Discrete Variable Representations of Large-amplitude Ro-vibrational States in a generalised Coordinate System

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We present a formulation of the triatomic ro-vibrational nuclear motion problem in a set of generalised coordinates using a discrete variable representation (DVR). These coordinates are expressed in terms of two distances and an included angle, and contain many well known coordinate systems. Applications to LiCN, Na_3 and H_3^+ which illustrate the power of the method are described. The resulting energy levels and wavefunctions are discussed. Our Na_3 fundamental frequencies are found to be in good agreement with experiment.

1. Introduction

Highly excited small molecular systems are now an area of much study for both the experimentalist and the theorist. Improved technology in the form of lasers and molecular beams has allowed spectroscopists to study high-lying ro-vibrational levels. More suitable and efficient methodologies are helping the theorist, as are of course the great advances in computer facilities. It is challenging to try to understand the spectroscopy and dynamics of highly excited systems, and the idea of quantum 'chaos' attracts much interest.

Conventional variational methods, using basis-set expansions, now allow the determination of low-lying ro-vibrational states of triatomic molecules, in some cases to spectroscopic accuracy. For a given potential-energy function, these techniques, applied within the Born–Oppenheimer approximation, are used to solve the nuclear motion on the hypersurface. Effectively one constructs the Hamiltonian matrix in the basis of some truncated set of polynomial (or numerical) functions and diagonalises this matrix to yield the eigenvectors and eigenvalues. The general approach is variational in that the eigenvalues will converge monotonically from above to their exact values as the size of the set of functions in each coordinate increases indefinitely.

For relatively high-lying states, however, it has become increasingly apparent that these finite-basis representations (FBRs) begin to become intractable, owing primarily to the extremely large basis sets required for convergence of the higher levels. This is particularly the case with molecules that can exhibit very large-amplitude motion in one or more of the internal coordinates and display large anisotropy in the potential-energy surface. These systems are 'floppy' and tend to isomerise, or may encounter other features of the potential-energy surface. The problem is that the conventional FBR methods may fail to provide a good representation when the molecule is executing very delocalised motions and is accessing highly anharmonic regions of the potential.

The past five years have seen Bačić, Light and co-workers[1] develop the discrete variable representation (DVR) as an attempt to overcome the difficulties encountered with the FBR techniques. The notion, essentially, is that the basis expansion of the FBR can be operated on by an orthogonal DVR transformation matrix to give a representation in coordinate space rather than in function space. This part of the theory relies on standard transformation properties and was first suggested by Harris *et al.*[2] The second part of the DVR theory utilizes the notion of successive diagonalisation and truncation of intermediate, reduced-dimensionality Hamiltonian matrices. This effectively gives one the power to create basis sets of different types and sizes at different grid points over the potential-energy function, thus ensuring a more physical and realistic representation of the physics, and winning major computational savings over FBR methods. One is also at liberty in coordinate space to reject quadrature points that may be energetically inaccessible. The procedures will be explained in detail in section 2.

The most popular DVR approach so far, in the ro-vibrational study of 'floppy' triatomic systems, employs Jacobi coordinates. The angular coordinate θ is usually expressed in a DVR whilst the radial coordinates remain in an FBR. (Light and co-workers usually like to use a distributed Gaussian basis in the radial coordinates.[3]) It is also possible to discretise more than one and sometimes all of the internal coordinates.

In this paper we develop the theory for the DVR in a generalised set of body-fixed coordinates, prescribed by parameters g_1 and g_2 which has, for example, Jacobi, Radau and bond length-bond angle coordinates as special cases. The coordinate system is most general in that it represents any two lengths and the included angle (see fig. 1). The angular coordinate has been discretised *via* a transformation in associated Legendre polynomials and the radial coordinates use an FBR in either Morse oscillator-type functions[4] or spherical oscillators.[5] Rotational excitation is accounted for using the two-step variational approach of Tennyson and Sutcliffe.[6]

This formalism has been used by us for a series of calculations on floppy triatomic systems. In this work we discuss the calculations on LiCN, H_3^+ and Na_3. Na_3 illustrates the power of the DVR particularly well in that we were able to converge many energy levels, whereas our FBR efforts failed to converge even the lowest-lying states satisfactorily.

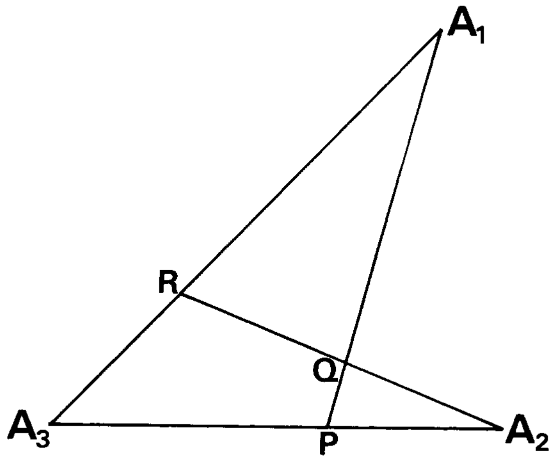

Fig. 1. Coordinate system. A_i represents atom *i*. The coordinates in the text are given by $r_1 = A_2\text{–}R$, $r_2 = A_1\text{–}P$ and $\theta = A_1\hat{Q}A_2$.

