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The discrete variable representation of a triatomic Hamiltonian in bond length–bond angle coordinates

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The discrete variable representation (DVR) is used to calculate vibrational energy levels of H_2O and SO_2 . The Hamiltonian is written in terms of bond length–bond angle coordinates and their conjugate momenta. It is shown that although these coordinates are not orthogonal and the appropriate kinetic energy operator is complicated, the discrete variable representation is quite simple and facilitates the calculation of vibrational energy levels. The DVR enables one to use an internal coordinate Hamiltonian without expanding the coordinate dependence of the kinetic energy or evaluating matrix elements numerically. The accuracy of previous internal coordinate calculations is assessed.

INTRODUCTION

New experimental techniques such as stimulated emission pumping¹ have enabled experimentalists to probe vibrational and vibrational–rotational transitions well beyond the energy levels which may be accurately determined by standard harmonic analysis.² To understand the spectra of highly excited states spectroscopists are using perturbation theory,^{3,4} the self-consistent field method,⁵ and the adiabatic approximation, but more and more they are resorting to variational calculations.⁶ It is, however, difficult to apply variational methods to polyatomic molecules and it is important to hone the computational techniques on triatomic molecules before attempting molecules with more than three vibrational degrees of freedom.

Although the conventional perturbative approach³ to molecular spectroscopy employs rectilinear coordinates, curvilinear coordinates are better suited to the description of highly excited large amplitude vibrations. It is desirable to write the Hamiltonian operator in terms of internal, curvilinear coordinates, and their conjugate momenta, and to set up the Hamiltonian matrix using basis functions which are functions of the internal coordinates for two reasons. First, curvilinear coordinates give a more accurate representation of the potential energy surface.⁷ A simple polynomial expansion in internal coordinates more accurately approximates the potential than the corresponding expansion in Cartesian coordinates. If, on the basis of spectroscopic information near the minimum, one wants to obtain the best possible potential, it is important to express the potential in terms of coordinates which describe the potential as compactly as possible. The internal-coordinate expansion parameters also have the advantage of being isotope independent (within the Born–Oppenheimer approximation). Second, internal coordinates facilitate the choice of good basis functions. Not only the potential but also the wave functions are more succinctly represented in terms of internal coordinates. A direct product of functions of the internal coordinates more closely approximates the true wave function than a direct product of functions of Cartesian coordinates. It is important to be able to choose basis

functions which approximate as exactly as possible the exact wave functions to reduce the size of the variational matrix which must be diagonalized. The essential disadvantage of internal coordinates is the complicated kinetic energy operator one is forced to deal with if the Hamiltonian is written in terms of internal coordinates and their conjugate momenta. The complexity of the kinetic energy operator in internal coordinates is dealt with either by expanding the coordinate dependence of the G matrix elements in terms of functions whose matrix elements may be calculated analytically and inexpensively^{8,9} or by calculating the necessary matrix elements numerically.⁶

It has recently been shown that variational calculations may be considerably simplified by employing two representations, one in which the potential is diagonal and another in which the kinetic energy matrix is simple.^{10–13} The powerful discrete variable representation (DVR) of Light and co-workers is a representation in terms of finite basis approximations to delta functions. The transformation between the discrete representation and the polynomial basis set representation is well understood. The DVR has proved very useful for calculating energy levels when the kinetic energy operator of the Hamiltonian is relatively simple. It has not yet been used to determine energy levels using a Hamiltonian written in terms of coordinates which are not orthogonal and whose kinetic energy does not lend itself to a simple matrix representation in terms of some polynomial basis functions.

APPLICATION OF THE DVR TO AN INTERNAL COORDINATE HAMILTONIAN

If the wave functions are normalized so that $\int \Psi^*(\mathbf{r})\Psi(\mathbf{r})d\mathbf{r} = 1$ with the volume element $d\mathbf{r} = dr_1 dr_2 d\theta$ the quantum mechanical Hamiltonian of a triatomic molecule, X_2Y , in terms of the two bond lengths and the enclosed angle is

$$H = T + V, \quad (1)$$

where

$$\begin{aligned}
2T = & p_1 G_{11} p_1 + p_2 G_{22} p_2 + p_\theta G_{\theta\theta} p_\theta + p_1 G_{12} p_2 + p_2 G_{12} p_1 \\
& + p_1 G_{1\theta} p_\theta + p_\theta G_{1\theta} p_1 + p_2 G_{2\theta} p_\theta + p_\theta G_{2\theta} p_2 \\
& - \frac{\hbar^2}{2m_Y} \frac{\cos \theta}{r_1 r_2} - \frac{\hbar^2}{8} G_{\theta\theta} (1 + \csc^2 \theta), \quad (2)
\end{aligned}$$

where

$$p_1 = -i\hbar \frac{\partial}{\partial r_1}, \quad p_2 = -i\hbar \frac{\partial}{\partial r_2}, \quad p_\theta = -i\hbar \frac{\partial}{\partial \theta}$$

and

$$\begin{aligned}
G_{11} = G_{22} &= \frac{1}{m_X} + \frac{1}{m_Y}, \\
G_{\theta\theta} &= \frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} - \frac{2 \cos \theta}{m_Y r_1 r_2}, \\
G_{12} &= \frac{\cos \theta}{m_Y}, \quad G_{1\theta} = \frac{-\sin \theta}{m_Y r_2}, \quad G_{2\theta} = \frac{-\sin \theta}{m_Y r_1},
\end{aligned}$$

where

$$\frac{1}{\mu_1} = \frac{1}{m_Y} + \frac{1}{m_X} = \frac{1}{\mu_2},$$

and r_1 , r_2 , and θ are the two bond lengths and the enclosed angle and V is the potential energy.¹⁴ Each term in the Hamiltonian has the form

$$h(r_1, r_2, \theta) = f_1(r_1) f_2(r_2) f_3(\theta).$$

The factors f_i may include not only functions with respect to the appropriate variable but also derivatives with respect to it. For example, one term in the Hamiltonian is

$$\begin{aligned}
p_\theta \frac{\cos \theta}{m_Y r_1 r_2} p_\theta &= \left(\frac{1}{r_1} \right) \left(\frac{1}{r_2} \right) \left[p_\theta \left(\frac{\cos \theta}{m_Y} \right) p_\theta \right] \\
&= f_1(r_1) f_2(r_2) f_3(\theta).
\end{aligned}$$

