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# DVR1D: programs for mixed pointwise/basis set calculation of ro-vibrational spectra

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DVR1D calculates vibrational energy levels and wavefunctions for triatomic molecules in either scattering (Jacobi) or Radau coordinates for a given potential. The program uses a discrete variable representation (DVR) for the angular coordinate and a choice of basis functions for the radial coordinates. The program is particularly appropriate for high lying vibrational states. The accompanying program ROTLEV2 is driven by DVR1D and calculates rotationally excited states of $AB_2$ molecules such as water using Radau coordinates and a "bisector" axis embedding which properly reflects the symmetry of the system. DVR1D can also drive ROTLEVD, DIPOLE and hence SPECTRA from the TRIATOM program suite (Tennyson et al., Comput. Phys. Commun., previous article).

## PROGRAM SUMMARY

*Title of program*: DVR1D

*Catalogue number*: ACNC

*Program obtainable from*: CPC Program Library, Queen's University of Belfast, N. Ireland (see application form this issue)

*Licensing provisions*: none

*Computer*: Convex C3840 running BSD unix; *Installation*: University of London Computer Centre

*Other machines on which program has been tested*: Cray-XMP/48, Cray-YMP8i, IBM RS6000

*Programming language used*: FORTRAN 77

*Memory required to execute with typical data*: case dependent

*Peripherals used*: card reader, line printer, disk files

*No. of lines in distributed program, including test data, etc.*: 3709

*Keywords*: ro-vibrational, body-fixed, discrete variable representation, finite elements, vectorised

*Nature of physical problem*
DVR1D calculates the bound vibrational levels of a triatomic system using body-fixed coordinates (either Jacobi or Radau) [1].

*Method of solution*
The angular coordinate is treated using a discrete variable representation (DVR) based on (associated) Legendre polynomials and the radial coordinates are represented by a basis constructed as a product of either Morse oscillator-like or spherical oscillator functions. Intermediate diagonalisation and truncation is used to construct the final secular problem. For rotationally excited states DVR1D provides data necessary to drive ROTLEV2 [2] or ROTLEVD [3].

*Restrictions on the complexity of the problem*
The size of matrix that can practically be diagonalised. DVR1D dimensions arrays dynamically at execution time and

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in the present version the total space available is a single parameter which can be reset as required.

*Typical running time*
Case depenent but dominated by matrix diagonalisation. The sample data takes 23 s for $J = 0$ and 47 s for $J = 1$ (Coriolis decoupled) on the Convex C3840.

*Unusual features of the program*
A user supplied subroutine containing the potential energy as an analytic function (optionally a Legendre polynomial expansion) is a program requirement.

*References*

[1] J. Tennyson and J.R. Henderson, J. Chem. Phys. 91 (1989) 3815.
[2] J.R. Henderson and J. Tennyson, this article, second program (ROTLEV2).
[3] J. Tennyson, S. Miller and C.R. Le Sueur, Comput. Phys. Commun. 75 (1993) 339, this issue.

## PROGRAM SUMMARY

*Title of program*: ROTLEV2

*Catalogue numbers*: ACND

*Program obtainable from*: CPC Program Library, Queen's University of Belfast, N. Ireland (see application form this issue)

*Licensing provisions*: none

*Computer*: Convex C3840 running BSD unix; *Installation*: University of London Computer Centre

*Other machines on which program has been tested*: Cray-XMP48, Cray-YMP8i

*Programming language used*: FORTRAN 77

*Memory required to execute with typical data*: case dependent

*Peripherals used*: card reader, line printer, at least two disk files

*No. lines in distributed program, including test data, etc.*: 4401

*Keywords*: rotationally excited state, Coriolis coupling, secondary variational method, sparse matrix, vectorised, discrete variable representation

*Nature of physical problem*
ROTLEV2 performs the second step in a two-step variational calculation for the bound ro-vibrational levels of an $AB_2$ molecule using Radau coordinates [1].

*Method of solution*
A basis is constructed from the energy selected solutions of the Coriolis decoupled problem. The resulting sparse matrix is then diagonalised to give the solutions.

*Restrictions on the complexity of the problem*
The time taken to transform the required matrix elements.

*Typical running time*
Highly case dependent. The sample data takes 873 s on the Convex C3840.

*Unusual features of the program*
Most data is read directly from DVR1D [2].

*References*

[1] J. Tennyson and B.T. Sutcliffe, Int. J. Quantum Chem. 42 (1992) 941.
[2] J.R. Henderson and J. Tennyson, first program, this article.

## LONG WRITE-UP

### 1. Introduction

The use of the discrete variable representation (DVR) by Light, Bačić and co-workers [1] has given new impetus to the theoretical study of highly excited vibrational states of small molecules. This is development has proved timely because of the great increase in experimental activity in this area.

In practice most DVR calculations (see e.g. refs. [2–11]) on the ro-vibrational levels of triatomic systems have been hybrids. One coordinate, usually the angular coordinate, has been treated using a

DVR and the two remaining, radial, coordinates have been expanded within a finite basis representation (FBR). This method has proved highly successful and the only significant computational difference between the works cited above has been between the form of the functions used to carry the radial motion. These calculations show that the $\mathrm{DVR}^1$–$\mathrm{FBR}^2$ [12] method can routinely deliver an accurate representation of several hundred vibrational states of most triatomics. This is significantly more than can easily be obtained using comparable pure FBR ($\mathrm{FBR}^3$) methods [8].