2. Theory

2.1 The Hamiltonian Operator

DVR techniques have been well reviewed recently by Bačić and Light.[1] In this section we present the DVR theory using a generalised body-fixed Hamiltonian operator, as developed by Sutcliffe and Tennyson.[7] The DVR in any of the internal coordinates is obtained by transforming the respective FBR Hamiltonian matrix elements.

First then, before applying the transformation, we present the Hamiltonian operator in the FBR. We use the close-coupling approach of Arthurs and Dalgarno,[8] and follow Tennyson and Sutcliffe.[4] Effectively this entails defining angular basis functions of the form

$$|j, k\rangle = \Theta_{j,k}(\theta) D^{J}_{Mk}(\alpha, \beta, \gamma) \tag{1}$$

where $\Theta_{j,k}(\theta)$ is an associated Legendre polynomial (assumed to be normalised) in the phase convention of Condon and Shortley,[9] and $D^{J}_{Mk}(\alpha, \beta, \gamma)$ is a Wigner rotation matrix in the Euler angles (α, β, γ). In this notation J is the total angular momentum of the system and k is the projection of J onto the body-fixed z axis.

One then lets this exact Hamiltonian operator[7] act on $|j, k\rangle$, multiplies from the right by $\langle j', k'|$ and integrates over all the angular variables. This results in an effective radial Hamiltonian of the form

$$\hat{H}(r_1, r_2) = \hat{K}^{(1)}_{V} + \hat{K}^{(2)}_{V} + \hat{K}^{(1)}_{VR} + \hat{K}^{(2)}_{VR} + \delta_{k'k}\langle j'k|V(r_1, r_2, \theta)|jk\rangle_{\theta} \tag{2}$$

where $V(r_1, r_2, \theta)$ is the potential-energy function. The kinetic energy operators are given by

$$\hat{K}^{(1)}_{V} = \delta_{j'j}\delta_{k'k}\left[-\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial r_2^2} + \frac{\hbar^2}{2} j(j+1)\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right)\right] \tag{3}$$

$$\hat{K}^{(1)}_{VR} = \delta_{j'j}\delta_{k'k}\frac{\hbar^2}{2\mu_1 r_1^2}[J(J+1) - 2k^2] - \delta_{j'j}\delta_{k'k\pm 1}\frac{\hbar^2}{2\mu_1 r_1^2} C^{\pm}_{JK} C^{\pm}_{jk} \tag{4}$$

$$\hat{K}^{(2)}_{V} = -\delta_{j'j+1}\delta_{k'k} d_{jk}\frac{\hbar^2}{2\mu_{12}}\left(\frac{\partial}{\partial r_1} - \frac{j+1}{r_1}\right)\left(\frac{\partial}{\partial r_2} - \frac{j+1}{r_2}\right) - \delta_{j'j-1}\delta_{k'k} d_{j-1,k}\frac{\hbar^2}{2\mu_{12}}\left(\frac{\partial}{\partial r_1} + \frac{j}{r_1}\right)\left(\frac{\partial}{\partial r_2} + \frac{j}{r_2}\right) \tag{5}$$

$$\hat{K}^{(2)}_{VR} = \delta_{j'j+1}\delta_{k'k\pm 1}\frac{\hbar^2}{2\mu_{12}} C^{\pm}_{Jk}\frac{a_{j,\pm k}}{r_1}\left(\frac{j+1}{r_2} - \frac{\partial}{\partial r_2}\right) + \delta_{j'j-1}\delta_{k'k\pm 1}\frac{\hbar^2}{2\mu_{12}} C^{\pm}_{Jk}\frac{b_{j,\pm k}}{r_1}\left(\frac{j}{r_2} - \frac{\partial}{\partial r_2}\right). \tag{6}$$

The angular factors used above are defined as

$$C^{\pm}_{jk} = [J(J+1) - k(k \pm 1)]^{1/2} \tag{7}$$

$$d_{jk} = \left[\frac{(j-k+1)(j+k+1)}{(2j+1)(2j+3)}\right]^{1/2} \tag{8}$$

$$a_{jk} = \left[\frac{(j+k+1)(j+k+2)}{(2j+1)(2j+3)}\right]^{1/2} \tag{9}$$

$$b_{jk} = \left[\frac{(j-k)(j-k-1)}{(4j^2-1)}\right]^{1/2}. \tag{10}$$

The above operators are for the body-fixed z axis embedded along the r_1 direction. Embedding the z axis along the r_2 direction necessitates the changes $r_1 \leftrightarrow r_2$ and $\mu_1 \leftrightarrow \mu_2$ in the terms involving the rotational quantum numbers J and k.