Note that $f_3(\theta)$ includes both functions of θ and derivatives with respect to θ . The DVR has not been used with Hamiltonians of this complexity. The multidimensional DVR we employ is a direct product of DVRs for the r_1 , r_2 , and θ degrees of freedom. For each of the three degrees of freedom the matrix \mathbf{T}_X , which relates the basis function representation to the discrete representation is determined by diagonalizing a function of the coordinate operator in the function basis,

$$\mathbf{X}^{\text{DVR}} = \mathbf{T}_X' \mathbf{X} \mathbf{T}_X, \quad \mathbf{X} = \mathbf{g}_1(r_1), \mathbf{g}_2(r_2), \theta, \quad (3)$$

where \mathbf{X}^{DVR} is a diagonal matrix. If the basis functions are orthogonal polynomials times a *common* weight function the diagonal elements of the matrix \mathbf{X}^{DVR} are the Gaussian points for the polynomial basis functions.¹³ The basis set representation of each term in the Hamiltonian has the form

$$\begin{aligned}
h_{ijk}^{i'j'k'} &= \langle \phi_i(r_1) | f_1(r_1) | \phi_{i'}(r_1) \rangle \langle \chi_j(r_2) | f_2(r_2) | \chi_{j'}(r_2) \rangle \\
&\quad \times \langle \Psi_k(\theta) | f_3(\theta) | \Psi_{k'}(\theta) \rangle \\
&= (\mathbf{f}_1)_{ii'} (\mathbf{f}_2)_{jj'} (\mathbf{f}_3)_{kk'},
\end{aligned}$$

where $\phi_i(r_1)$, $\chi_j(r_2)$, and $\Psi_k(\theta)$ are basis functions for the r_1 , r_2 , and θ degrees of freedom. In the direct product DVR the corresponding matrix is

$$\text{DVR } h_{\alpha\beta\gamma}^{\alpha'\beta'\gamma'} = (\mathbf{T}_{r_1}' \mathbf{f}_1 \mathbf{T}_{r_1})_{\alpha\alpha'} (\mathbf{T}_{r_2}' \mathbf{f}_2 \mathbf{T}_{r_2})_{\beta\beta'} (\mathbf{T}_\theta' f_3 \mathbf{T}_\theta)_{\gamma\gamma'}.$$

For the term considered above,

$$(\mathbf{T}_{r_1}' \mathbf{f}_1 \mathbf{T}_{r_1})_{\alpha\alpha'} = \left(\frac{1}{r_1^\alpha} \right) \delta_{\alpha\alpha'},$$

$$(\mathbf{T}_{r_2}' \mathbf{f}_2 \mathbf{T}_{r_2})_{\beta\beta'} = \left(\frac{1}{r_2^\beta} \right) \delta_{\beta\beta'},$$

$$(\mathbf{T}_\theta' f_3 \mathbf{T}_\theta)_{\gamma\gamma'} = \sum_{\gamma''} (\mathbf{T}_\theta' p_\theta \mathbf{T}_\theta)_{\gamma\gamma''} \left(\frac{\cos \theta_{\gamma''}}{m_Y} \right) (\mathbf{T}_\theta' p_\theta \mathbf{T}_\theta)_{\gamma''\gamma'},$$

where r_1^α is the value of r_1 associated with the α th eigenvalue of $g_1(r_1)$, r_2^β is the value of r_2 associated with the β th eigenvalue of $g_2(r_2)$, θ_γ is the γ th eigenvalue of θ , and we have assumed that $\mathbf{T}_X' f(\mathbf{X}) \mathbf{T}_X = f(\mathbf{X}^{\text{DVR}})$, $\mathbf{X} = \mathbf{g}(r_1)$, $\mathbf{g}(r_2)$, θ where \mathbf{X}^{DVR} is diagonal. The discrete representation of each of the terms in the Hamiltonian in Eq. (1) is constructed in this manner. We have also used DVRs of the Hamiltonian of Carter and Handy.⁶ Their Hamiltonian is equivalent to that of Eq. (1), but for the wave function normalized so that

$$\int dr_1 \int dr_2 \int d\theta \sin \theta \psi^*(r_1, r_2, \theta) \psi(r_1, r_2, \theta) = 1. \quad (4)$$

The discrete representation of the Carter–Handy Hamiltonian is determined in the same way.

CHOICE OF BASIS FUNCTIONS

In the discrete variable representation the potential matrix is always diagonal (this fundamental assumption of the DVR method is based on the accuracy of Gaussian quadrature). The discrete representation of the complete Hamiltonian is easily constructed if the basis set representation of the kinetic energy is simple. Basis functions are usually chosen so that the basis representation of the kinetic energy is diagonal or tridiagonal. For example, the angular part of the kinetic energy of an atom–diatom system in Jacobi coordinates in the body-fixed reference frame is diagonal in a Legendre polynomial basis.¹³ The internal coordinate Hamiltonian is sufficiently complicated that it is not possible to choose basis functions so that the basis function representation of the kinetic energy operator is diagonal.

For the stretching degrees of freedom we have considered two sets of basis functions: the eigenfunctions of a Morse oscillator and a set of orthogonal functions which tridiagonalizes the Morse oscillator Hamiltonian. It is natural to think that Morse eigenfunctions might define useful DVR points. From basis set variational calculations it is known that the Morse basis is very efficient.^{8,15} A useful set of discrete points may be obtained from the Morse eigenfunctions by following the original prescription of Harris *et al.*¹⁶ The eigenvalues of the Morse oscillator eigenfunction representation of the coordinate operator are not Gaussian quadrature points (because the basis functions do not

share a common weight function).¹⁷ The eigenvalues and eigenfunctions of the coordinate matrix may still, however, be used to construct an efficient discrete representation of the Hamiltonian to calculate eigenvalues. It is better to choose basis functions which efficiently represent the eigenfunctions of the Hamiltonian than to choose polynomial basis functions with a common weight function to achieve Gaussian accuracy. If the X - Y stretching potentials are represented by Morse oscillators, the Morse DVR points are excellent because the Morse oscillator eigenfunction finite basis set representation of the X - Y stretching Hamiltonian matrix elements is in this case exact. The points obtained from the Morse oscillator eigenfunction basis are not obviously the best points to choose if the X - Y stretching potentials are not exactly Morse.

