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DVR3D: for the fully pointwise calculation of ro-vibrational spectra of triatomic molecules

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Abstract

The DVR3D program suite calculates energy levels, wavefunctions, and where appropriate dipole transition moments, for rotating and vibrating triatomic molecules. Potential energy, and where necessary, dipole surfaces must be provided. The programs use an exact (within the Born–Oppenheimer approximation) Hamiltonian, offer a choice of Jacobi or Radau internal coordinates and several body-fixed axes. Rotationally excited states are treated using an efficient two-step algorithm. The programs use a Discrete Variable Representation (DVR) based on Gauss–Legendre and Gauss–Laguerre quadrature for all 3 internal coordinates and thus yields a fully pointwise representation of the wavefunctions. The vibrational step uses successive diagonalisation and truncation which is implemented for 4 of the 6 possible coordinate orderings. The rotational and transition dipole programs exploit the major savings offered by performing integrals on a DVR grid.

PROGRAM SUMMARY

Title of program: DVR3DRJ

Catalogue number: ADAK

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

Licensing provisions: none

Computer: Convex C3800 running BSD unix; *Installation:* University of London Computer Centre

Other machines on which program has been tested: Cray-YMP81, IBM RS6000

Programming language used: FORTRAN 77

Memory required to execute with typical data: case dependent

No. of lines in distributed program, including test data, etc.: 4740

Keywords: vibrations, body-fixed, discrete variable representation, Coriolis decoupled, finite elements, Gaussian quadrature, vectorised

Nature of physical problem

DVR3DRJ calculates the bound vibrational or Coriolis decoupled ro-vibrational states of a triatomic system in body-fixed Jacobi (scattering) or Radau coordinates [1,2].

Method of solution

All coordinates are treated in a discrete variable representation (DVR). The angular coordinate uses a DVR based on (associated) Legendre polynomials and the radial coordinates utilise a DVR based on either Morse oscillator-like or spherical oscillator functions. Intermediate diagonalisation and truncation is performed on the hierarchical expression of the Hamiltonian operator to yield the final secular problem. DVR3DRJ provides the vibrational wavefunctions necessary for DIPJ0DVR [3] to calculate vibrational band intensities, ROTLEV3 [4] or ROLEV3B [5] to

calculate rotationally excited states, and DIPOLE3 [6] to calculate ro-vibrational transition strengths

Restrictions on the complexity of the problem

(1) The size of the final Hamiltonian matrix that can practically be diagonalised. DVR3DRJ allocates arrays dynamically at execution time and in the present version the total space available is a single parameter which can be reset as required. (2) The order of integration in the radial coordinates that can be dealt within the machine exponent range. Some adjustment in the code may be necessary when large order Gauss–Laguerre quadrature is used.

Typical running time

Case dependent but usually dominated by the final (3D) matrix diagonalisation. A $J = 0$ calculation on the Convex C3800 takes 95 s for test run 1 and 48 s for test run 2. These test runs use 25 MB and 20 MB scratch disk space, respectively.

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.R. Henderson, J. Tennyson and B.T. Sutcliffe, *J. Chem. Phys.* 98 (1993) 7191.
- [2] N.G. Fulton, Ph.D. Thesis, University of London (1994).
- [3] J.R. Henderson, C.R. Le Sueur and J. Tennyson, *Comput. Phys. Commun.* 75 (1993) 379.
- [4] J. Tennyson, J.R. Henderson and N.G. Fulton, second program, this article (ROTLEV3).
- [5] J. Tennyson, J.R. Henderson and N.G. Fulton, third program, this article (ROTLEV3B).
- [6] J. Tennyson, J.R. Henderson and N.G. Fulton, fourth program, this article (DIPOLE3).

PROGRAM SUMMARY

Title of program: ROTLEV3

Catalogue number: ADAL

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

Licensing provisions: none

Computer: Convex C3800 running BSD unix; *Installation:* University of London Computer Centre

Other machines on which program has been tested: Cray-YMP81, IBM RS6000

Programming language used: FORTRAN 77

Memory required to execute with typical data: case dependent

No. of lines in distributed program, including test data, etc.: 4562

Keywords: rotationally excited state, Coriolis coupling, secondary variational method, sparse matrix, vectorised

Nature of physical problem

ROTLEV3 performs the second step in a two-step variational calculation for the bound ro-vibrational levels of a triatomic system represented in either Jacobi or unsymmetrised Radau coordinates [1].