This Hamiltonian operator is effective in the set of coordinates illustrated in fig. 1. The most general use of these coordinates is given by Sutcliffe and Tennyson.[7] For our use it is sufficient to use the parameters g_1 and g_2 given by (see fig. 1)

$$g_1 = \frac{A_3 - P}{A_3 - A_2}; \qquad g_2 = \frac{A_3 - R}{A_3 - A_1}. \tag{11}$$

The reduced masses are defined in terms of the parameters g_1 and g_2 $(0 \leqslant g_1, g_2 \leqslant 1)$;

$$\mu_1^{-1} = g_2^2 m_1^{-1} + m_2^{-1} + (1 - g_2)^2 m_3^{-1} \tag{12}$$

$$\mu_{12}^{-1} = (1 - g_1)(1 - g_2) m_3^{-1} - g_2 m_1^{-1} - g_1 m_2^{-1} \tag{13}$$

$$\mu_2^{-1} = g_1^2 m_2^{-1} + m_1^{-1} + (1 - g_1)^2 m_3^{-1}. \tag{14}$$

Note that orthogonal coordinate systems are those for which $\mu_{12}^{-1} = 0$, and hence $\hat{K}^{(2)}_{V} = \hat{K}^{(2)}_{VR} = 0$. Such systems include scattering (or Jacobi) and Radau coordinates, and any other (g_1, g_2) solutions of $\mu_{12}^{-1} = 0$.

The above close-coupled equations (2) are in an FBR, labelled by j, corresponding to the rotational functions forming the angular basis for any particular J and k. This set of equations can now be transformed to yield a representation labelled by a set of discrete angles.

2.2 The Discrete Variable Representation

We would like to switch from amplitudes expressed in the associated Legendre polynomials to amplitudes represented at Gauss-associated Legendre quadrature points. Dickinson and Certain[10] showed that if the functions involved are a set of $j_{\max} + 1$ classical orthogonal polynomials, then there exists an orthogonal transformation to switch to a representation at $j_{\max} + 1$ suitably weighted Gauss-polynomial quadrature points. Furthermore, from their work one can define the particular transformation required in this case. If $\chi_{k\alpha}(= \cos\theta_{k\alpha})$ and $\omega_{k\alpha}$ are the points and weights of N-point $(\alpha = 1, N)$ Gauss-associated Legendre quadrature, then the DVR transformation can be written

$$T^{k}_{j\alpha} = N_{jk}\,\omega_{k\alpha}^{1/2}\,\Theta_{jk}(\theta_{k\alpha}) \tag{15}$$

where N_{jk} normalises Θ_{jk}.

One can now transform the effective Hamiltonian operator in the FBR to yield

$$\begin{aligned}
\hat{H}_{k'\alpha',k\alpha} &= \sum_{j=k}^{N+k-1}\sum_{j'=k'}^{N'+k'-1} T^{k'}_{j'\alpha'}\hat{H}(r_1, r_2) T^{k}_{j\alpha} \\
&= \delta_{k'k}\delta_{\alpha'\alpha}\left[-\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial r_2^2} + \frac{\hbar^2}{2\mu_1 r_1^2} \times [J(J+1) - 2k^2] + V(r_1, r_2, \theta_{k\alpha})\right] \\
&\quad + \delta_{k'k}\frac{\hbar^2}{2}\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right) L^{k}_{\alpha'\alpha} \\
&\quad - \delta_{k'k}\frac{\hbar^2}{2\mu_{12}}\left[M^{(1)k}_{\alpha'\alpha}\frac{\partial^2}{\partial r_1\,\partial r_2} - M^{(2)k}_{\alpha'\alpha}\left(\frac{1}{r_1}\frac{\partial}{\partial r_2} + \frac{1}{r_2}\frac{\partial}{\partial r_1}\right) + M^{(3)k}_{\alpha'\alpha}\frac{1}{r_1 r_2}\right] \\
&\quad - \delta_{k'k\pm 1}\frac{\hbar^2}{2\mu_1 r_1^2} C^{\pm}_{Jk} Q^{k\pm}_{\alpha'\alpha} \\
&\quad - \delta_{k'k\pm 1}\frac{\hbar^2}{2\mu_{12} r_1} C^{\pm}_{Jk}\left[R^{(1)k\pm}_{\alpha'\alpha}\frac{\partial}{\partial r_2} + R^{(2)k\pm}_{\alpha'\alpha}\frac{1}{r_2}\right].
\end{aligned} \tag{16}$$