We have also used the DVR points associated with the basis functions

$$\chi_n(z) = \left[\frac{\alpha n!}{\Gamma(2\gamma + n + 1)} \right]^{1/2} z^{\gamma+1/2} \exp(-z/2) L_n^{2\gamma}(z), \quad (5)$$

where

$$z = \left(\frac{2}{\alpha \hbar} \right) (2\mu D)^{1/2} \exp[-\alpha(r - r_e)],$$

μ is the reduced mass, r_e is the equilibrium bond length, α and D are the Morse parameters, where the Morse potential is

$$V(r) = D\{1 - \exp[-\alpha(r - r_e)]\}^2, \quad (6)$$

$L_n^{2\gamma}(z)$ is an associated Laguerre polynomial and γ is greater than $-1/2$ but otherwise arbitrary.¹⁸ If the Morse oscillator Hamiltonian is written,

$$\begin{aligned} H &= \frac{1}{2\mu} P_r^2 + D\{1 - \exp[-\alpha(r - r_e)]\}^2 \\ &= \frac{\omega \hbar c}{2} (P_q^2 + Q^2) \\ &= \frac{\omega \hbar c}{2} \left[P_q^2 + \frac{1}{\beta^2} \left(1 - \frac{\beta^2 z}{2} \right)^2 \right], \end{aligned} \quad (7)$$

where

$$\beta = \left(\frac{-2x}{\omega} \right)^{1/2},$$

$$q = \frac{\alpha}{\beta} (r - r_e),$$

$$P_q = \frac{\beta}{\alpha \hbar} P_r,$$

$$Q = (1 - e^{-\beta q})/\beta = \frac{1}{\beta} - \frac{z\beta}{2},$$

$$x = -\frac{\alpha^2 \hbar^2}{2\hbar c \mu},$$

$$\omega \hbar c = \hbar \left(\frac{2\alpha^2 D}{\mu} \right)^{1/2},$$

the matrix elements required to set up a matrix representation of the Hamiltonian are¹⁸

$$(P_q)_{n,n+1} = \left(\frac{\beta}{2} \right) \left(\frac{1}{i} \right) [(n+1)(n+2\gamma+1)]^{1/2},$$

$$(P_q^2)_{n,n} = \frac{\beta^2}{4} [2n(n+2\gamma+1) + 2\gamma+1],$$

$$\begin{aligned} (P_q^2)_{n,n+2} &= \frac{-\beta^2}{4} [(n+2)(n+1)(n+2\gamma+2) \\ &\quad \times (n+2\gamma+1)]^{1/2}, \end{aligned}$$

$$(\chi_n | z | \chi_n) = 2n + 2\gamma + 1,$$

$$(\chi_n | z | \chi_{n-1}) = (\chi_{n-1} | z | \chi_n) = -[n(n+2\gamma)]^{1/2},$$

$$\begin{aligned} (\chi_n | z^2 | \chi_n) &= (n+1)(n+2\gamma+1) + n(n+2\gamma) \\ &\quad + (2n+2\gamma+1)^2, \end{aligned}$$

$$\begin{aligned} (\chi_n | z^2 | \chi_{n-1}) &= (\chi_{n-1} | z^2 | \chi_n) \\ &= [n(n+2\gamma)]^{1/2} (n+\gamma)(-4), \end{aligned}$$

$$\begin{aligned} (\chi_n | z^2 | \chi_{n-2}) &= (\chi_{n-2} | z^2 | \chi_n) \\ &= [n(n-1)(n+2\gamma)(n+2\gamma-1)]^{1/2}. \end{aligned}$$

The matrix representation of the Morse oscillator Hamiltonian in this basis is tridiagonal and this basis will be referred to as the tridiagonal-Morse basis. Such basis functions have been used to construct finite basis representations.¹⁹ We use them here to generate a discrete representation. These functions *do* have a common weight function and the eigenvalues of the $n \times n$ coordinate matrix are exactly the roots of the appropriate n th polynomial. The tridiagonal-Morse basis has several important advantages. Unlike harmonic oscillator eigenfunctions the tridiagonal-Morse functions provide a very compact representation of the true wave functions. It has been clearly demonstrated in the past that harmonic oscillator basis functions are poor, but the usual solution is to use Morse eigenfunctions to construct the basis. The tridiagonal-Morse functions are better basis functions than Morse eigenfunctions. The Morse basis is not complete because eigenfunctions in the continuum are not included. This truncation of the basis is not important for low-lying energy levels but to calculate accurately highly excited energy levels it is essential that the corresponding eigenfunctions be well described by linear combinations of the basis functions and this description will become increasingly poorer if a Morse basis is used and continuum functions are neglected. Another advantage of the tridiagonal-Morse basis with respect to the Morse basis is the simplicity of the required matrix elements. The Morse matrix elements of Q or q and of P_q [both are required for a standard variational calculation and matrix elements of P_q are required for a DVR calculation with a Hamiltonian as tangled as the internal coor-

TABLE I. Comparison of eigenvalues of the Morse [Eq. (7)] and extended-Morse [Eq. (8)] oscillator Hamiltonians calculated using harmonic, Morse, and tridiagonal-Morse bases. N is the number of basis functions, Ne is used to define the tridiagonal-Morse functions [$\gamma = (-\omega/2x) - (Ne + 1)$], E_{ex} is the exact energy level, E_h , E_m and E_{tm} are the variational results obtained with the harmonic, Morse and tridiagonal-Morse bases. The parameters for the Morse potential are: $\alpha = 2.2241 \text{ \AA}^{-1}$, $D = 0.853\,045 \text{ aJ}$, and $\omega = 3886.92 \text{ cm}^{-1}$. The parameters for the extended-Morse potential are: $\alpha = 2.2241 \text{ \AA}^{-1}$, $\omega = 3886.92 \text{ cm}^{-1}$, $\beta = 0.212\,736$, $b = 0.05 (D/hc) \text{ cm}^{-1}$.