Method of solution

A basis is constructed from the solutions of the Coriolis decoupled problem provided by DVR3DRJ [2]. The angular coordinate is transformed back to a basis set representation [3]. The sparse Hamiltonian matrix can be diagonalised iteratively or in core.

Restrictions on the complexity of the problem

The size of matrix that can practically be diagonalised. ROTLEV3 dimensions arrays dynamically at execution time and in the present version the total space available is a single parameter which can be reset as required.

Typical running time

Case dependent. The sample data takes 44 s for a $J = 1$ calculation on the Convex C3800.

Unusual features of the program

Most data is read directly from DVR3DRJ [2]. ROTLEV3 can provide data to drive DIPOLE3 [4].

References

- [1] J. Tennyson and B.T. Sutcliffe, *Mol. Phys.* 58 (1986) 1067.
- [2] J. Tennyson, J.R. Henderson and N.G. Fulton, first program, this article (DVR3DRJ).
- [3] J. Tennyson, *J. Chem. Phys.* 98 (1993) 9658.
- [4] J. Tennyson, J.R. Henderson and N.G. Fulton, fourth program, this article (DIPOLE3).

PROGRAM SUMMARY

Title of program: ROTLEV3B

Catalogue number: ADAM

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

Licensing provisions: none

Computer: Convex C3800 running BSD unix; *Installation:* University of London Computer Centre

Other machines on which program has been tested: Cray-YMP81, IBM RS6000

Programming language used: FORTRAN 77

Memory required to execute with typical data: case dependent

No. of lines in distributed program, including test data, etc.: 5352

Keywords: rotationally excited state, Coriolis coupling, secondary variational method, sparse matrix, vectorised, bisector embedding

Nature of physical problem

ROTLEV3B performs the second step in a two-step variational calculation [1] for the bound ro-vibrational levels of a triatomic system represented symmetrised Radau coordinates using a bisector embedding [2].

Method of solution

A basis is constructed from the solutions of the Coriolis decoupled problem provided by DVR3DRJ [3]. The problem is constructed entirely within the DVR [4]. The Hamiltonian matrix can be diagonalised iteratively or in core.

Restrictions on the complexity of the problem

The size of matrix that can practically be diagonalised. ROTLEV-3B dimensions arrays dynamically at execution time and in the present version the total space available is a single parameter which can be reset as required.

Typical running time

Case dependent. The sample data takes 391 s for a $J = 1$ calculation on the Convex C3800.

Unusual features of the program

Most data is read directly from DVR3DRJ [2]. ROTLEV3B can provide data to drive DIPOLE3 [5].

References

- [1] J. Tennyson and B.T. Sutcliffe, Mol. Phys. 58 (1986) 1067.
- [2] J. Tennyson and B.T. Sutcliffe, Int. J. Quantum Chem. 42 (1992) 941.
- [3] J. Tennyson, J.R. Henderson and N.G. Fulton, first program, this article (DVR3DRJ).
- [4] O.L. Polyansky, P. Jensen and J. Tennyson, J. Chem. Phys. (submitted).
- [5] J. Tennyson, J.R. Henderson and N.G. Fulton, fourth program, this article (DIPOLE3).

PROGRAM SUMMARY

Title of program: DIPOLE3

Catalogue number: ADAN

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

Licensing provisions: none

Computer: Convex C3800 running BSD unix; *Installation:* University of London Computer Centre

Other machines on which program has been tested: Cray-YMP81, IBM RS6000

Programming language used: FORTRAN 77

Memory required to execute with typical data: case dependent

No. of lines in distributed program, including test data, etc.: 2167

Keywords: transition intensities, linestrengths, vectorised

Nature of physical problem

DIPOLE3 calculates dipole transition intensities between previously calculated wavefunction for both rotational and ro-vibrational transitions [1].