The new, transformed matrices that are diagonal in k are given by

$$L^{k}_{\alpha'\alpha} = \sum_{j=k}^{N+k-1} T^{k}_{j\alpha'} j(j+1) T^{k}_{j\alpha} \tag{17}$$

$$M^{(i)k}_{\alpha'\alpha} = \sum_{j=k}^{N+k-1} T^{k}_{j+1,\alpha'}[(j+1)^{i-1}d_{jk} + (j)^{i-1}d_{j-1,k}]T^{k}_{j\alpha}. \tag{18}$$

The off-diagonal, Coriolis matrices are given by

$$Q^{k\pm}_{\alpha'\alpha} = \sum_{j} T^{k\pm 1}_{j\alpha'} C^{\pm}_{jk} T^{k}_{j\alpha} \tag{19}$$

$$R^{(i)k\pm}_{\alpha'\alpha} = \sum_{j} T^{k\pm 1}_{j+1,\alpha'}[(j+1)^{(i-1)}a_{j,\pm k} + (-1)^{i}(j)^{(i-1)}b_{j,\pm k}]T^{k}_{j\alpha} \tag{20}$$

where the sum goes from max(k, $k \pm 1$) to min($N + k - 1$, $N' + k \pm 1 - 1$).

The details of each matrix have been given, particularly as the non-orthogonal contributions have not been published before. Note that each of these transformed matrices is formed by effectively the same operation and so all of them can be computed at the same time.

One can express eqn (15) in a more compact notation as

$$\hat{\boldsymbol{H}} = \hat{\boldsymbol{H}}^{k} + \hat{\boldsymbol{K}}^{VR} \tag{21}$$

where

$$\hat{\boldsymbol{H}}^{k} = \hat{\boldsymbol{h}}^{k}(r_1, r_2)\boldsymbol{I} + w_0(r_1, r_2)\boldsymbol{L}^{k} + \sum_{i=1}^{3}(-1)^{i} w_i(r_1, r_2)\boldsymbol{M}^{(i)k} \tag{22}$$

$$\hat{\boldsymbol{K}}^{VR} = -u_0(r_1, r_2)\boldsymbol{Q}^{k\pm} - \sum_{i=1}^{2} u_i(r_1, r_2)\boldsymbol{R}^{(i)k}. \tag{23}$$

In deriving eqn (15) we have assumed the usual DVR approximation in that the potential function is diagonal across the grid points, *i.e.*

$$\sum_{j,j'=k}^{N+k-1} T^{k}_{j'\alpha}\langle j'k | V(r_1, r_2, \theta) | jk >_{\theta} T^{k}_{j\alpha} \approx \delta_{\alpha\alpha'} V(r_1, r_2, \theta_{k\alpha}). \tag{24}$$

This is equivalent to N-point Gauss-associated Legendre quadrature.[10] This quadrature approximation means that the DVR method is not strictly variational, owing to the number of functions being inextricably linked to the number of points. It is observed, however, that the method behaves variationally (as one would expect) if N is sufficiently large.

As a consequence of eqn (24) the potential is now diagonal in the angles, and the only angle-coupling is provided by the transformed matrices, which are relatively simple to evaluate.

The DVR procedure then is to solve the two-dimensional (2D) Hamiltonian $\hat{\boldsymbol{h}}^{k}$, contained in $\hat{\boldsymbol{H}}^{k}$, for each different angle α. This can be thought of as finding solutions at various 2D 'cuts' across the potential-energy surface. The 2D eigenvectors obtained can then be used as a well adapted basis in which to represent the fully coupled problem. The major benefit is that not all the solutions of these lower-dimensional problems are required to converge the desired states of $\hat{\boldsymbol{H}}$. One can select a subset of each of the 2D solutions at each angle according to an energy cut-off criterion, then the final basis constructed from these will be of reduced size and hence offer great computational savings.

The elements in $\hat{\boldsymbol{h}}^{k}$ are block-diagonal in angle, with all other terms spanning the whole $\hat{\boldsymbol{H}}^{k}$. Clearly one could either include the diagonal contributions from the angle-coupling matrices in the 2D calculations or in the final, 3D calculation. It is generally considered better to include them in the 3D calculation as one can then assign a physical meaning to the 2D solutions, as eigenvalues of the stretching vibrations (rather like an adiabatic approximation). Essentially, by taking this option, the 2D eigenvalues are independent of the number of DVR points and faster convergence of final solutions is achieved.

The full expression for $\hat{\boldsymbol{H}}$ in a DVR has been given for completeness, and indeed one can go ahead from this and obtain ro-vibrational solutions entirely in a DVR in the generalised coordinates. For vibrational problems ($J = 0$) it is seen that $\hat{\boldsymbol{K}}^{VR} = 0$ and so one purely solves $\hat{\boldsymbol{H}}^{k}$ in the DVR for $k = 0$. To account for rotational excitation ($J > 0$) one could now solve $\hat{\boldsymbol{H}}^{VR}$ also in a DVR, for all k.

