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Coordinate ordering in the discrete variable representation

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The problem of what order to treat the coordinates in the scheme of successive diagonalisations and truncations commonly used in multidimensional discrete variable representation (DVR) calculations is analysed. Test calculations in 4 different coordinate orderings are performed for the vibrational band origins of the HCN and H_3^+ molecules. These tests show that calculations which place the coordinate with the densest DVR grid *last* require considerably less computer time and converge significantly faster than the other options.

1. Introduction

The discrete variable representation (DVR) has proved very powerful for studying highly excited vibrational states of small molecules. The application of the DVR to molecular vibrations was pioneered by Light and coworkers [1] following original developments in the sixties [2,3]. More recently DVR based methods have also been used to study heavy particle scattering [4,5].

The advantage of the DVR over the conventional finite basis representation (FBR) results from writing the problem as a heirachy of Hamiltonians. The Hamiltonian matrices are diagonalised in turn and the lowest energy solutions used as a basis for the next Hamiltonian in the heirachy. This diagonalisation and truncation technique leads to final Hamiltonians which are heavily truncated compared to the initial set of grid points [4,6,7]. It should be noted that although prediagonalisation and truncation ("contraction") has been used in FBR techniques [8], the DVR gives an optimal method of doing this [9], which is particularly efficient at treating cases of strong mode coupling.

So far most DVR calculations on multidimensional problems have actually been FBR–DVR hybrids with a DVR used only for one coordinate. However, a number of studies on H_3^+ [10–12] have used a DVR in all three vibrational coordinates. The most recent of these studies have yielded spectacular results with estimates of *all* the bound vibrational states of this system. This represents a fivefold increase in the number of converged states compared to an early study which used an FBR for two coordinates and a DVR in the third [13].

When using a DVR in more than one dimension, there is a choice over how one orders the coordinates for the successive diagonalisation and truncation procedure. So far the question of whether calculations are sensitive to how coordinates are ordered has received little attention. It has been stated that the best method should be to treat the coordinates in order of decreasing density of associated vibrational states [11,14]. Conversely it has also been suggested that the ordering of the coordinates in the calculations is of little significance [10].

In this paper we present a number of test calculations on the molecules HCN and H_3^+ de-

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signed to illustrate the behaviour of multidimensional DVR calculations as a function of coordinate order. We show that the efficiency of the calculation is strongly influenced by the ordering of the coordinates and we suggest that the optimal procedure is given by placing the coordinate with the largest number of DVR points (and hence the densest associated vibrational spectrum) *last*.

2. Theory

Consider a triatomic vibrational problem with total angular momentum $J=0$ and coordinate system (r_1, r_2, θ). As the DVR is very much more efficient in orthogonal coordinates, these coordinates could be Radau (see ref. [15]) or scattering (Jacobi) coordinates [1]. For these coordinates an FBR Hamiltonian matrix element can be written [16],

$$\begin{aligned}\langle m, n, j | \hat{H} | m', n', j' \rangle &= \langle m | \hat{h}^{(1)} | m' \rangle \delta_{n,n'} \delta_{j,j'} + \langle n | \hat{h}^{(2)} | n' \rangle \delta_{m,m'} \delta_{j,j'} \\ &\quad + \big(\langle m | \hat{g}^{(1)} | m' \rangle \delta_{n,n'} \\ &\quad + \langle n | \hat{g}^{(2)} | n' \rangle \delta_{m,m'} \big) j(j+1) \delta_{j,j'} \\ &\quad + \langle m, n, j | V(r_1, r_2, \theta) | m', n', j' \rangle, \end{aligned} \tag{1}$$

where it has been assumed that the angular basis functions $|j\rangle$ are Legendre polynomials and it will be assumed that the radial basis functions can also be expressed as weighted orthogonal polynomials. In eq. (1), V is the potential and the kinetic energy integrals are given by

$$\langle t | \hat{h}^{(i)} | t' \rangle = \langle t | \frac{-\hbar^2}{2\mu_i r_i^2} \frac{\partial^2}{\partial r_i^2} | t' \rangle, \tag{2}$$

where $|t\rangle = |m\rangle$ for $i=1$ and $|t\rangle = |n\rangle$ for $i=2$, and

$$\langle t | \hat{g}^{(i)} | t' \rangle = \langle t | \frac{\hbar^2}{2\mu_i r_i^2} | t' \rangle, \tag{3}$$

where μ_i is the appropriate reduced mass [16].

