}(\alpha'_2, \alpha_3)} K_{\alpha'_1, \alpha_1}^{(r_1)} u_{\alpha_1, \alpha'_2, \alpha_3} \quad (22)$$

It is useful to determine, e.g., for scanning scheme (1), $\alpha_3^{\max}(\alpha_1, \alpha_2)$ and $\alpha_3^{\min}(\alpha_1, \alpha_2)$ before evaluating matrix-vector products, because this obviates the need to determine whether basis functions should be included or excluded *during* the Lanczos iteration. If $\alpha_3^{\max}(\alpha_1, \alpha_2)$ and $\alpha_3^{\min}(\alpha_1, \alpha_2)$ are determined before computing the matrix-vector products, it is possible to evaluate them by summing only over index values that correspond to basis functions that are included in the basis. It would obviously be more difficult to do the same thing for a more complicated (e.g., multiwell) potential. In this case, one could map the discontinuous regions into one continuous region by

reindexing the points before determining which basis functions are to be retained and before evaluating matrix-vector products.

Rather than including DVR functions centered about points at which the potential is less than V_{\max} (using either of the two scanning schemes described above), one could select DVR functions to include by proceeding as follows: retain the values of α_1 that satisfy the condition $V(r_1^{\alpha_1}, r_2^e, \theta^e) \leq V_{\max}$; for each value of α_1 retain the values of α_2 that satisfy the condition $V(r_1^{\alpha_1}, r_2^{\alpha_2}, \theta^e) \leq V_{\max}$; for each pair of (α_1, α_2) values retain the values of α_3 that satisfy the condition $V(r_1^{\alpha_1}, r_2^{\alpha_2}, \theta^{\alpha_3}) \leq V_{\max}$. Using equations similar to those presented above, constrained matrix-vector products can also be computed for this constraint system. Because the range of allowed values of the second index is constrained, the total cost with this constraint system would be somewhat lower. If there is little coupling there is not much difference between this procedure for imposing constraints and schemes (1) and (2) described above. Due to coupling, DVR functions centered about points at which the potential is less than V_{\max} may be excluded if one uses this constraint system. This is a disadvantage of this method of choosing which points to include.

For H₂O, we find that the number of matrix-vector products

required to converge the lowest energy level is decreased only slightly from 2324 to 2063 but that the cost of each matrix-vector product is reduced by a factor of 2. The ratio of the cost of the constrained basis calculation to the cost of the full direct product basis calculation is approximately proportional to the ratio of the constrained basis size to the full direct product basis size. (See Table 3.) We compare constrained and unconstrained calculations with no symmetry adaptation. It would be possible to use the symmetry-adapted Lanczos (SAL) method^{36,37} and constrain basis index ranges. In fact, we have used SAL to determine symmetries of the H₂O states we calculated.

III. Conclusion

To calculate vibrational (or rovibrational) energy levels, one must choose a basis set with which to construct a matrix representation of the Hamiltonian operator and an eigensolver to calculate eigenvalues of the matrix. Both choices have an important effect on the efficiency of the calculation. The choice of the basis set and the choice of the eigensolver are not independent. For example, if one chooses a direct product basis, then it is clear that it is better to use an iterative (e.g., Lanczos) rather than an explicit (e.g., Householder) eigensolver. Direct product basis functions do not represent wave functions compactly, but it is very easy to compute a direct product basis representation of the Hamiltonian, and it is easy to evaluate matrix-vector products with a product basis Hamiltonian matrix.

The number of direct product basis functions for a molecule with f degrees of freedom is n^f (where n is a representative number of 1-d basis functions). Because n is typically between 10 and 20, this number is huge for a molecule with six degrees of freedom. There are two obvious ways to improve the basis: (1) make new (better) basis functions by taking appropriate linear combinations of the direct product functions; (2) exclude from the direct product basis functions that are not necessary for calculating the energy levels of interest. There is a great deal of evidence suggesting that option (1) is a very good strategy. However, it has the disadvantage that generating better basis functions requires devising a contraction scheme, and choosing parameters. It also has the disadvantage that matrix-vector products in the new basis are more complicated and costly than their direct product counterparts. In this paper we have demonstrated that option (2) is, for some problems, a good choice. If one excludes direct product basis functions by restricting the range of basis function indices, it is straightforward to evaluate the matrix-vector products required to use iterative methods to compute energy levels. Excluding basis functions by restricting index ranges is practical and effective.

We have applied two different schemes for excluding direct product basis functions. We excluded VBR product basis functions by imposing a constraint on the allowed values of the 1-d quantum numbers. For silane, this works extremely well. Excluding basis functions enables us to reduce the number of Lanczos iterations required to converge the desired energy levels

and also to reduce the cost of each matrix-vector product. We have also tested excluding basis functions from a direct product PODVR basis by removing basis functions peaked about points at which the potential is larger than V_{\max} . In this case the number of iterations required is not reduced significantly, but we are able to reduce the number of basis functions and the cost of the matrix-vector products by about a factor of 2. We have used a simple criterion (V_{\max}) for excluding basis functions, but it should also be possible to use more sophisticated criteria for excluding points with the method we employ.