The treatment that we prefer, however,[11] partly because of the computational considerations, is to treat the non-Coriolis coupled ($\hat{\boldsymbol{H}}^{k}$ only) problem in a DVR, for each k. Take the lowest of these solutions (for each k), back-transform to an FBR and then couple the ks to solve the full Coriolis-coupled Hamiltonian, using the solutions of each k calculation, expressed in an FBR, as a basis to solve the final $\hat{\boldsymbol{H}}$. Of course the advantage here again is that not all of the non-Coriolis solutions are required; one chooses the lowest M. This is a neat way of performing ro-vibrational calculations utilising both a DVR and the two-step variational approach of Tennyson and Sutcliffe.[6]

3. Applications/Results

3.1 Scattering Coordinates: LiCN, H_3^+

We discuss here some recent studies using the DVR in scattering (or Jacobi) coordinates. In terms of fig. 1, these are obtained when point R coincides with atom A_1 and point P is at the centre of mass of the diatom $A_2A_3\{g_1 = [m_2/(m_2 + m_3)], g_2 = 0\}$. These orthogonal coordinates are particularly suitable for atom–diatom systems that tend to be 'floppy' and isomerise.

Henderson and Tennyson[12] have recently studied the vibrational ($J = 0$) states of the LiCN system using the SCF potential-energy surface of Essers *et al.*[13] with the CN bond frozen at its equilibrium value. This potential has an absolute minimum for linear LiNC ($\theta = 180°$) and a metastable minimum for LiCN ($\theta = 0°$). These isomers are separated by a relatively low barrier.

The r_2 coordinate, the Li—CN stretch, was treated in an FBR using Morse oscillator-like functions. The DVR method proved to be powerful in that some 900 vibrational states were converged (with respect to basis-set truncation). This calculation involved diagonalising a final Hamiltonian matrix of dimension 1870. The best FBR calculation on this system[14] converged only the lowest 80 levels.

In the high-energy region studied all the states are sufficiently energetic to cross the LiNC/LiCN barrier. Most vibrational states were found to be irregular and delocalised. However, Henderson and Tennyson found states corresponding to LiNC normal modes, LiCN normal modes and free-rotor states where the Li^+ orbits the CN^-, throughout the energy range studied.

Approximate mode excitation assignments could be made for these states by examining contour plots of the wavefunction. Indeed, state 900 is found to be an LiNC state with 20 quanta of stretching energy in the Li—CN bond! Fig. 2 shows some of the wavefunction structures for various states.

The large number of levels involved enabled a reliable statistical analysis to be made on nearest-neighbour level spacings. Fits were made to a Brody parameter,[15] for various