Morse potential					Extended Morse potential			
	E_{ex}	$E_h - E_{ex}$	$E_m - E_{ex}$	$E_{tm} - E_{ex}$	E_{ex}	$E_h - E_{ex}$	$E_m - E_{ex}$	$E_{tm} - E_{ex}$
$N=10$								
	$Ne=6$							
0	1 921.473	0.000	0.000	0.000	1 924.708	0.000	0.000	0.000
1	5 632.487	0.072	0.000	0.000	5 648.437	0.061	0.002	0.000
2	9 167.593	3.430	0.000	0.000	9 208.396	2.994	0.008	0.000
3	12 526.790	58.995	0.000	0.000	12 603.908	52.853	-0.041	-0.003
4	15 710.079	414.324	0.000	0.000	15 834.312	383.790	-0.703	-0.030
5	18 717.459	1 461.305	0.000	0.000	18 898.968	1 389.482	-4.366	-0.075
6	21 548.930	3 414.156	0.000	0.000	21 797.251	3 301.355	-16.338	-3.207
7	24 204.493	6 919.493	0.000	-1397.711	24 528.551	6 817.753	-38.363	-1516.785
8	26 684.147	9 990.919	0.000	-1777.524	27 092.271	9 910.745	-56.660	-2060.520
9	28 987.893	27 986.552	0.000	2253.356	29 487.825	30 257.330	-106.669	2177.169
$N=34$ (22 for Morse basis) $Ne=21$								
0	1 921.473	0.000	0.000	0.000	1 924.708	0.000	0.000	0.000
1	5 632.487	0.000	0.000	0.000	5 648.437	0.000	0.000	0.000
2	9 167.593	0.000	0.000	0.000	9 208.396	0.000	0.000	0.000
3	12 526.790	0.000	0.000	0.000	12 603.908	0.000	0.001	0.000
4	15 710.079	0.000	0.000	0.000	15 834.312	0.000	0.006	0.000
5	18 717.459	0.006	0.000	0.000	18 898.968	0.004	0.026	0.000
6	21 548.930	0.260	0.000	0.000	21 797.251	0.148	0.076	0.000
7	24 204.493	5.642	0.000	0.000	24 528.551	3.447	0.142	0.000
8	26 684.147	61.191	0.000	0.000	27 092.271	41.425	0.059	0.000
9	28 987.893	328.486	0.000	0.000	29 487.825	248.597	-0.690	0.000
10	31 115.730	1 012.219	0.000	0.000	31 714.641	834.775	-3.127	0.000
11	33 067.659	2 195.261	0.000	0.000	33 772.153	1 911.288	-8.562	0.000
12	34 843.679	3 875.084	0.000	0.000	35 659.804	3 487.755	-17.669	0.000
13	36 443.790	6 036.380	0.000	0.000	37 377.047	5 551.109	-29.137	0.000
14	37 867.993	8 669.219	0.000	0.000	38 923.338	8 092.262	-39.425	0.000
15	39 116.287	11 769.620	0.000	0.000	40 298.141	11 108.430	-45.368	0.000
16	40 188.673	15 338.363	0.000	0.000	41 500.924	14 602.101	-47.779	0.000
17	41 085.150	19 380.331	0.000	0.000	42 531.156	18 580.391	-50.655	0.000
18	41 805.718	23 904.244	0.000	0.000	43 388.314	23 054.787	-54.394	-0.001
19	42 350.378	28 923.153	0.000	0.000	44 071.871	28 041.857	-51.224	-0.002
20	42 719.130	34 455.266	0.000	0.000	44 581.307	33 564.202	-32.975	0.032
21	42 911.973	40 523.850	0.000	0.000	44 916.185	39 650.642	6.858	0.471

dinate Hamiltonian in Eq. (1)] are complicated,²⁰ but the matrix elements of Q and P_q are simple for the tridiagonal-Morse basis. If one chooses to use a discrete variable representation, the points associated with the tridiagonal-Morse basis are better than the Morse points because the tridiagonal-Morse points are Gaussian quadrature points and the Morse points are not. The accuracy of a DVR calculation is determined by two things: the dimension of the Hamiltonian matrix and the quality of the quadrature scheme used to compute the matrix elements. The tridiagonal-Morse points are optimized (they are Gaussian quadrature points), the Morse points are not and, therefore, the quadrature scheme associated with the tridiagonal-Morse basis is superior. One way to visualize this advantage of the tridiagonal-Morse basis is to think in terms of the approximation method introduced by Harris *et al.*¹⁶ The quadrature approximation is equivalent to assuming that the finite basis set representation of $g(q)$ raised to some power is equal to products of $g(q)$, where $g(q)$ is the finite basis set representation of the coordinate

function diagonalized. The function $z=g(q)$ is tridiagonal in the tridiagonal-Morse representation, whereas z is a full matrix in the Morse representation. The finite basis set representation of $g(q)$ raised to some power is more nearly equal to products of $g(q)$ if the matrix representation of $g(q)$ is tridiagonal. The quality of the tridiagonal-Morse basis functions and the associated points is demonstrated in Table I. In this table we compare the eigenvalues obtained using harmonic, Morse, and tridiagonal-Morse bases for a Morse oscillator and an extended Morse oscillator Hamiltonian. The extended Morse oscillator Hamiltonian is

$$H = \frac{hc\omega}{2} (P_q^2 + Q^2) + hcbQ^4. \quad (8)$$

The discrete representation of the Morse oscillator Hamiltonian in the Morse and tridiagonal-Morse bases is

$${}^{\text{DVRM}}\mathbf{H}_M = \mathbf{T}_M^t \mathbf{E} \mathbf{T}_M$$

and

$$\text{DVRTM} \mathbf{H}_{\text{TM}} = \mathbf{T}_{\text{TM}}^t \mathbf{M} \mathbf{T}_{\text{TM}},$$