In this work we present our $\mathrm{DVR}^1$–$\mathrm{FBR}^2$ program, DVR1D, which has been successfully used to study the vibrational states of $H_3^+$ [6], LiCN [7], $Na_3$ [8], $H_2O$ [10], KCN [11] and $H_2Se$ [13]. Rotational excitation of $H_3^+$ [6], $H_2S$ [14], $H_2O$ [15] and $H_2Se$ [13] have been studied using either ROTLEVD [16] or ROTLEV2 (this article). The computationally efficient [15] option of using ROTLEVD involves back-transforming the DVR to an FBR. By this means it also possible to calculate transition intensities using DIPOLE [16] either for individual ro-vibrational transitions [17] or for complete vibrational bands [18].

## 2. Method

### 2.1. The vibrational problem: DVR1D

Following Sutcliffe and Tennyson [14,19] one write can an effective radial Hamiltonian operator

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

This Hamiltonian is obtained by letting the full body-fixed Hamiltonian of the problem act on the angular functions, multiplying from the left by the complex conjugate of these functions and integrating over all angular variables. Appropriate angular functions are given by

$$|\, j, k\rangle = \Theta_{j,k}(\theta) \,|\, J, M, k\rangle, \tag{2}$$

where $\Theta_{j,k}(\theta)$ is a normalised associated Legendre polynomial with the Condon and Shortley [20] phase conventions. $|\, J, M, k\rangle$ is an angular momentum eigenfunction [21] given in terms of the Euler angles $(\alpha, \beta, \gamma)$ which are defined by the embedding. In eq. (2), $J$ is the total angular momentum which is a good quantum number of the system; $M$ is the projection of $J$ on the space-fixed $z$-axis and will not be considered further; $k$ is the projection of $J$ onto the body-fixed $z$-axis.

For orthogonal coordinates, such as scattering (Jacobi) or Radau coordinates, the effective vibrational kinetic energy operator of eq. (1), which is independent of the axis embedding, is given by

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

where the reduced masses are given in terms of the atomic masses, $m_i$:

$$\mu_1^{-1} = g_2^2 m_1^{-1} + m_2^{-1} + (1-g_2)^2 m_3^{-1}, \qquad \mu_2^{-1} = m_1^{-1} + g_1^2 m_2^{-1} + (1-g_1)^2 m_3^{-1}. \tag{4}$$

The parameters $(g_1, g_2)$ are defined by the coordinate system. For scattering (Jacobi) coordinates:

$$g_1 = \frac{m_2}{m_2 + m_3}, \qquad g_2 = 0; \tag{5}$$

and for Radau coordinates [19]:

$$g_1 = 1 - \frac{\alpha}{\alpha + \beta - \alpha\beta}, \quad g_2 = 1 - \frac{\alpha}{1 - \beta + \alpha\beta}, \quad \alpha = \left( \frac{m_3}{m_1 + m_2 + m_3} \right)^{1/2}, \quad \beta = \frac{m_2}{m_1 + m_2}. \tag{6}$$

For systems with two like atoms ($AB_2$ molecules), the identical atoms are 2 and 3 in scattering coordinates when $g_1 = \frac{1}{2}$. In Radau coordinates the like atoms are 1 and 2; in this case $g_1 = g_2$.

Transformation of the Hamiltonian of eq. (1) to a DVR in $\theta$ is achieved by

$$\mathbf{H}^{\mathrm{DVR}} = \mathbf{T}^{\mathrm{T}}\mathbf{H}\mathbf{T}. \tag{7}$$

The feature which distinguishes the DVR from other finite element approaches is that grid points are defined by an appropriate Gaussian quadrature. The transformation matrix for the angular coordinate is thus

$$T_{j\alpha}^{k} = \omega_{k\alpha}^{1/2} \Theta_{jk}(\theta_{k\alpha}), \tag{8}$$

where $\boldsymbol{\theta}_k$ and $\boldsymbol{\omega}_k$ are the points and weights of $N$-point Gauss-associated Legendre quadrature points for associated Legendre polynomials of order $k$.

An important feature of the DVR is the quadrature approximation [22]. This is used to evaluate the contribution due to the potential which is diagonal in the DVR:

$$\sum_{j,j'=k}^{N+k-1} T_{j'\alpha'}^{k} \langle j'k \,|\, V(r_1, r_2, \theta) \,|\, jk \rangle_\theta T_{j\alpha}^{k} \simeq \delta_{\alpha\alpha'} V(r_1, r_2, \theta_{k\alpha}). \tag{9}$$

This means that all angular off-diagonal contributions arise from the kinetic energy operator via the **L** matrix which is given by

$$L_{\alpha\alpha'}^{k} = \sum_{j=k}^{N+k-1} T_{j\alpha'}^{k} j(j+1) T_{j\alpha}^{k}. \tag{10}$$

The resulting $J = k = 0$ effective radial Hamiltonian is

$$\hat{H}_{\alpha\alpha'} = \delta_{\alpha\alpha'} \left( \frac{-\hbar}{2\mu_1} \frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial r_2^2} + V(r_1, r_2, \theta_{k\alpha}) \right) + \tfrac{1}{2}\hbar^2 \left( \frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} \right) L_{\alpha\alpha'}^{0}. \tag{11}$$

The solution strategy in the DVR is to solve the effective radial Hamiltonian for each $\alpha$ on the DVR grid. The lowest solutions, selected either by number or energy cut-off, are then used to construct a full 3D Hamiltonian matrix which is diagonalised to yield the eigenenergies and values for the wavefunctions at the DVR grid points. In this approach there is choice as to whether the diagonal parts of the angular kinetic energy term (the "$W$-matrix" of ref. [6]) are included in the 2D or 3D problems [23]. Our experience has shown that the latter gives better convergence.