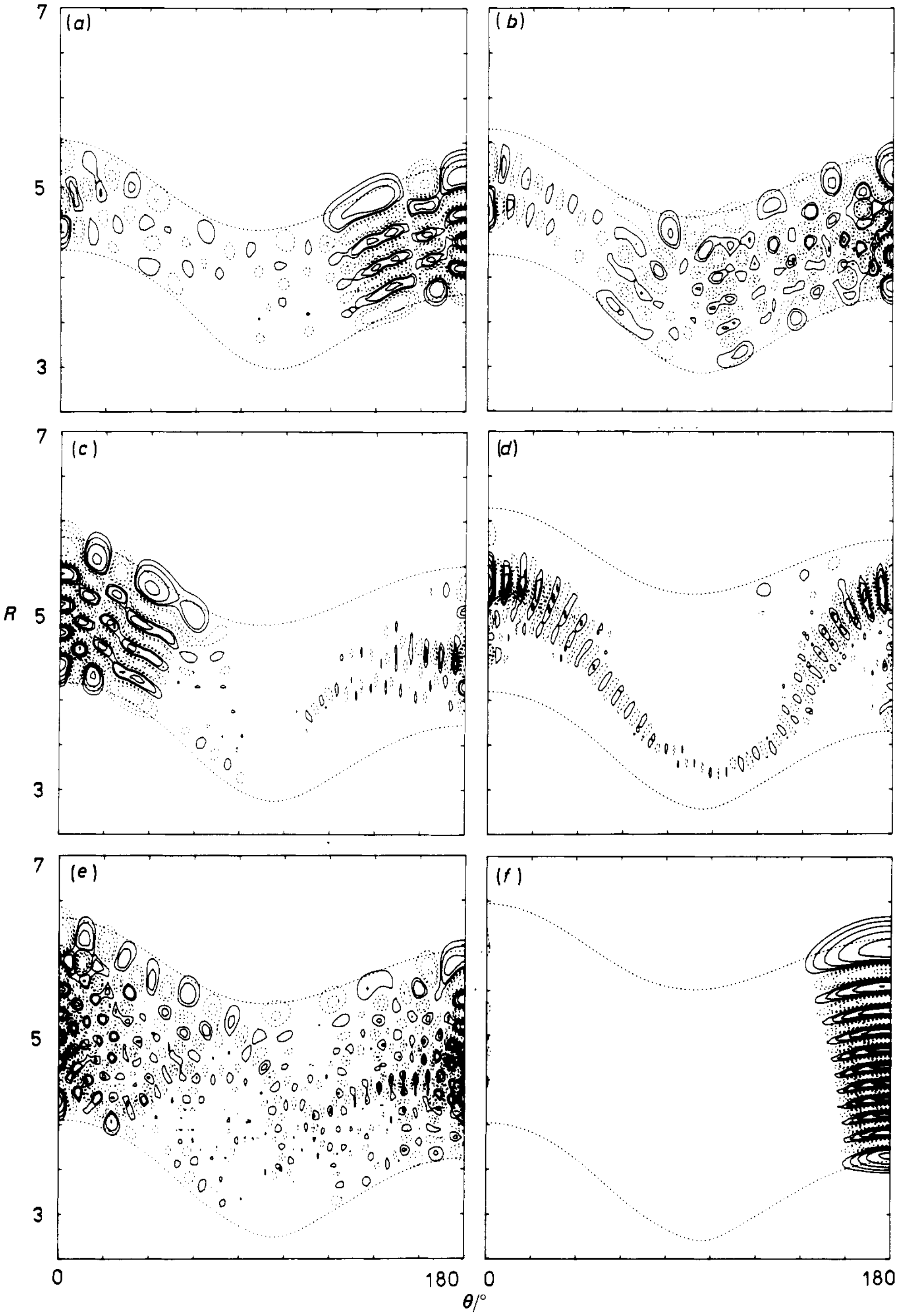

Fig. 2. Contour plots of six typical wavefunctions for the LiNC/LiCN system. Approximate assignments are; (*a*) state 180, LiNC normal mode (7, 4); (*c*) state 353, LiCN normal mode (7, 6); (*d*) state 609, free-rotor (0, 65); (*f*) state 900, LiNC normal mode (20, 0), where (v_s, v_b) corresponds to (no. of stretching quanta in the Li—CN bond, no. of quanta in the bend). States 250 and 750 [(*b*) and (*e*)] are irregular and cannot be assigned. Solid (dashed) contours enclose regions where the wavefunction has positive (negative) amplitude. Contours are drawn at 4, 8, 16, 32 and 64% of the maximum amplitude of the wavefunction. The outer dashed contours represent the classical turning point of the potential for the associated eigenvalue.

ranges of levels, and indicated increases in irregularity with energy. This finding was consistent with the decreasing number of states that could be assigned even approximate quantum numbers.

H_3^+ is a system that has been studied extensively in recent years by both experimentalists and theorists. This electronically simple species has proved to be of great interest to the theoretical nuclear dynamicist and spectroscopist. The observation by Carrington and Kennedy,[16] of 27000 transitions in a 222 cm^{-1} near-dissociation region provides much motivation in this area. This spectrum remains unassigned and largely unexplained.

Tennyson and co-workers[17,18] recently performed a series of parallel quantum and classical 2D calculations on H_3^+ with θ frozen at 90°. The two radial coordinates were expressed in an FBR: Morse-like functions in r_1 and spherical oscillator functions in r_2. The spherical oscillators were used to carry r_2 as the Morse-type functions do not behave correctly when r_2

approaches zero, *i.e.* as the system becomes linear. This geometry is sampled at *ca.* one third of the H_3^+ dissociation energy.

These calculations studied the structure of the wavefunctions for all the bound states of the system, using two different potential-energy functions. A variety of rotationally excited states was examined. An important result of these calculations was the observation of 'horseshoe' states in quantum calculations (see fig. 3). Classical studies[19] had suggested that this horseshoe motion was responsible for the underlying structure in the Carrington–Kennedy spectrum. This spectrum, the transitions of which are between quasi-bound states, can only be fully understood by calculations including both vibrational and rotational excitation.

Tennyson and Henderson, using the highly accurate *ab initio* surface of Meyer *et al.*,[20] performed similar calculations for a range of other angles, and this 2D basis was employed for the full 3D calculations using a DVR in θ.[11]

The lowest 180 vibrational ($J = 0$) solutions were obtained and $J = 1 \leftarrow 0$ excitation energies were computed for the lowest 41 vibrational states. This considerably extended the range of ro-vibrational states studied, and showed the convergence difficulties suffered in previous calculations.[21]

This work identified 'horseshoe' states *for the first time in a full 3D quantum-mechanical study.* These states may actually be thought of as the highly excited bending motion of a quasi-linear molecule. Fig. 3 shows a wavefunction contour plot for a 'horseshoe' state from a 2D calculation, and fig. 4 shows the same state in a 3D calculation. The authors are currently developing a multi-dimensional DVR program to make a serious attempt, at the very highest energies, to reproduce the Carrington–Kennedy spectrum quantum-mechanically.