where

$$E_{nn'}/hc = [\omega(n + \frac{1}{2}) + x(n + \frac{1}{2})^2] \delta_{nn'},$$

$$\begin{aligned} M_{nn'}/hc = & \left[-\frac{\beta^2 \omega}{2} \left[n + \left(\gamma + \frac{1}{2} \right)^2 + \left(\frac{1}{\beta^2} - \gamma - n - 1 \right) (2n + 2\gamma + 1) \right] + \frac{\omega}{2\beta^2} \right] \delta_{nn'} + \frac{\beta^2 \omega}{2} \left[\left(\frac{1}{\beta^2} - \gamma - n \right) \right. \\ & \times [n(n + 2\gamma)]^{1/2} \delta_{n,n'+1} + \frac{\beta^2 \omega}{2} \left[\left(\frac{1}{\beta^2} - \gamma - n - 1 \right) [(n+1)(n+1+2\gamma)]^{1/2} \right] \delta_{n,n'-1} \end{aligned}$$

and T_M and T_{TM} are the transformation matrices which diagonalize \mathbf{z} (or \mathbf{Q}). The discrete representation of the extended Morse Hamiltonian in the Morse and tridiagonal-Morse bases is

$$\text{DVRM} \mathbf{H}_{\text{EM}} = \mathbf{T}_M^t \mathbf{E} \mathbf{T}_M + hcb(\Lambda_M)^4$$

and

$$\text{DVRTM} \mathbf{H}_{\text{EM}} = \mathbf{T}_{\text{TM}}^t \mathbf{M} \mathbf{T}_{\text{TM}} + hcb(\Lambda_{\text{TM}})^4,$$

where

$$\mathbf{T}_M^t \mathbf{Q} \mathbf{T}_M = \Lambda_M,$$

$$\mathbf{T}_{\text{TM}}^t \mathbf{Q} \mathbf{T}_{\text{TM}} = \Lambda_{\text{TM}}.$$

The \mathbf{T} matrices are obtained from diagonalizing \mathbf{Q} (or for the harmonic and tridiagonal-Morse bases from the Gaussian points and weights). For the Morse potential the tridiagonal-Morse basis is almost as good as the Morse basis (with which one obtains exact results) and both are far superior to the harmonic basis. For the extended Morse Hamiltonian the tridiagonal-Morse basis is excellent. The best value of γ might be determined variationally. If $\gamma = (-\omega/2x) - (Ne+1)$ then diagonalizing the $(Ne+1) \times (Ne+1)$ tridiagonal-Morse representation of the Morse oscillator Hamiltonian yields the first $Ne+1$ energy levels exactly. We choose γ equal to the value which would generate exact eigenvalues if b were equal to zero. For the extended-Morse potential one obtains much better results with the Morse basis if the parameters for the basis are chosen so that ω is equal to the harmonic frequency of the extended-Morse potential and β is determined from the actual dissociation energy of the extended-Morse potential (and not from the dissociation energy of the corresponding potential with $b=0$). For the extended-Morse of Table I we have used $0.212\,736/(1+0.05)^{1/2}$ for β and $2.2241/(1+0.05)^{1/2} \text{ \AA}^{-1}$ for α in the definition of the Morse basis functions.

To determine accurate energy levels from the DVR associated with the tridiagonal-Morse basis it is important to take more discrete points than the number of tridiagonal-Morse basis functions which would be required if the Hamiltonian matrix elements were evaluated exactly. For example, for a Morse oscillator Hamiltonian, the eigenvalues of an $N \times N$ tridiagonal-Morse representation are exactly the first N energy levels, if the matrix elements are computed exactly, but in the DVR one must diagonal-

ize a slightly large matrix to obtain the first N energy level accurately. The advantages of the tridiagonal-Morse basis are more important if one wants to calculate many energy levels. The transformation from the variational basis representation to the discrete variable representation is more accurate for the tridiagonal-Morse basis because the matrix representation of \mathbf{Q} is a tridiagonal matrix and not a full matrix. To calculate many energy levels one requires a large basis set and for a large matrix the difference between a tridiagonal and a full matrix is more important.

For the bending degree of freedom we have applied DVRs obtained from a harmonic basis, a Legendre basis, and the basis which tridiagonalizes a Morse oscillator Hamiltonian. The kinetic energy formula of Carter and Handy was used with the Legendre basis, the calculations with the harmonic and tridiagonal-Morse bases were performed with the Hamiltonian of Eq. (1). It is natural to assume that a Morse-type basis would be good for stretching degrees of freedom and it is less obvious that Morse-type basis functions would provide a good representation of bending eigenfunctions. Morse-type basis functions actually provide quite a good basis for the bend of a (well-bound) triatomic molecule. There is a natural limit on the size of the harmonic and tridiagonal-Morse bases which one can use. If the number of basis functions, and hence the number of points, is too large, some of the DVR points correspond to values of the bending angle larger than π and one obtains nonsensical results.

The tridiagonal-Morse and the Morse functions are both excellent bases for the stretches because they mimic well the true stretching wave functions. Choosing points associated with square integrable functions which resemble appropriate one-dimensional eigenfunctions reduces the dimension of the variational matrix for the coupled problem because the points are optimal. The Morse-type functions are useful even for the bend, but there is a better way to choose optimized DVR points for the bending degree of freedom.

Using the Legendre basis we diagonalize the zeroth-order bending Hamiltonian. $\cos(\theta)$ is then diagonalized in a basis of the eigenvectors of the one-dimensional bending Hamiltonian to define an optimized DVR. This optimized DVR is used for the full three dimensional calculations. We take as many eigenvectors of the zeroth-order bending

TABLE II. Comparison of eigenvalues of the pure bending vibration of water calculated using harmonic (E_h), tridiagonal-Morse (E_{tm}), Legendre (E_l) and optimized-Legendre (E_{op}) bases. The number of basis functions is 17. The optimized Legendre basis is obtained using 30 (E_{op30}) or 35 (E_{op35}) Legendre functions. E_{ex} is the exact energy level. The Hamiltonian parameters are $f_{\theta\theta}=35\,591.175\text{ cm}^{-1}$, $F_e=39.285\,276\text{ cm}^{-1}$, $\theta_e=104.439\,76^\circ$, $f_0^{(2)}=18\,975.6\text{ cm}^{-1}$, $f_0^{(3)}=1728\text{ cm}^{-1}$, $f_0^{(4)}=5154\text{ cm}^{-1}$, $\omega_b=1672.249$. The Morse and tridiagonal-Morse parameters are $\alpha=0.169\,28\text{ \AA}^{-1}$, $\gamma=730.828$.