A three-dimensional DVR is obtained by applying the transformation

$$\begin{aligned} H_{\alpha,\alpha',\beta,\beta',\gamma,\gamma'} &= \sum_{m,n,j} \sum_{m',n',j'} \left(T^{\alpha,\beta,\gamma}_{m,n,j} \right)^{\mathrm{T}} \\ &\quad \times \langle m, n, j | H | m', n', j' \rangle T^{\alpha',\beta',\gamma'}_{m',n',j'}. \end{aligned} \tag{4}$$

The 3D transformation can be written as a product of 1D transformations

$$T^{\alpha,\beta,\gamma}_{m,n,j} = T^{\alpha}_{m} T^{\beta}_{n} T^{\gamma}_{j}. \tag{5}$$

The 1D transformations are defined in terms of points, η, and weights, w_η, of the N-point Gaussian quadrature associated with the orthogonal polynomial used for the FBR in that coordinate:

$$T^{\eta}_{t} = (w_\eta)^{1/2} | t(\eta) \rangle, \tag{6}$$

where $|t\rangle = |m\rangle$, $|n\rangle$, $|j\rangle$ for $\eta = \alpha$, β, γ, respectively.

The transformed Hamiltonian is written at the DVR grid points as

$$\begin{aligned} {}^{(3\mathrm{D})}H_{\alpha,\alpha',\beta,\beta',\gamma,\gamma'} &= K^{(1)}_{\alpha,\alpha'} \delta_{\beta,\beta'} \delta_{\gamma,\gamma'} + K^{(2)}_{\beta\beta'} \delta_{\alpha,\alpha'} \delta_{\gamma,\gamma'} \\ &\quad + L^{(1)}_{\alpha,\alpha',\gamma,\gamma'} \delta_{\beta,\beta'} + L^{(2)}_{\beta,\beta',\gamma,\gamma'} \delta_{\alpha,\alpha'} \\ &\quad + V(r_{1\alpha}, r_{2\beta}, \theta_\gamma) \delta_{\alpha,\alpha'} \delta_{\beta,\beta'} \delta_{\gamma,\gamma'}, \end{aligned} \tag{7}$$

where the potential energy operator is diagonal because of the quadrature approximation [3] and $(r_{1\alpha}, r_{2\beta}, \theta_\gamma)$ is the value of (r_1, r_2, θ) at grid point (α, β, γ). The kinetic energy terms are represented by

$$K^{(i)}_{\eta,\eta'} = \sum_{tt'} (T^{\eta}_{t})^{\mathrm{T}} \langle t | \hat{h}^{(i)} | t' \rangle T^{\eta'}_{t'}, \tag{8}$$

and, again applying the quadrature approximation,

$$L^{(i)}_{\eta,\eta',\gamma,\gamma'} = \sum_{jj'} \frac{\hbar^2}{2\mu_i r_{i\eta}^2} (T^{\gamma}_{j})^{\mathrm{T}} j(j+1) T^{\gamma'}_{j'} \delta_{\eta,\eta'}. \tag{9}$$

To illustrate the diagonalisation and trunction schemes, consider the case where the coordinates are treated in the order r_1 then r_2 then θ, i.e. α

then β then γ. The 1D problems, which need to be solved for each value of β and γ, are given by

$$^{(1\mathrm{D})}H^{\beta,\gamma}_{\alpha,\alpha'} = K^{(1)}_{\alpha,\alpha'} + V(r_{1\alpha}, r_{2\beta}, \theta_\gamma)\, \delta_{\alpha,\alpha'}. \tag{10}$$

Amplitudes for the kth level, with eigenenergy $\epsilon^{\beta,\gamma}_k$, are given at the grid points by $c^{\beta,\gamma}_{\alpha,k}$.

Solutions with eigenenergies above a certain cutoff value, $E^{1\mathrm{D}}_{\max}$, are discarded prior to the next step. The $N^{2\mathrm{D}}$ solutions with $\epsilon^{\beta,\gamma}_k \le E^{1\mathrm{D}}_{\max}$ are then used to solve 2D problems for each value of γ. This gives

$$^{(2\mathrm{D})}H^{\gamma}_{\beta,\beta',k,k'} = \epsilon^{\beta,\gamma}_k \delta_{\beta,\beta'} \delta_{k,k'} + \sum_{\alpha} c^{\beta,\gamma}_{\alpha,k} K^{(2)}_{\beta,\beta'} c^{\beta',\gamma}_{\alpha,k'}. \tag{11}$$

Solutions for the lth level, with eigenenergy ϵ^{γ}_l, are given by $c^{\gamma}_{\beta,l,k}$.