The 2D radial Hamiltonians are diagonalised using radial basis functions similar to those employed in our $\mathrm{FBR}^3$ program [16]. These are either Morse oscillator-like functions or spherical oscillators. The Morse oscillator-like functions are defined as [24]

$$|n\rangle = H_n(r) = \beta^{1/2} N_{n,\alpha+1/2} \exp(-\tfrac{1}{2}y)\, y^{(\alpha+1)/2} L_n^{\alpha}(y), \quad y = A \exp[-\beta(r - r_e)], \tag{12}$$

where

$$A = 4D_e/\beta, \qquad \beta = \omega_e(\mu/2D_e)^{1/2}, \qquad \alpha = \text{integer}(A). \tag{13}$$

The parameters $\mu$, $r_e$, $\omega_e$ and $D_e$ can be associated with the reduced mass, equilibrium separation, fundamental frequency and dissociation energy of the relevant coordinate respectively. In practice ($r_e$, $\omega_e$, $D_e$) are treated as variational parameters and optimised accordingly. $N_{n\alpha}L_n^{\alpha}$ is a normalised associated Laguerre polynomial [25].

The spherical oscillator functions are particularly useful for systems which have significant amplitude for $r_2 = 0$. These functions are defined by [26]

$$|n\rangle = H_n(r) = 2^{1/2}\beta^{1/4}N_{n\alpha+1/2}\exp\left(-\tfrac{1}{2}y\right)\, y^{(\alpha+1)/2}L_n^{\alpha+1/2}(y), \quad y = \beta r^2, \tag{14}$$

where

$$\beta = (\mu\omega_e)^{1/2} \tag{15}$$

and ($\alpha$, $\omega_e$) are treated as variational parameters.

For either set of radial functions, integration over the potential is performed using Gauss–Laguerre quadrature [27]. Details of how the integrals over the radial kinetic energy operators are computed can be found in the previous article [16].

For an $AB_2$ system in scattering coordinates the permutation symmetry of the like atoms is carried by the angular coordinate. In the DVR this leads to a modified, symmetrised $\mathbf{L}$ matrix [6]:

$$L_{\alpha\alpha'}^{kq} = 2\sum_{j=k}^{N/2+k-1} T_{2j+q,\alpha'}^{k}(2j+q)(2j+q+1)T_{2j+q,\alpha}^{k}, \quad q = 0, 1. \tag{16}$$

In a symmetrised DVR only the term which differs between even ($q = 0$) and odd ($q = 1$) calculations is provided by the $\mathbf{L}$ matrix which means that the same solutions of the 2D problems can be used for both $q = 0$ and $q = 1$ calculations if the diagonal portion of $\mathbf{L}$ is only included in the 3D Hamiltonian.

In Radau coordinates symmetry is carried by the radial functions provided the same functions are used for the $r_1$ and $r_2$ coordinates (denoted $|m\rangle$ and $|n\rangle$, respectively). Symmetrised radial functions can be written as

$$|m, n, q\rangle = 2^{-1/2}(1+\delta_{mn})^{-1/2}\left(|m\rangle|n\rangle + (-1)^q|n\rangle|m\rangle\right), \quad m \geq n+q, \quad q = 0, 1. \tag{17}$$

### 2.2. Rotational excitation

#### 2.2.1. Driving ROTLEVD

If the $z$-axis is taken to lie parallel to either $\boldsymbol{r}_1$ or $\boldsymbol{r}_2$, then the vibration-rotation term in Hamiltonian (1) is given by [19]

$$\hat{K}_{VR} = \delta_{j'j}\delta_{k'k}\frac{\hbar^2}{2\mu_1 r_1^2}\left(J(J+1) - 2k^2\right) - \delta_{j'j}\delta_{k',k\pm1}\frac{\hbar^2}{2\mu_1 r_1^2}(1+\delta_{k0}+\delta_{k'0})^{1/2}C_{Jk}^{\pm}C_{jk}^{\pm}, \tag{18}$$

where

$$C_{Jk}^{\pm} = \left[J(J+1) - k(k\pm1)\right]^{1/2}. \tag{19}$$

The first, diagonal in $k$, term in (18) can be included as part of the effective "vibrational" problem discussed in the previous section. The second, off-diagonal in $k$, Coriolis coupling term is then the only remaining operator that needs to be considered. This is the problem solved by ROTLEVD [16]. The $i$th solution, $c^{ki}$ of the effective vibrational operator in the DVR can be transformed to an FBR, using [6]

$$d_{jmn}^{ki} = \sum_{\alpha} T_{j\alpha}^{k}c_{\alpha mn}^{ki}. \tag{20}$$

The FBR eigenvector coefficients, $\boldsymbol{d}^{ki}$, and corresponding eigenenergies, $\epsilon_i^k$ form the necessary input to ROTLEVD. When $J = k = 0$ these coefficients can also be used to drive DIPOLE [16] directly.