	E_{ex}	$E_h - E_{ex}$	$E_{tm} - E_{ex}$	$E_l - E_{ex}$	$E_{op30} - E_{ex}$	$E_{op35} - E_{ex}$
0	810.829 698	0.000 000	0.000 000	-0.000 359	0.000 000	0.000 000
1	2 457.227 854	0.000 001	0.000 000	-0.067 196	0.000 000	0.000 000
2	4 073.093 571	0.000 048	0.000 002	1.010 890	0.000 000	0.000 000
3	5 650.440 637	0.002 150	0.000 057	-9.073 218	0.000 000	0.000 000
4	7 178.539 188	0.066 384	0.000 732	18.582 580	0.000 000	0.000 000
5	8 640.577 830	1.394 938	0.001 172	-29.581 380	0.000 000	0.000 000
6	10 004.807 310	17.979 326	-0.068 273	-197.227 995	0.000 000	0.000 000
7	11 233.071 204	112.320 595	0.070 123	221.237 371	0.000 001	0.000 000

Hamiltonian as is necessary to obtain converged results.

In Table II we compare the eigenvalues calculated with four bases for the pure bending Hamiltonian⁶

$$H = -F_e \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} \right) + V_0,$$

where the bending potential is⁹

$$V_0 = f_0^{(2)} x^2 + f_0^{(3)} x^3 + f_0^{(4)} x^4, \quad x = \cos \theta - \cos \theta_e.$$

For the Legendre and optimized Legendre bases we use points defined by $\cos \theta$ and the volume element of Eq. (4). For the harmonic and tridiagonal-Morse bases we use points defined by $\theta - \theta_e$ and the volume element $dr_1 dr_2 d\theta$, but there is an additional effective potential term $-(0.5 + 0.25 \cot^2 \theta) F_e$ in the Hamiltonian.

RESULTS

We have used the DVR to calculate eigenvalues of the internal coordinate Hamiltonian for triatomic molecules (with the two normalizations mentioned above). Here we present results for H_2O and SO_2 . For H_2O we have calculated energy levels for two potentials, both of which were determined by least squares fitting using a basis function variational approach.^{8,9} The variational calculations of Ref. 8 are not converged for the higher bending states but nonetheless the potential reproduces experimental results fairly well. The potential of Ref. 9, determined with the MORBID variational method of Jensen, is more accurate and his variational calculation seems to be good. The expansion of the coordinate dependence of the kinetic energy (or possibly the inadequacy of the chosen basis set) seems to affect the calculated eigenvalues by several cm^{-1} (the biggest difference is about 15 cm^{-1}). Our calculations and the original variational calculations of Ref. 9 are compared in Table III. We use the Carter-Handy Hamiltonian and a basis set of 12 tridiagonal-Morse points for each stretch and optimized DVR points obtained from 21 eigenvectors of a 35×35 Legendre polynomial representation of the zeroth-order bending Hamiltonian for the bend (a 70×70 Legendre representation for the bend gave exactly the same results). Similar results were obtained using the tridiagonal-Morse functions for all three degrees of free-

dom. The power of the DVR is the simplicity of the potential in the discrete representation but there is a price to pay: the quality of the DVR eigenvalues is limited not only by the size of the matrix representations but also by the accuracy of the associated or implicit quadrature scheme. Increasing the number of basis functions can actually increase eigenvalues. Our calculated energy levels in Table III are well converged. Differences between the energy levels calculated with 10 tridiagonal-Morse functions for the stretch and 21 eigenvectors of the bend and those computed with 10 tridiagonal-Morse functions and 17 bend eigenvectors are all less than 0.005 cm^{-1} except for one level. For this level the difference between a calculation with 10 tridiagonal-Morse functions and 21 bend eigenvectors and one with 11 tridiagonal-Morse functions and 21 bend eigenvectors is less than 0.005 cm^{-1} . The eigenvalues calculated in Ref. 9 may be closer to the experimentally observed energy levels than are our results for the same potential because the potential was determined so that one obtains the experimental results when the coordinate dependence of the kinetic energy is expanded and truncated; we do not expand and truncate the coordinate dependence. Indeed, the agreement between the calculated eigenvalues and the observed energy levels improves if we decrease the number of stretch basis functions from ten to eight or seven. Reducing the number of basis functions does not change some levels which differ substantially from the results of Ref. 9; for these levels it is clear that the discrepancy is due to truncation of the kinetic energy expansion.

The potential for SO_2 was determined²¹ using the method of Ref. 8. Our variational results and those of Ref. 21 (compared in Table IV) differ by as much as several wave numbers but most eigenvalues are within one wave number. This discrepancy may be due either to our better basis set or to higher order terms in the kinetic energy which are neglected in Ref. 21. Our basis set includes 10 tridiagonal-Morse points for each stretch and 17 optimized bending points obtained from a 70×70 Legendre representation of the bending Hamiltonian. Although there are recent experimental results for highly excited states of SO_2 , it is difficult to compare our calculated energy levels with the experimental observations because the experimentalists²²

TABLE III. Comparison of the DVR vibrational energy levels and those calculated by expanding the coordinate dependence of the kinetic energy (Ref. 9) for the H₂O potential of Ref. 9. The assignment is that of Ref. 8 (based on analysis of the eigenvectors of the Hamiltonian matrix). O-C denotes observed-calculated. The observed (Obs.) values are those cited in Refs. 8 and 9.