3.2 Radau Coordinates: Na_3

The Na_3 cluster presents a very challenging problem. This Jahn–Teller system has a very complicated potential-energy surface.[22] Below the conical intersection there are three symmetry-related absolute minima and three metastable minima, separated by six saddle points. There are a further three low-lying saddle points at linear geometries. The linear saddle points are a long way from the minima and the conical intersection resulting in long, narrow and nearly flat portions of the surface.

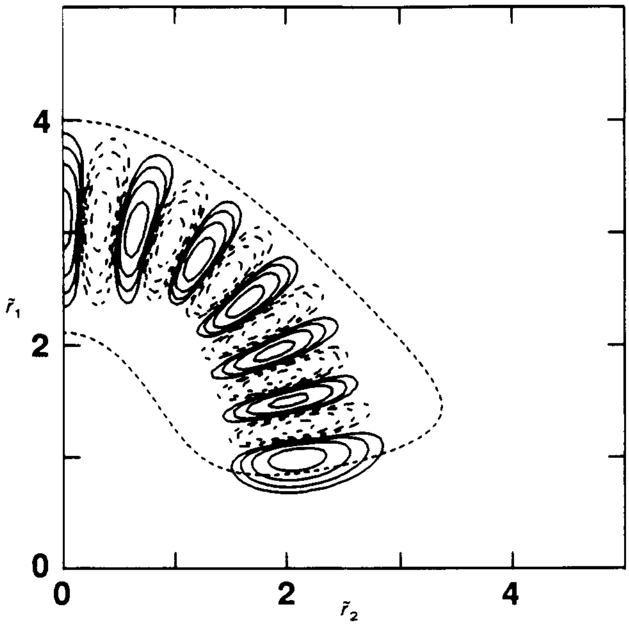

Fig. 3. A wavefunction of a $J = 0$ 'horseshoe' state of H_3^+ obtained from a 2D ($\theta = 90°$) calculation (see text). This state (number 54) contains 12 quanta of excitation in the 'horseshoe' mode. Contours are for 64, 32, 16 and 8% of the maximum amplitude with solid (dashed) curves enclosing regions of positive (negative) amplitude. The outer contour gives the classical turning point. The radial coordinates are mass weighted so that $\tilde{r}_1 = \alpha r_1$ and $\tilde{r}_2 = r_2/\alpha$, where $\alpha = (3/4)^{1/4}$.

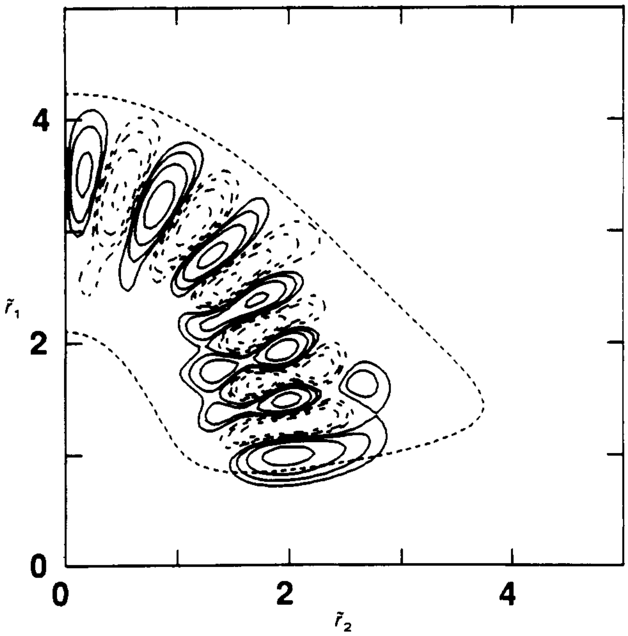

Fig. 4. Cuts through the 3D wavefunction of state 150 of the $J = 0$ even states containing 12 quanta in the 'horseshoe' mode. The angle θ is fixed at 90° for this plot. The contours and radial coordinates are as given in fig. 3.

A number of spectroscopic studies have been performed on Na_3. The most intriguing, by Broyer *et al.*,[23] found a very dense spectrum at relatively low energy. Classical calculations[24] suggested that this behaviour could be associated with classical chaos and in particular with the asymmetric stretching mode which, with relatively small amounts of excitation, links the absolute minima.

We therefore decided to perform a quantum-mechanical study of this system using the single *ab initio* potential-energy surface of Thompson *et al.*[22] Initially we attempted an FBR calculation. We tried using scattering ($g_1 = \frac{1}{2}$, $g_2 = 0$), bondlength–bond angle ($g_1 = g_2 = 0$) and Radau [$g_1 = g_2 = \sqrt{3}/(1 + \sqrt{3})$] coordinates. None of these calculations gave satisfactory results. The best results were obtained using Radau coordinates and even then the lowest levels were converged to only *ca.* 0.5 cm^{-1} with very poor results for higher levels, see table 1.