### 2.2.2. Bisector embedding: ROTLEV2

If, in Radau coordinates, the $z$-axis is placed along a direction $\frac{1}{2}\theta$ from either $\boldsymbol{r}_1$ or $\boldsymbol{r}_2$, the vibration–rotation operator in (1) is given by [14]

$$\begin{aligned}\hat{K}_{VR} = {} & \delta_{k'k}\frac{\hbar^2}{8}(J(J+1)-3k^2)\left(\frac{1}{\mu_1 r_1^2}+\frac{1}{\mu_2 r_2^2}\right)I^{(1)}_{j',k,j,k} \\ & + \delta_{k'k}\frac{\hbar^2}{16}(J(J+1)-k^2)\delta_{j'j}\left(\frac{1}{\mu_1 r_1^2}+\frac{1}{\mu_2 r_2^2}\right) \\ & + \delta_{k'k\pm 1}\frac{\hbar^2}{4}C^{\pm}_{Jk}\left(\frac{1}{\mu_2 r_2^2}-\frac{1}{\mu_1 r_1^2}\right)\left(\delta_{j'j}C^{\pm}_{jk}+(k\pm\tfrac{1}{2})I^{(2)}_{j',k',j,k}\right) \\ & + \delta_{k'k\pm 2}\frac{\hbar^2}{32}C^{\pm}_{Jk\pm 1}C^{\pm}_{Jk}\left(\frac{1}{\mu_1 r_1^2}+\frac{1}{\mu_2 r_2^2}\right)\left(2I^{(1)}_{j',k',j,k}-I^{(3)}_{j',k',j,k}\right),\end{aligned} \tag{21}$$

where $C^{\pm}_{Jk}$ is defined above and the other angular factors are

$$a_{jk} = \left(\frac{(j+k+1)(j+k+2)}{(2j+1)(2j+3)}\right)^{1/2}, \tag{22}$$

$$b_{jk} = \left(\frac{(j-k)(j-k-1)}{(4j^2-1)}\right)^{1/2}. \tag{23}$$

The integrals in (21) are

$$I^{(1)}_{j',k',j,k} = \left\langle j'k'\left|\frac{1}{(1-\cos\theta)}\right|jk\right\rangle, \tag{24}$$

$$I^{(2)}_{j',k',j,k} = \left\langle j'k'\left|\frac{1+\cos\theta}{\sin\theta}\right|jk\right\rangle \tag{25}$$

and

$$I^{(3)}_{j',k',j,k} = \langle j'k' \mid jk\rangle. \tag{26}$$

The integrals $I^{(1)}$ and $I^{(2)}$ are in fact singular for $k = k' = 0$, although inspection of (21) shows this only to be serious in the case of $I^{(1)}$. However, for $k = k'$ one can apply the quadrature approximation in the DVR:

$$\sum_{j,j'=k}^{N+k-1} T^k_{j'\alpha'}I^{(1)}_{j'k,j,k}T^k_{j\alpha} \simeq \delta_{\alpha\alpha'}\frac{1}{(1-\cos\theta_{k\alpha})}. \tag{27}$$

In all cases where $k \neq k'$, the integrals can be evaluated quickly and accurately using an appropriate Gauss-associated Legendre quadrature scheme and then transformed into the DVR.

Of course evaluating in the DVR does not actually remove the singularity, it is simply avoided. For a general molecule in Radau coordinates the singularity occurs when $\theta = 0°$ or $180°$. However, for an $AB_2$

system using the symmetrised basis functions (17), the singularity is confined to $\theta = 0°$: see Tennyson and Sutcliffe [14] for a detailed discussion of how to symmetrise (21). This corresponds to a linear ABB geometry which is energetically unfavourable for many molecules. If this is so the effects of the singularity can be suppressed by forcing the wavefunction to be have zero amplitude near $\theta = 0°$. This is the procedure used by ROTLEV2 which is thus only appropriate for $AB_2$ molecules in Radau coordinates.

## 3. Program structure

The key program in the suite is DVR1D which has to be run in all cases. If rotationally excited states are being considered then eigenvalues, eigenvectors and some matrix elements generated by DVR1D are passed to either ROTLEVD [16] or ROTLEV2. The input wavefunctions for DIPOLE [16] come from either DVR1D or ROTLEVD.

Card input is needed for both DVR1D and ROTLEV2. The amount required is kept to a minimum by passing as much information as possible from previous modules and by the use of default settings for many parameters. Both programs follow the convention that names beginning with letters A–H and O–Y are for 8-byte real variables, I–N are for integers and variables whose name begins with Z are logicals.

The calling sequences of DVR1D and ROTLEV2 are given in figs. 1 and 2. The role of the individual subroutines is described in comment cards included in the source programs.

DVR1D and ROTLEV2 used dynamical assignment of array space in which one big vector is sub-divided in routine CORE. In the current versions, this array is a single fixed length array ARRAY of dimension NAVAIL (set to 500000 in the versions supplied) in subroutine GTMAIN. For efficient storage management a call to a local GETMAIN, MEMORY or HPALLOC command should be implemented.

The CPU time requirement of DVR1D is dominated by matrix diagonalisation. The required diagonaliser has to give all eigenvalues and eigenvectors of a real symmetric matrix. The present implementation uses subroutine EGVQR [28] to mimic NAG routine F02ABF [29]. We would strongly recommend that EGVQR is replaced either by the local NAG implementation or by some diagonaliser appropriate to the architecture of the machine.

ROTLEV2 uses NAG routine F02FJF [29] which is a sparse matrix diagonaliser based on the algorithm of Nikolai [30]. The supplied source for this should be discarded if a local implementation of NAG is available. In ROTLEV2 the major consumer of CPU time is routine MXMB which performs vector–matrix and matrix–matrix multiplies for both the transformation and diagonalisation step. Replacing MXMB by a version customized for any particular machine is strongly recommended.