n_1, n_2, n_3	Obs.	Jensen	This work	
		O-C	O-C	Calc.
0,1,0	1 594.75	0.50	-0.43	1 594.32
0,2,0	3 151.63	-0.25	0.38	3 152.01
1,0,0	3 657.05	0.72	-0.57	3 656.49
0,0,1	3 755.92	0.20	0.00	3 755.92
0,3,0	4 666.81	-0.70	0.89	4 667.70
1,1,0	5 234.99	1.12	-0.70	5 234.29
0,1,1	5 331.24	-0.25	0.82	5 332.06
0,4,0	6 134.03	0.16	0.08	6 134.11
1,2,0	6 775.10	0.70	-0.07	6 775.03
0,2,1	6 871.52	-1.10	1.95	6 873.47
2,0,0	7 201.54	-0.65	1.13	7 202.67
1,0,1	7 249.82	-0.53	1.11	7 250.93
0,0,2	7 445.07	0.72	-0.14	7 444.93
0,5,0				7 539.79
1,3,0	8 273.98	1.53	-0.73	8 273.24
0,3,1	8 373.85	-0.73	1.79	8 375.64
2,1,0	8 761.58	-0.19	1.29	8 762.87
1,1,1	8 807.00	-1.21	2.59	8 809.59
0,6,0				8 863.20
0,1,2	9 000.14	-0.76	2.00	9 002.14
1,4,0				9 719.75
0,4,1	9 833.58	2.27	-1.00	9 832.58
0,7,0				10 073.81
2,2,0	10 284.40	0.60	1.34	10 285.74
1,2,1	10 328.72	-1.49	3.68	10 332.40
0,2,2	10 524.30	0.60	1.30	10 525.60
3,0,0	10 599.66	-1.51	3.11	10 602.77
2,0,1	10 613.41	-0.57	2.18	10 615.59
1,0,2	10 868.86	0.86	0.47	10 869.33
0,0,3	11 032.40	-0.20	1.69	11 034.09
1,3,1	11 813.19	0.43	2.28	11 815.47
3,1,0	12 139.20	-2.00	5.26	12 144.46
2,1,1	12 151.26	-1.92	5.27	12 156.53
1,1,2	12 407.64	1.80	0.78	12 408.42
0,1,3	12 565.00	-0.50	2.04	12 567.04
2,2,1	13 652.65	-1.64	-4.91	13 647.74
4,0,0	13 828.30	2.20	1.41	13 829.71
3,0,1	13 830.92	2.55	1.10	13 832.03
1,2,2	13 910.80	2.60	0.92	13 911.72
0,2,3	14 066.19	-6.01	9.78	14 075.97
2,0,2	14 221.14	0.09	2.36	14 223.51
1,0,3	14 318.80	0.00	2.69	14 321.49
0,0,4	14 536.87	-1.70	4.43	14 541.30
2,3,1	15 119.03	1.81	3.55	15 122.58
4,1,0	15 344.50	0.47	5.66	15 350.16
3,1,1	15 347.95	-0.68	7.34	15 355.29
2,1,2	15 742.79	3.07	1.32	15 744.11
1,1,3	15 832.76	-1.36	6.34	15 839.10
4,2,0	16 821.63	4.97	2.22	16 823.84
3,2,1	16 825.23	6.41	0.81	16 826.04
5,0,0	16 898.42	7.48	1.06	16 899.48
4,0,1	16 898.83	7.79	0.72	16 899.55
2,2,2	17 227.70	7.20	-1.61	17 226.09
1,2,3	17 312.54	-1.24	-0.16	17 312.38
3,0,2	17 458.20	1.91	2.66	17 460.86
2,0,3	17 495.52	3.44	1.51	17 497.02

TABLE IV. Comparison of the DVR vibrational energy levels and those calculated by expanding the coordinate dependence of the kinetic energy for the SO₂ potential of Ref. 21. Assignments are given for levels which may be clearly associated with experimental observations. O-C denotes observed-calculated. The observed (Obs.) values are those cited in Ref. 21.

n_1, n_2, n_2	Obs.	K & H	This work	
		O-C	O-C	Calc.
0,1,0	517.87	0.09	0.28	518.15
0,2,0	1035.13	0.26	0.64	1035.77
1,0,0	1151.71	0.22	-0.08	1151.63
0,0,1	1362.06	0.02	-0.42	1361.64
0,3,0	1551.10	-0.20	1.77	1552.87
1,1,0	1666.33	0.53	0.52	1666.85
0,1,1	1875.80	-0.17	0.05	1875.85
0,4,0	2066.87	-0.22	2.59	2069.46
1,2,0	2179.51	0.07	2.06	2181.57
2,0,0	2295.81	0.11	0.17	2295.98
0,2,1	2388.92	-0.25	0.55	2389.47
1,0,1	2499.87	-0.16	-0.30	2499.57
0,5,0	2582.30	0.03	3.25	2585.55
1,3,0				2695.81
0,0,2	2715.46	2.23	-3.23	2712.23
2,1,0	2807.19	0.71	1.05	2808.24
0,3,1				2902.53
1,1,1	3010.32	-0.19	0.53	3010.85
0,6,0				3101.13
1,4,0				3209.56
0,1,2	3222.25	-1.10	0.28	3222.53
2,2,0				3320.02
0,4,1				3415.02
3,0,0	3431.19	-1.44	1.86	3433.05
1,2,1				3521.58
0,7,0				3616.24
2,0,1	3629.61	-0.84	0.29	3629.90
				3722.85
0,2,2	3730.90	-1.76	1.30	3732.20
				3831.35
1,0,2	3837.06	-0.93	-0.37	3836.69
				3926.95
3,1,0	3939.90	0.06	2.41	3942.31
				4031.76
0,0,3	4054.26	0.64	-2.50	4051.76
0,3,2	4241.50	0.30	-0.25	4241.25
2,4,0	4342.70		-0.48	4342.22
3,2,0	4446.90	0.51	4.22	4451.12
4,0,0	4560.10	-2.21	-1.89	4558.21
3,0,1	4751.23	-2.05	-1.52	4749.71
1,2,2	4848.14		2.68	4850.82
3,3,0	4958.00		1.49	4959.49
4,1,0	5070.30	4.35	-1.24	5069.06
1,0,3	5165.64	0.25	-2.62	5163.02
0,5,2	5261.90		-1.89	5260.01
3,4,0	5465.60		1.86	5467.46

high. The results we present in Table IV are well converged. Differences between the energy levels calculated with ten tridiagonal-Morse functions for the stretch and 17 eigenvectors of the bend and those computed with 9 tridiagonal-Morse functions and 16 bend eigenvectors are all less than 0.002 cm^{-1} .