Method of solution

Integrals over dipole surfaces are constructed in the DVR for the radial coordinates and by Gauss-(associated) Legendre quadrature for the angular coordinate [2]. The wavefunctions generated by DVR3DRJ [3] and ROTLEV3 [4] or ROTLEV3B [5] are then used to give transition intensities for individual pairs of states.

Restrictions on the complexity of the problem

The complexity of problem that can be solved by DVR3DRJ, ROTLEV3 or ROTLEV3B.

Typical running time

Case dependent but usually less than DVR3DRJ. The test runs take 26 s (run 1) and 13 s (run 2) on the Convex C3800.

Unusual features of the program

Most data is read directly from DVR3DRJ [3] and ROTLEV3 [4] or ROTLEV3B [5]. DIPOLE provides data to drive SPECTRA [6].

References

- [1] S. Miller, J. Tennyson and B.T. Sutcliffe, Mol. Phys. 66 (1989) 429.
- [2] A.E. Lynas-Gray, S. Miller and J. Tennyson, J. Mol. Spectrosc. (submitted).
- [3] J. Tennyson, J.R. Henderson and N.G. Fulton, first program, this article (DVR3DRJ).
- [4] J. Tennyson, J.R. Henderson and N.G. Fulton, second program, this article (ROTELEV3).
- [5] J. Tennyson, J.R. Henderson and N.G. Fulton, third program, this article (ROTELEV3B).
- [6] J. Tennyson, S. Miller and C.R. Le Sueur, Comput. Phys. Commun. 75 (1993) 339.

LONG WRITE-UP

1. Introduction

The calculation of rotation-vibration spectra for triatomic species has become almost routine for molecules with a single low-lying potential energy surface. This has led to increasing activity looking at highly excited states of such molecules and using the observed spectroscopic data to determine highly accurate potential energy surfaces by successive refinement of the surface [1].

Over the last decade or so a number of methods have been developed which will compute molecular spectra using Hamiltonians which are exact within the Born–Oppenheimer approximation and basis function expansions to represent the nuclear wavefunctions [2–4]. These variational procedures have proved very successful, particularly for problems where highly excited states are not required.

An alternative procedure, based on finite element representations of the nuclear wavefunctions, has been developed by Light and co-workers [5–7]. This approach, generally known as the discrete variable representation or DVR, was based on earlier work by Harris et al. [8]. The DVR is not strictly variational, but has a number of advantages over the more traditional basis set methods in both the development of compact representations for multi-dimensional Hamiltonians and the simplicity of most of the matrix elements. This latter property has recently been exploited in a number of methods using iterative diagonalisation, see [9].

In our work we have increasingly shifted from basis set methods to the DVR. Our most recent and largest fit of a potential to experimental data [10] and our largest transition linelist [11,12] have used DVR based programs simply because they were computationally more efficient than the equivalent basis set algorithms.

In 1993 Tennyson and co-workers published 3 program suites for calculating triatomic ro-vibrational spectra in this journal. TRIATOM [13] was a complete ro-vibrational spectra package which used basis functions. DVR1D [14] was a hybrid DVR-basis function procedure which was designed to link into the triatomic package. DVR3D [15] used a DVR in all three dimensions to solve vibrational problems and to obtain vibrational band intensities using the associated program DVRDIPJ0.

In this work we present a full, triatomic rotation-vibration spectroscopic package based on a three-dimensional DVR. To our knowledge this is the first such package to be made generally available. The package comprises the main driver program DVR3DRJ. This program is an extended version of the original DVR3D [15,16] which now also allows for symmetrized Radau coordinates [17] and provides the first step in Tennyson and Sutcliffe's [18] two-step procedure for rotationally excited states. ROTLEV3 performs the second step calculation for rotationally excited states using the DVR for the radial coordinates and transforming back to a basis set for the angle [19]. This program is appropriate for calculations in scattering (Jacobi) coordinate or Radau coordinates with no symmetry. ROTLEV3B performs the second step calculation for rotationally excited states using the DVR in all 3 coordinates and a bisector embedding of the body-fixed axes [10,20]. This program works in Radau coordinates and is needed for cases, like water, where the molecule has two like atoms. DIPOLE3 takes the wavefunctions generated by these programs and computes line strengths for rotation-vibration transitions [12]. It generates a transition list which program SPECTRA, published previously [13], can use to generate synthetic spectra. DVR3DRJ will also drive program DVRDIPJ0, published earlier [15], which calculates vibrational band intensities using the theory of Le Sueur et al. [22].