## 4. Program use

### 4.1. The potential subroutine

DVR1D requires a user supplied potential energy subroutine. There are two ways of supplying the potential. If it is specified as a Legendre expansion,

$$V(r_1, r_2, \theta) = \sum_{\lambda} V_\lambda(r_1, r_2)\, P_\lambda(\theta), \tag{28}$$

which corresponds to option ZLPOT = .TRUE., then the expansion must be supplied by

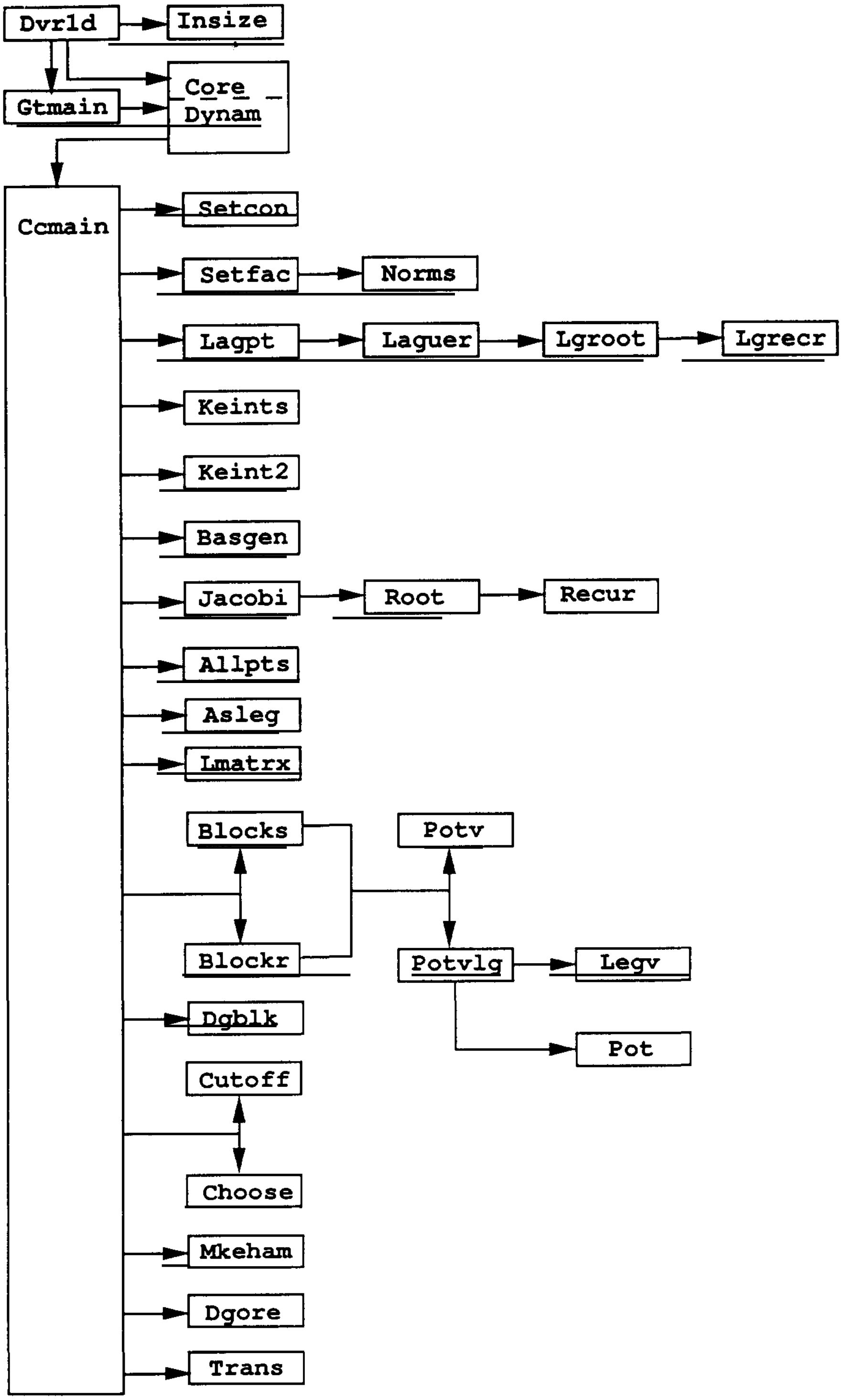

Fig. 1. Structure of program DVR1D. Service routines TIMER, GETROW and OUTROW have been omitted.