CONCLUSION

Early attempts to calculate vibrational energy levels of triatomic molecules with large amplitude vibrations or

give a range of values (each determined from a different spectrum) for each energy level and the density of states is

with nearly linear equilibrium structures using normal coordinate Hamiltonians and basis functions^{6,23} revealed the inadequacy of normal coordinates for such molecules. General internal coordinate variational methods were developed to enable one to calculate accurately energy levels of any triatomic molecule.²⁴ The kinetic energy operator in internal coordinates is a complicated function of internal coordinates and derivatives with respect to internal coordinates. This complexity was dealt with by expanding the coordinate dependence and calculating matrix elements exactly^{8,9} or by calculating matrix elements numerically.⁶ The kinetic energy of the normal coordinate Hamiltonian is much simpler, but the development of an internal coordinate variational technique permitted Carter and Handy and co-workers to go beyond the limitations of a normal coordinate formalism.⁶

In this paper we show that the discrete variable representation which has proved to be so powerful for Hamiltonians with kinetic energy operators whose basis set representations are simple (usually diagonal or tridiagonal) is also extremely useful for Hamiltonians with very complicated kinetic energy operators. The discrete variable representation of any term in the internal coordinate kinetic energy is obtained by calculating matrix elements of coordinate functions in the discrete basis and matrix elements of derivatives in a square integrable function basis and transforming back and forth between the two representations. This is complicated for a complex kinetic energy operator but the advantages of the internal coordinate Hamiltonian make it worth the effort. The DVR of the internal coordinate kinetic energy is in part complicated because the internal coordinates are not orthogonal. Although not orthogonal r_1 , r_2 , and θ are natural coordinates for many triatomic molecules. They are natural coordinates in the sense that the potential is compactly described in terms of these coordinates and natural in the sense that direct products of functions of the internal coordinates provide a very good basis (and hence a small Hamiltonian matrix). The matrix elements of the Carter–Handy vibrational Hamiltonian with the correct Jacobian are not singular for any value of θ and the Hamiltonian could be used even for linear molecules.

For a triatomic molecule it would be simpler to use Radau coordinates, which are orthogonal, but very similar to the bond length–bond angle coordinates we employ. The kinetic energy of a triatomic molecule, in terms of Radau coordinates and their conjugate momenta, does not contain terms with different momentum operators and this simplifies calculation of the discrete representation of the kinetic energy.²⁵ While it is possible to circumvent dealing with kinetic energy cross terms for a triatomic molecule, such cross terms are unavoidable for larger molecules. In this paper we have shown that it is not difficult to calculate energy levels using nonorthogonal coordinates and a kinetic energy operator with cross terms. The technique we use is directly applicable to larger molecules.

Although the Hamiltonian in Radau coordinates is simpler, the bond length–bond angle Hamiltonian has some important advantages. The basis functions we choose

are excellent if the one dimensional stretch potentials are very close to Morse potentials. With the bond angle and one of the bond lengths frozen at their equilibrium values the potential along the other bond length coordinate is very Morse-like. The potential as a function of the distance from a hydrogen atom to the canonical point of the Radau coordinate system is less Morse-like. We have used the Radau Hamiltonian to calculate the vibrational energy levels of water using Jensen's potential and we are unable to obtain perfectly converged results for all the levels reported in this paper. Using the bond angle–bond length Hamiltonian, with a basis of 12 tridiagonal-Morse functions, all energy levels were converged to 0.01 cm^{-1} . Using the Radau Hamiltonian, we find that it takes 17 tridiagonal-Morse functions to converge all of the energy levels to 0.01 cm^{-1} . It seems clear that the Morse-type basis we use is better suited to the bond angle–bond length coordinate system.

We have not made use of the ray-eigenvector contraction procedure of Light and co-workers which is often used to reduce the size of variational matrices.¹³ Rather than contract the basis in this fashion, we have used DVR points adapted to the potential. The points for the stretching degrees of freedom are chosen using Morse or tridiagonal-Morse eigenfunctions and represent the stretches very compactly. It is not obvious how to choose points adapted to the bending potential.⁶ For the bending degree of freedom we have used discrete points determined by diagonalizing $\cos(\theta)$ in a basis composed of the eigenfunctions of the zeroth-order bending Hamiltonian. We have independently developed what Echave and Clary call the potential optimized discrete variable representation.²⁶ Although we have not tried combining the optimized DVR with the ray-eigenvector contraction scheme, Echave and Clary claim that the contracted optimized DVR is more expensive than the simple optimized DVR because the extra CPU time required to transform the Hamiltonian matrix more than compensates for the additional basis set reduction.

If one assumes that, like the potential, the coordinate dependence of the kinetic energy is diagonal in the discrete representation the DVR permits one to determine eigenvalues of the internal coordinate Hamiltonian without expanding the coordinate dependence of the kinetic energy or calculating integrals numerically. Despite the complexity of the internal coordinate kinetic energy operator the kinetic energy matrix in the discrete representation is quite simple. In the discrete representation all functions of coordinates are diagonal. Different degrees of freedom are coupled only by cross terms in the kinetic energy and because no term in the kinetic energy involves more than two derivatives there are no terms in the Hamiltonian which couple more than two degrees of freedom in the discrete representation.

Vibrations, even large amplitude vibrations, in many polyatomic molecules are well described by internal curvilinear coordinates. Unfortunately, it is difficult to use Hamiltonians in nonorthogonal curvilinear coordinates to calculate energy levels because of their complexity. By

evaluating matrix elements of functions of coordinates in a discrete representation and derivatives in a basis set of square integrable functions one greatly simplifies the use of internal coordinate Hamiltonians.

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