The solutions with $\epsilon^{\gamma}_l \le E^{2\mathrm{D}}_{\max}$ are then used to solve the full 3D problem of dimension $N^{3\mathrm{D}}$:

$$\begin{aligned} &^{(3\mathrm{D})}H_{\gamma,\gamma',l,l'} \\ &\quad = \epsilon^{\gamma}_l \delta_{\gamma,\gamma'} \delta_{l,l'} + \sum_{\beta,k,k'} \Bigg[c^{\gamma}_{\beta,l,k} c^{\gamma'}_{\beta,l',k'} \\ &\qquad \times \left(L^{(2)}_{\beta,\beta,\gamma,\gamma'} + \sum_{\alpha} \left[c^{\beta,\gamma}_{\alpha,k} L^{(1)}_{\alpha,\alpha,\gamma,\gamma'} c^{\beta,\gamma'}_{\alpha,k'} \right) \right]. \end{aligned} \tag{12}$$

Diagonalisation of this yields final energies and wavefunction coefficients.

Clearly it is possible to formulate similar diagonalisation and truncation schemes for the five other possible orderings of (r_1, r_2, θ). Note that it is possible to include the diagonal (in γ) contributions earlier on this solution scheme, for example $L^{(1)}_{\alpha,\alpha,\gamma,\gamma'}$ in the α step and $L^{(2)}_{\beta,\beta,\gamma,\gamma'}$ in the β step. However, previous experience [14] shows that this procedure produces intermediate vectors which are less well adapted and have worse convergence properties.

3. Calculations

The 3D DVR program developed by us has four possible coordinate orderings: (r_1, r_2, θ), (r_2, r_1, θ), (θ, r_1, r_2) and (θ, r_2, r_1). Although there is no problem in principle with having θ as the second coordinate, we have not included this option as it is would require considerable reprogramming. As we show below, the major consideration is the final coordinate and the above options allow for all three possibilities.

Our calculations focussed on the triatomic molecules HCN and H_3^+. All calculations were performed in scattering coordinates. In general we did not aim to produce fully converged calculations as these would have been prohibitively expensive for some coordinate orderings. Instead we chose to compare the results between orderings, both in terms of computational resources used and convergence, for standardized calculations using the same grid points and cutoff parameters. In fact cutoff's can be expressed both in terms of energies $(E^{1\mathrm{D}}_{\max}, E^{2\mathrm{D}}_{\max})$ and numbers of functions selected $(N^{2\mathrm{D}}, N^{3\mathrm{D}})$. For ease of comparison with the vibrational band origins quoted below, all the energy cutoffs are given relative to the vibrational ground state of the relevant system.

3.1. HCN

HCN was chosen for initial studies as scattering coordinates give a reasonable approximation to the vibrational motions of the molecule. Thus θ approximates the bending mode for both HCN and HNC isomers, and the reaction coordinate between the two minima. As the bending modes are of much lower frequency than the stretching modes one would expect the θ coordinate to represent the densest set of vibrational states.

The calculations used the HCN potential of Murrell et al. [17] used in previous FBR [18] and DVR [9,19,20] studies on the high-lying vibrational states of HCN. The calculations used Morse oscillator-like functions [16] in both coordinates. All calculations here used $N_1 = 30$ points in the r_1 coordinate, $N_2 = 40$ points in r_2 and $N_\theta = 74$ in θ. This grid is almost certainly denser than is necessary to obtain useful results for HCN – for example Bačić and Light used $N_\theta = 45$ in their calculations – but this serves our purpose for illustrating the effect of coordinate ordering. Note that the number of grid points in each coordinate

Table 1
Band origins in cm^{-1} for HCN as a function of coordinate order. All calculations used the same grid and energy cutoffs.