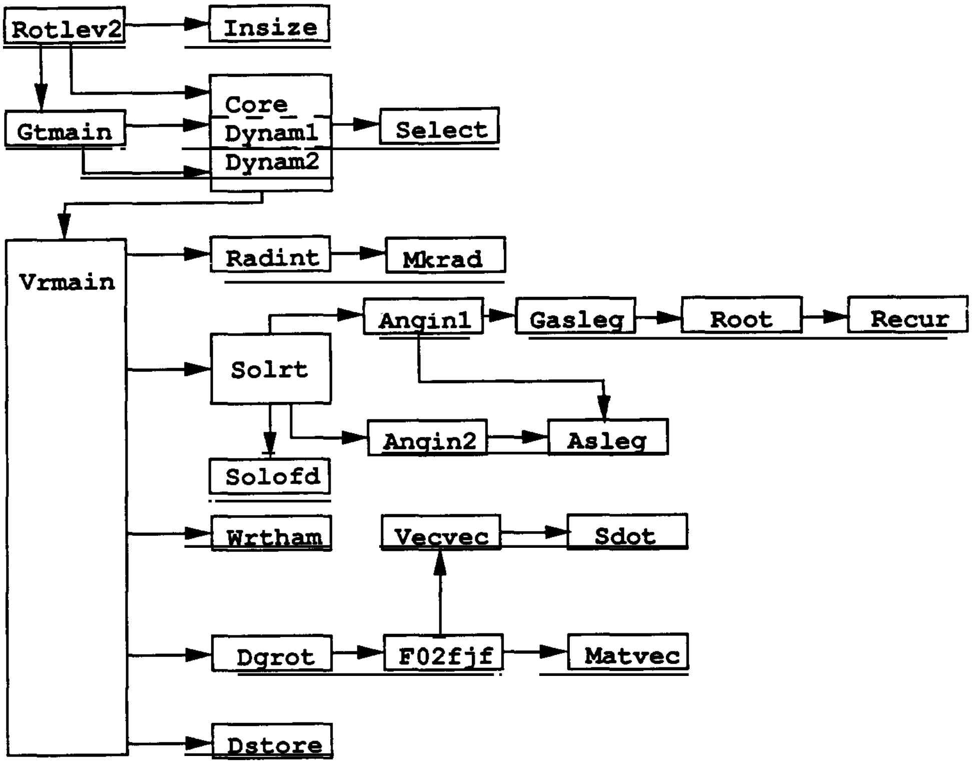

Fig. 2. Structure of program ROTLEV2. Service routines TIMER, GETROW, OUTROW and MXMB have been omitted.

SUBROUTINE POT(V0, VL, R1, R2)

which returns V0 = $V_0(r_1, r_2)$ and VL($\lambda$) = $V_\lambda(r_1, r_2)$ in Hartree for R1 = $r_1$ and R2 = $r_2$ in Bohr. If |IDIA| = 2, only even $V_\lambda$ are needed. If NCOORD = 2, R1 contains the rigid diatom bondlength $r_e$. If NCOORD > 1 then $V_\lambda$ has dimensions LPOT.

If a general potential function, ZLPOT = .FALSE., is to be used then

SUBROUTINE POTV(V, R1, R2, XCOS)

must be supplied. POTV returns the potential $V$ in Hartree for an arbitrary point given by R1 = $r_1$, R2 = $r_2$ (both in Bohr) and XCOS = cos $\theta$.

DVR1D includes COMMON/MASS/XMASS(3), G1, G2 where XMASS contains the atomic masses in atomic units (*not* amu), G1 = $g_1$ and G2 = $g_2$. This enables users to write flexible potential subroutines which allow for changes in coordinates or isotopic substitution. See, for example, the version of POTV supplied.

### 4.2. Input for DVR1D

DVR1D requires 9 lines of card input for *all* runs. Cards giving data not required or for which the defaults [given below in parenthesis] are sufficient should be left blank.

Card 1: NAMELIST/PRT/

| | |
|---|---|
| ZPHAM[F] | = T, requests printing of the Hamiltonian matrix. |
| ZPRAD[F] | = T, requests printing of the radial matrix elements. |
| ZP2D [F] | = T, requests printing of the solutions of the 2D radial problems. |

| | |
|---|---|
| ZPMIN[F] | = T, requests only minimal printing. |
| ZPVEC[F] | = T, requests printing of the eigenvectors. |
| ZLMAT[F] | = T, requests printing of the $L$-matrix. |
| ZCUT[F] | = T, final basis selected using an energy cut-off given by EMAX.<br>= F, LOWEIG (LOWEIG2) final basis functions selected. |
| ZDIAG[T] | = T, requests diagonalisation of the final Hamiltonian matrix. |
| ZROT[F] | = T, DVR1D to perform first step in a two-step variational calculation. |
| ZLADD[F] | only used if ZROT = T:<br>= T, number of DVR points (NDVR) fixed with (J, k);<br>= F, number decreases with $(J, k)$. |
| ZEMBED[T] | Used only in conjunction with ROTLEVD<br>= T, $z$-axis embedded along $r_2$;<br>= F, $z$-axis embedded along $r_1$. |
| ZMORSE[T] | = T, use Morse oscillator-like functions for $r_2$ coordinate;<br>= F, use spherical oscillator functions. |
| ZLPOT[F] | = T, potential supplied in POT;<br>= F, potential supplied in POTV. |
| ZWBLK[F] | = T, include $W$-matrix in the 2D Hamiltonians. |
| ZTEST[F] | Used only in conjunction with IDIA = $-2$ and JROT > 0.<br>= T, force suppression of functions at last DVR point. |
| ZTWOD[F] | = T, perform 2D calculation only at specified grid point. |
| ZVEC[F] | = T, data for ROTLEVD or ROTLEV2 to be written to stream IVEC(IVEC2). |
| IVEC[4] | stream for ROTLEVD or ROTLEV2 data. |
| IVEC2[7] | second stream for ROTLEVD data if IPAR = 2. |
| ZPFUN[F] | = T, eigenvalues concatenated on stream ILEV.<br>Warning, the first eigenvalues on this file must be for $J = 0$, $q = 0$. |
| ILEV[14] | stream for eigenvalues data. |
| IHAM[25] | stream for intermediate vectors. |
| IHAM2[1] | stream for partial Hamiltonian matrix if IPAR = 2. |

Card 2: NCOORD (I5)

NCOORD[3] the number of vibrational coordinates of the problem:
= 1 for a diatomic (useful for basis set optimisation),
= 2 for an atom rigid diatom system (not valid for IDIA = $-2$),
= 3 for a full triatomic.