References and Notes

- (1) Bačić, Z.; Light, J. C. *Annu. Rev. Phys. Chem.* **1989**, *40*, 469.
- (2) Sibert, E. L. *Int. Rev. Phys. Chem.* **1990**, *9*, 1.
- (3) Carrington, T., Jr. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; John Wiley & Sons: New York, 1998; Vol. 5.
- (4) Light, J. C.; Carrington, T., Jr. *Adv. Chem. Phys.* **2000**, *114*, 263.
- (5) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in Fortran*, Second Edition; Cambridge University Press: Cambridge, 1992.
- (6) Carter, S.; Handy, N. C. *Mol. Phys.* **1986**, *57*, 175.
- (7) Bačić, Z.; Light, J. C. *J. Chem. Phys.* **1987**, *86*, 3065.
- (8) Tennyson, J.; Henderson, J. R. *J. Chem. Phys.* **1989**, *91*, 3815.
- (9) Bowman, J. M.; Gazdy, B. *J. Chem. Phys.* **1991**, *94*, 454.
- (10) LeQuéré, F.; Leforestier, C. *J. Chem. Phys.* **1990**, *92*, 247.
- (11) Iung, C.; Leforestier, C. *J. Chem. Phys.* **1989**, *90*, 3198.
- (12) Bentley, J. A.; Brunet, J.-P.; Wyatt, R. E.; Friesner, R. A.; Leforestier, C. *Chem. Phys. Lett.* **1989**, *161*, 393.
- (13) McNichols, A.; Carrington, T., Jr. *Chem. Phys. Lett.* **1993**, *202*, 464.
- (14) Bramley, M. J.; Carrington, T., Jr. *J. Chem. Phys.* **1993**, *99*, 8519.
- (15) Bramley, M. J.; Tromp, J. W.; Carrington, T., Jr.; Corey, G. C. *J. Chem. Phys.* **1994**, *100*, 6175.
- (16) Bramley, M. J.; Carrington, T., Jr. *J. Chem. Phys.* **1994**, *101*, 8494.
- (17) Leforestier, C.; Braly, L. B.; Liu, K.; Elrod, M. J.; Saykally, R. J. *J. Chem. Phys.* **1997**, *106*, 8527.
- (18) Sarkar, P.; Poulin, N.; Carrington, T., Jr. *J. Chem. Phys.* **1999**, *110*, 10269.
- (19) Cullum, J.; Willoughby, R. A. *Lanczos Algorithm for Large Symmetric Eigenvalue Computations*; Birkhäuser: Boston, 1985.
- (20) Echave, J.; Clary, D. C. *Chem. Phys. Lett.* **1992**, *190*, 225.
- (21) Wei, H.; Carrington, T., Jr. *J. Chem. Phys.* **1992**, *97*, 3029.
- (22) Halonen, L.; Child, M. S. *Comput. Phys. Comm.* **1988**, *51*, 173.
- (23) Carter, S.; Handy, N. C. *Comput. Phys. Rep.* **1986**, *5*, 115.
- (24) Lehoucq, R. B.; Gray, S. K.; Zhang, D.-H.; Light, J. C. *Comput. Phys. Comm.* **1998**, *109*, 15.
- (25) Friesner, R. A.; Bentley, J. A.; Menou, M.; Leforestier, C. *J. Chem. Phys.* **1993**, *99*, 324.
- (26) Wu, X. T.; Hayes, E. F. *J. Chem. Phys.* **1997**, *107*, 2705.
- (27) Wyatt, R. E.; Iung, C.; Leforestier, C. *J. Chem. Phys.* **1992**, *97*, 3458.
- (28) Wyatt, R. E.; Iung, C.; Leforestier, C. *J. Chem. Phys.* **1992**, *97*, 3477.
- (29) Friesner, R. A.; Wyatt, R. E.; Hempel, C.; Criner, B. *J. Comput. Phys.* **1986**, *64*, 220.
- (30) Manthe, U.; Koeppel, H. *J. Chem. Phys.* **1993**, *93*, 345.
- (31) Wang, X.-G.; Sibert, E. L. *J. Chem. Phys.* **2000**, *113*, 5384.
- (32) Martin, J. M. L.; Baldrige, K. K.; Lee, T. J. *Mol. Phys.* **1999**, *97*, 945.
- (33) Colbert, D. T.; Miller, W. H. *J. Chem. Phys.* **1992**, *96*, 1982.
- (34) Dumont, R. S.; Assalone, R. *J. Chem. Phys.* **1999**, *111*, 4362.
- (35) Sutcliffe, B. T.; Tennyson, J. *Int. J. Quantum Chem.* **1991**, *39*, 183.
- (36) Wang, X.-G.; Carrington, T., Jr. *J. Chem. Phys.* **2001**, *114*, 1473.
- (37) Chen, R.; Guo, H. *J. Chem. Phys.* **2001**, *114*, 1467.