Order:	$r_1 \to r_2 \to \theta$	$r_2 \to r_1 \to \theta$	$\theta \to r_1 \to r_2$	$\theta \to r_2 \to r_1$
N^{2D}_{max}:	94	89	301	381
N^{2D}_{tot}:	4231	3730	4455	4455
N^{3D}:	589	597	734	642
t (s):	289	325	690	580
Band	Band origins (cm^{-1})			
1	1418.5	1418.4	1420.5	1418.8
21	6554.6	6532.8	6570.5	6570.5
41	8305.6	8300.1	8370.2	8348.4
61	9673.9	9644.3	9795.0	9742.4
81	10654.5	10638.7	10863.0	10791.8
101	11590.5	11521.1	11972.8	11789.4
121	12391.4	12337.3	12834.8	12737.4
141	13089.0	13059.5	13876.3	13598.8

Table 2
Band origins, in cm^{-1}, for HCN as a function of coordinate order. All calculations used the same grid and value of E^{2D}_{max} but E^{1D}_{max} n the θ first calculations was lowered to give N^{2D}_{max} similar to those of the θ last calculations.

Order:	$r_1 \to r_2 \to \theta$	$r_2 \to r_1 \to \theta$	$\theta \to r_1 \to r_2$	$\theta \to r_2 \to r_1$
N^{2D}_{max}:	94	89	82	115
N^{2D}_{tot}:	4239	3730	738	932
N^{3D}:	589	597	580	538
t (s):	270	312	450	476
Band	Band origins (cm^{-1})			
1	1418.5	1418.4	1460.3	1445.2
21	6554.5	6532.8	7628.1	7274.7
41	8305.6	8300.1	11107.2	10058.9
61	9673.1	9644.3	13236.3	12292.5
81	10654.4	10638.7	16247.9	14475.7
101	11589.8	11521.1	19073.1	16730.0
121	12391.2	12337.3	21319.4	18578.8
141	13088.9	13059.5	24011.5	20891.0

is an approximate measure of the density of the vibrational spectrum in that coordinate.

Table 1 compares the four coordinate orderings for an unconverged calculation on HCN using the cutoff $E^{1D}_{max} = 16\,144$ cm^{-1} and $E^{2D}_{max} = 13\,132$ cm^{-1}. For comparison the total number of 1D solutions selected, N^{2D}_{tot}, the maximum size of a 2D problem, N^{2D}_{max} and the size of the final Hamiltonian, N^{3D}, are given. The CPU time taken, t, in Convex C240 single processor seconds, is also given. It is clear from table 1 that the runs which place θ last are superior *and* use less CPU time than the calculations with θ first.

A feature of table 1 is the comparatively large values of N^{2D}_{max} used in the θ first runs. Table 2 gives an alternative comparison, again with constant $E^{2D}_{max} = 13\,132$ cm^{-1}, in which an attempt has been made to make the size of N^{2D}_{max} comparable between the runs. The result of this is also to bring the values of N^{3D} close together but to further degrade the convergence of the θ first calculations. Indeed these calculations no longer give satisfactory results for the HCN bending fundamental (band origin 1).

Table 3 presents calculations on HCN using much larger intermediate energy cuttoffs ($E^{1D}_{max} = 26\,124$ cm^{-1}, $E^{2D}_{max} = 22\,104$ cm^{-1}) which aimed for convergence. At this level the band origins for the (r_2, r_1, θ) calculations agree to within 1 cm^{-1} with those of Bačić and co-workers [19,20] who only considered band origins up to 12540 cm^{-1}.

Again the θ last calculations give much better convergence and require less CPU time, although the difference in the size of the final Hamiltonians, N^{3D}, is less marked. Indeed it is interesting

Table 3
Band origins, in cm^{-1}, for HCN as a function of coordinate order. All calculations used the same grid and energy cutoffs. The energy cutoffs were chosen so that the (r_2, r_1, θ) results converged.

Order:	$r_1 \to r_2 \to \theta$	$r_2 \to r_1 \to \theta$	$\theta \to r_1 \to r_2$	$\theta \to r_2 \to r_1$
N^{2D}_{max}:	208	154	597	815
N^{2D}_{tot}:	11882	8282	11078	11078
N^{3D}:	2180	2200	2958	2095
t (s):	4338	4420	11055	6145
Band	Band origins (cm^{-1})			
1	1418.4	1418.4	1418.4	1418.4
41	8295.4	8295.3	8296.8	8295.9
81	10619.9	10619.4	10623.3	10620.3
121	12208.9	12206.9	12222.6	12212.0
161	13425.4	13414.2	13448.5	13425.0
201	14325.8	14323.1	14366.2	14345.9
241	15344.0	15338.2	15381.0	15353.0
281	16226.3	16218.7	16271.3	16242.7
321	17002.3	16996.3	17074.0	17031.5

Table 4
Band origins in cm^{-1}, for H_3^+ as a function of coordinate order. All calculations used the same grid and energy cutoffs. The converged results of Henderson et al. [12] are shown for comparison.