Card 3: NPNT2, NMAX2, JROT, NEVAL, NDVR, LOWEIG, IDIA, KMIN, NPNT1, NMAX1, IPAR, LOWEIG2, LPOT (14I5)

| | |
|---|---|
| NPNT2[2*NMAX2 + 1] | order of Gaussian quadrature in the $r_2$ coordinate. |
| NMAX2 | order of the largest radial basis function $H_n(r_2)$, giving an $r_2$ basis of NMAX2 + 1 functions. |
| JROT[0] | total angular momentum quantum number of the system. |
| NEVAL[10] | number of eigenvalues and eigenvectors required. |

If NCOORD = 1 the rest of the card is ignored.

| | |
|---|---|
| NDVR | number of DVR points in $\theta$ from Gauss–(associated) Legendre quadrature. |
| LOWEIG | Maximum dimension of largest final Hamiltonian. |

| | |
|---|---|
| | If ZCUT = F, it is the actual dimension,<br>if ZCUT = T, LOWEIG must be ≥ than the number of functions selected. |
| IDIA | = 1 for scattering coordinates with a hetronuclear diatomic,<br>= 2 for scattering coordinates with a homonuclear diatomic,<br>= $-1$ for Radau coordinates with an ABC molecule, or Radau coordinates for an $AB_2$ system with $J > 0$ driving ROTLEVD,<br>= $-2$ for Radau coordinates with an $AB_2$ molecule. |
| KMIN[0] | = $k$ for JROT > 0 and ZROT = F,<br>= $(1-p)$ for JROT > 0 and ZROT = T.<br>Note: if KMIN = 2 in ROTLEV2 or ROTLEVD, KMIN must be 1 in DVR1D. |
| NPNT1[2*NMAX1 + 1] | order of Gaussian quadrature in the $r_1$ coordinate. |
| NMAX1 | order of the largest radial basis function $H_m(r_1)$, giving an $r_1$ basis of NMAX1 + 1 functions. |
| IPAR[0] | parity of basis if diatomic homonuclear ($\lvert$IDIA$\rvert$ = 2).<br>IPAR = 0 for even parity and = 1 for odd.<br>IPAR = 2: do both even and odd in same calculation (IDIA = 2 only). |
| LOWEG2[LOWEIG] | Maximum dimension of smaller final Hamiltonian. Only used if ZROT = T and IDIA = $-2$. |
| LPOT | If ZLPOT = T, highest value of $\lambda$ in Legendre expansion of the potential must be consistent with subroutine POT.<br>If ZLPOT = F, ignored. |

Card 4: TITLE (9A8)
A 72 character title.

Card 5: FIXCOS (F20.0)
If ZTWOD = T, FIXCOS is the fixed value of cos $\theta$ for the run.
If ZTWOD = F, this card is read but ignored.

Card 6: (XMASS(I), I = 1, 3) (3F20.0)
XMASS(I) contains the mass of atom I in atomic mass units.
If NCOORD = 1, XMASS(3) is set to zero, the diatom comprising atoms 1 and 2.

Card 7: EMAX (F20.0)
If ZCUT = T, EMAX is the cut-off energy in $cm^{-1}$ with the same energy zero as the potential.
If ZCUT = F, this card is read but ignored.

Card 8: RE1, DISS1, WE1 (3F20.0)
If NCOORD = 1, this card is read but ignored.
If NCOORD = 2, RE1 is the fixed diatomic bondlength, DISS1 and WE1 ignored.
If NCOORD = 3, RE1 = $r_e$, DISS1 = $D_e$ and WE1 = $\omega_e$ are Morse parameters for the $r_1$ coordinate in a.u.

Card 9: RE2, DISS2, WE2 (3F20.0)
If IDIA = $-2$, this card is read but ignored.
If ZMORSE = T, RE2 = $r_e$, DISS2 = $D_e$ and WE2 = $\omega_e$ are Morse parameters for the $r_2$ coordinate.
If ZMORSE = F, RE2 is ignored; DISS2 = $\alpha$ and WE2 = $\omega_e$ are spherical oscillator parameters for the $r_2$ coordinate in a.u.

### *4.3. Card input for ROTLEV2*

Most of the data for ROTLEV2, which must have been prepared previously by DVR1D, is read from streams IVEC (and IVEC2). Note that when $J > 1$ a copy of steam IVEC *must* be supplied on IVEC2. Three lines of data are read from cards.

Card 1: NAMELIST/PRT/

TOLER[0.0d0] tolerance for convergence of the eigenvalues, zero gives machine accuracy. 1.0D-4 is usually sufficient for most applications.

ZPVEC[F] = T, requests printing of the eigenvectors.

THRESH[0.1d0] threshold for printing eigenvector coefficients, zero requests the full vector (only used if ZPVEC = T).

ZPHAM[F] = T, requests printing of the Hamiltonian matrix.

ZPRAD[F] = T, requests printing of the radial matrix elements.

IVEC[4] stream for input data from TRIATOM.

IVEC2[7] second stream for input data from TRIATOM. Note that the files on units IVEC and IVEC2 should be identical.

ZVEC[F] = T, eigenvalue and eigenvector data to be written to disk fle. ( = T, forced if ZTRAN = T).

JVEC[3] stream for first set of eigenvalue and eigenvector output.