DVR calculations were therefore attempted using scattering and Radau coordinates. Again the Radau coordinates gave the better results. In this case satisfactorily converged (to within 0.1 cm^{-1} or better) results were obtained for the 70-plus levels lying below the linear saddle points (table 1). These calculations were successful because we were able to use large radial basis sets to obtain converged solutions for the 2D radial Hamiltonians. The lowest of these solutions then gave a very satisfactory basis for the full 3D problem. Effectively, these calculations mimicked FBR calculations with in excess of 30 000 basis functions! We note that Bačić *et al.*[25] used Radau coordinates for a successful DVR calculation on the vibrational states of water.

Rather surprisingly the very low-lying levels of Na_3, including the fundamental frequencies, are well represented by the harmonic approximation. Table 2 compares our fully

Table 1. Convergence of $J = 0$ vibrational calculations on Na_3 levels with odd symmetry performed in Radau coordinates

	FBR		DVR		
level	$L = 2100$	$L = 2460$	$L = 1200$	$L = 1500$	$L = 1800$
1	−2953.6	−2953.9	−2954.17	−2954.17	−2954.17
6	−2812.1	−2813.7	−2816.34	−2816.34	−2816.34
11	−2758.8	−2758.9	−2762.57	−2762.57	−2762.57
16	−2716.0	−2721.8	−2726.82	−2726.82	−2726.82
21	−2678.5	−2681.5	−2710.06	−2710.06	−2710.06
26	−2654.6	−2660.3	−2671.30	−2671.30	−2671.30
31	−2619.9	−2625.8	−2662.71	−2662.71	−2662.71
36	−2594.1	−2603.8	−2627.08	−2627.09	−2627.09
41	−2577.8	−2581.1	−2618.80	−2618.81	−2618.81

The energies of the selected levels are given in cm^{-1} relative to dissociation. The finite-basis representation (FBR) calculations used quantum number selection[29] to give a final secular matrix of dimension L. These calculations used up to 71 Legendre polynomials for θ and up to 19 Morse oscillator-like functions in the radial coordinates. The discrete variable representation (DVR) selected the L lowest solutions from a grid of 70 Gauss–Legendre quadrature points. The vibrational problem was solved for the 35 unique points[11] using up to 30 Morse oscillator-like functions in each radial coordinate.

coupled results with Thompson *et al.*'s harmonic calculations and experiment.[26] These results show that Thompson *et al.*'s potential-energy surface is accurate in the region about the minima. For completeness we also give the tunnelling splitting of the levels we calculate. These splittings are all small for the fundamentals.

The $J = 0$ high-lying solutions of the Na_3 problems that we have obtained show interesting structure that does not immediately bear out the predictions of the classical calculations.[24] A thorough analysis of these results as well as calculations on rotationally excited states is in progress and full results will be given elsewhere.[27]

4. Conclusions

We have presented a discrete variable representation, in one internal coordinate θ, of a most generalised coordinate system. A summary of recent DVR calculations using Jacobi and Radau coordinates has been given. The systems discussed here exemplify different strengths of the DVR method. For LiCN results were obtained for some 900 vibrational states. For H_3^+ high-lying rotationally excited states were obtained. These calculations also necessitated a clever use of C_{2v} symmetry in coordinate space. For Na_3, where FBR methods failed to converge even the lowest states, we managed to converge over 70 vibrational levels.

The generalised coordinates also encompass an infinite set of non-orthogonal coordinate systems which have now been presented in a DVR. Non-orthogonal coordinates are not usually those of choice owing to the extra computational effort required for cross-terms and the mixed derivatives. In some situations however, they are desirable if not necessary. Sutcliffe and Tennyson,[28] for example, when working on HeHD* found that it was necessary to prescribe the non-orthogonal, 'geometric', coordinates defined by $g_1 = 0.5$ and $g_2 = 0.0$. The use of Jacobi coordinates led to unconverged results owing to the loss of the symmetry in the potential.

Recently the authors have developed a computer program to treat all three internal coordinates in a DVR using the same coordinate systems presented here. Whitnell and Light[21] have already employed a 3D-DVR and used a hyperspherical coordinate system to study H_3^+. In a multidimensional DVR the diagonalisation–truncation procedure leads to a rather elegant expression of the problem and offers a most systematic solution strategy. The only problem is deciding in which order one should solve for the internal coordinates. Also of course, one might ask which internal coordinates should be in a DVR and which in an FBR? These questions are under investigation.

Table 2. Comparison of Na_3 band origins in cm^{-1}

			DVR	
band	harmonic[a]	expt.[b]	frequency	splitting
ν_0			−2954.2	0.0006
ν_2	58	49.5	54.0	0.0070
ν_3	94	87	92.5	0.0200
$2\nu_2$			105.2	0.0440
ν_1	142	139	137.8	0.0101

The absolute energy of the ground state, relative to dissociation, is given for comparison. [a] Ref. (22). [b] Ref. (26).

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