Order:	$r_1 \to r_2 \to \theta$	$r_2 \to r_1 \to \theta$	$\theta \to r_1 \to r_2$	$\theta \to r_2 \to r_1$	$\theta \to r_1 \to r_2$
$N_{\max}^{2D}$:	793	862	412	467	446
N_{tot}^{2D}:	11731	12993	11650	11650	14287
N^{3D}:	876	876	693	799	5500
t (s):	3097	3888	1013	1296	89136
Band	Band origins (cm^{-1})				
1	2521.4	2521.4	2521.3	2521.3	2521.3
41	14223.5	14223.5	14214.4	14225.7	14210.9
81	18238.9	18238.9	18224.7	18230.8	18208.6
121	20814.1	20814.1	20806.6	20816.1	20759.4
161	22791.9	22792.0	22794.1	22819.9	22687.9
201	24572.8	24572.8	24584.4	24643.9	24356.4
241	26418.2	26418.3	26340.4	26379.8	25834.1

to note that although the (θ, r_2, r_1) calculation had the smallest final Hamiltonian, this calculation required nearly 50% more CPU time than the θ last calculations. This can be attributed to the significantly larger value of $N_{\max}^{2D}$ in this calculation.

Tables 1–3 all show that the θ last calculations converge better and are quicker than the θ first calculations for HCN. They also indicate that the (r_2, r_1, θ) ordering converges better than (r_1, r_2, θ).

3.2. H_3^+

As mentioned in the introduction H_3^+ has been the focus of several 3D DVR calculations. Our previous calculations [11,12,14] have all used a (θ, r_1, r_2) coordinate ordering * based on some preliminary tests [14].

For this work, calculations were performed using the ab initio potential due to Meyer et al. (MBB) [21]. The grid of points used is given by $N_1 = 36$, $N_2 = 40$ and $N_\theta = 32$. Because of the symmetry of the system it is only necessary to consider half the θ grid points [13].

The calculations closely followed those of Henderson and Tennyson [11]. These calculations have since been criticised for displaying non-variational behaviour [22]. In this work we only consider even symmetry calculations which *do* behave variationally [22,23]. A full discussion of the problems with variational behaviour and the 3D DVR can be found elsewhere [12].

Table 4 presents even symmetry band origins for H_3^+ performed with a common set of cutoff parameters, $E_{\max}^{1D} = 55\,936$ cm^{-1} and $E_{\max}^{2D} = 26\,091$ cm^{-1}. For comparison highly converted results, based on the study by Henderson et al. [12], are also shown. This calculation used $E_{\max}^{1D} = 65\,936$ cm^{-1} and $E_{\max}^{2D} = 51\,052$ cm^{-1}.

The results of table 4 again show variations in convergence and CPU usage. In general the (θ, r_1, r_2) ordering gives the lower results, although the (r_1, r_2, θ) and (r_2, r_1, θ) calculations are lower in the intermediate energy region. It should be noted, however, that these θ last calculations require more than 3 times the CPU time of the (θ, r_1, r_2) calculation.

4. Conclusions

These test calculations show that 3D discrete variable calculations (DVR) show a strong sensitivity to the order in which the coordinates are tackled in the calculation. This sensitivity mani-

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* Note that the coordinate ordering used by Henderson and Tennyson was (θ, r_1, r_2), not (r_2, r_1, θ) as stated in ref. [11].

fests itself in two ways: through convergence of the eigenenergies and through the CPU time required to perform calculations with equivalent energy cutoffs. Fortunately the effects work in the same direction; the ordering of coordinates which displays the best convergence properties is also generally the cheapest computationally.

Analysing simply the CPU time characteristics of the results presented above, it is easy to see that the best calculations are those which place the coordinate with the largest number of grid points last. For the systems studied this coordinate is also one with the greatest density of vibrational states, i.e. the lowest frequency mode at high energy.

From the CPU timings the optimal coordinate ordering is obtained by treating the coordinates in the order sparsest DVR grid to densest DVR grid. However, this ordering does not give the fastest convergence for HCN and it is clearly dangerous to be too prescriptive on this, especially as the increase in CPU time on swapping the order of the first two coordinates is small.

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