JVEC2[2] stream for second set of eigenvalue and eigenvector output. (KMIN = 2 only.)

ISCR[1] stream for scratch file storing array OFFDG.

IRES[0] restart flag:
= 1, full restart.
= 2, restart second diagonalisation only (for KMIN = 2 only).
= − 1, perform vector transformation only (stream JVEC must be supplied).

ZPFUN[F] = T, eigenvalues concatenated on stream ILEV. The first eigenvalues on this file must (with $J = 0$, $q = 0$) be already present.

ILEV[14] stream for eigenvalue data.

Card 2: NVIB, NEVAL, KMIN, IBASS, NEVAL2, NPNT (6I5)

NVIB number of vibrational levels from DVR1D for each $k$ to be read, and perhaps selected from, in the second variational step.

NEVAL[10] the number of eigenvalues required for the first set.

KMIN[0] = 0, f or p = 1 parity calculation.
= 1, e or p = 0 parity calculation.
= 2, do both e and f parity calculation.

IBASS[0] = 0 or > NVIB*(JROT + KMIN), use all the vibrational levels. Otherwise, select IBASS levels with the lowest energy.

NEVAL2[NEVAL] the number of eigenvalues required for the second set.

NPNT[NDVR from DVR1D] number of Gauss associated Legendre quadrature points used for integral evaluation.

Card 3: TITLE (9A8)

A 72 character title.

### 4.4. Test output

Two test decks have been prepared. Both use Radau coordinates and the $H_2S$ potential of Senekowitch et al. [31]. The first run use DVR1D to drive programs ROTLEVD, DIPOLE and SPECTRA [16]. Because of constraints on ROTLEVD, this run does not use the permutation symmetry of the $H_2S$ molecule.

The second test run, which is for even ($q = 0$) symmetry, uses DVR1D to drive ROTLEV2. Both these runs mimic benchmark calculations on $H_2S$ transisitions performed by Carter et al. [32], although the size of the calculations have been reduced in the test data.

The LiCN (CN frozen) scattering coordinate surface of Essers et al. [33] is supplied in subroutine POT.

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# TEST RUN OUTPUT

```
     Program DVR1D (version of 16 Sept 1992)
     TITLE: H2S: J=0 even USING Radau COORDINATES


     FULL TRIATOMIC VIBRATIONAL PROBLEM WITH

        13   POINT NUMERICAL INTEGRATION FOR
         6   TH ORDER R1 RADIAL BASIS FUNCTIONS
        13   POINT NUMERICAL INTEGRATION FOR
         6   TH ORDER R2 RADIAL BASIS FUNCTIONS
        24   ANGULAR DVR POINTS USED, WITH
         5   LOWEST EIGENVECTORS CHOSEN FROM
UP TO  250   DIMENSION SECULAR PROBLEM

      250 EIGENVALUES SELECTED FROM     0.1234570024D-01 TO    0.1124049746D+00

LOWEST   5 EIGENVALUES IN WAVENUMBERS:

 0.329745806375D+04      0.448789879046D+04      0.566945382446D+04      0.591781365253D+04      0.684111928092D+04

     TITLE: H2S: J=1 even USING Radau COORDINATES

     Solutions with J =  1 k =  0

LOWEST 120 EIGENVALUES IN WAVENUMBERS:

 0.331115919072D+04      0.450177106869D+04      0.568351148338D+04      0.593132004304D+04      0.685537809984D+04

 0.710569781554D+04      0.801405916722D+04      0.827137720318D+04      0.846500257757D+04      0.856201591064D+04

     Solutions with J =  1 k =  1


LOWEST 120 EIGENVALUES IN WAVENUMBERS:

 0.594324176751D+04      0.711240611196D+04      0.827295003840D+04      0.846749436469D+04      0.942334477532D+04

 0.962010856633D+04      0.105644696838D+05      0.107642702850D+05      0.109012129129D+05      0.111010399294D+05

     PROGRAM ROTLEV2 (VERSION OF 15 Sept 1992):


     ROTATIONAL PART OF ROT-VIB CALCULATION  WITH:
      120   LOWEST VIBRATIONAL EIGENVECTORS SUPPLIED FROM
      672   DIMENSION VIBRATION SECULAR PROBLEM WITH
       24   ANGULAR DVR POINTS.
      120   LOWEST VIBRATIONAL EIGENVECTORS ACTUALLY USED
       24   POINT GAUSS-ASSOCIATED LEGENDRE INTEGRATION
       10   LOWEST ROTATIONAL EIGENVECTORS REQUIRED FOR
      200   DIMENSION ROTATION SECULAR PROBLEM
            WITH BASIS SELECTED BY ENERGY ORDERING

     TITLE:  H2S J=1 even, Radau CO-ORDINATES

      200 FUNCTIONS SELECTED FROM E =    0.1508675185D-01 TO    0.9494182951D-01

     J =  1 ROTATIONAL STATE,    200 BASIS FUNCTIONS
            E PARITY, SYMMETRIC |JK> + |J-K> FUNCTIONS IN BASIS
            EVEN PARITY RADIAL FUNCTIONS IN BASIS SET


LOWEST  10 EIGENVALUES IN WAVENUMBERS

 0.331114866624D+04      0.450172341048D+04      0.568342641401D+04      0.593130785002D+04      0.594324844233D+04

 0.685525557284D+04      0.710564462715D+04      0.711238035892D+04      0.801389871357D+04      0.827125402553D+04
```