2. Method

2.1. The vibrational problem: DVR3DRJ

2.1.1. The 3D DVR Hamiltonian matrix and its solution

We use a multidimensional DVR in scattering (Jacobi) or Radau coordinates. In scattering coordinates r_1 represents the 'diatom' distance between atom 1 and atom 2, and r_2 the separation of the third atom from the

diatom centre of mass. The angle between \underline{r}_1 and \underline{r}_2 is θ . A formal definition of (r_1, r_2, θ) in Radau coordinates is given below.

Using a finite basis representation (FBR), the zero rotational angular momentum ($J = 0$) Hamiltonian matrix can be written [2]

$$\begin{aligned} \langle m, n, j | \hat{H}^{J=0} | m', n', j' \rangle = & \langle m | \hat{h}^{(1)} | m' \rangle \delta_{n,n'} \delta_{j,j'} + \langle n | \hat{h}^{(2)} | n' \rangle \delta_{m,m'} \delta_{j,j'} \\ & + (\langle m | \hat{g}^{(1)} | m' \rangle \delta_{n,n'} + \langle n | \hat{g}^{(2)} | n' \rangle \delta_{m,m'}) j(j+1) \delta_{j,j'} + \langle m, n, j | V(r_1, r_2, \theta) | m', n', j' \rangle. \end{aligned} \quad (1)$$

For $J > 0$, we define the projection of J along the body-fixed z axis as k . If z is parallel to \underline{r}_1 or \underline{r}_2 then assuming k is a good quantum number simply adds an extra term to (1):

$$\langle m, n, j, J, k | \hat{H}^{J,k} | m', n', j', J, k \rangle = \langle m, n, j | \hat{H}^{J=0} | m', n', j' \rangle + \langle t | \hat{g}^{(i)} | t' \rangle \delta_{j,j'} \delta_{s,s'} (J(J+1) - 2k^2). \quad (2)$$

In (2), if the body-fixed z -axis is taken along \underline{r}_1 then $|t\rangle = |m\rangle$, $s = n$ and $i = 1$; conversely if z is along \underline{r}_2 , $|t\rangle = |n\rangle$, $s = m$ and $i = 2$. If the body-fixed x -axis is taken along $\frac{\theta}{2}$ ('the bisector'), then [20]:

$$\begin{aligned} \langle m, n, j, J, k | \hat{H}^{J,k} | m', n', j', J, k \rangle = & \langle m, n, j | \hat{H}^{J=0} | m', n', j' \rangle + (\langle m | \hat{g}^{(1)} | m' \rangle + \langle n | \hat{g}^{(2)} | n' \rangle) \\ & \times \left(\frac{1}{4} \langle jk | \frac{1}{(1 - \cos \theta)} | j'k \rangle (J(J+1) - 3k^2) + \frac{1}{8} \delta_{j,j'} (J(J+1) - k^2) \right). \end{aligned} \quad (3)$$

In the bisector embedding, $k = 1$ is a special case and has an extra term on the diagonal:

$$\begin{aligned} \langle m, n, j, J, k | \hat{H}^{J,k} | m', n', j', J, k \rangle = & \langle m, n, j, J, k | \hat{H}^{J,k} | m', n', j', J, k \rangle \\ & + \frac{(-1)^{1-p}}{16} (\langle m | \hat{g}^{(1)} | m' \rangle + \langle n | \hat{g}^{(2)} | n' \rangle) \langle jk | \frac{(1 + \cos \theta)}{(1 - \cos \theta)} | j'k \rangle J(J+1), \end{aligned} \quad (4)$$

where p , the rotational parity, is defined below. It will be assumed that, unlike the first two embeddings, the bisector embedding will only be used for AB_2 molecules represented in Radau coordinates.

A DVR is a unitary transformation of an FBR defined for some quadrature scheme associated with the FBR polynomials. In this work the angular basis functions $|j\rangle$ are associated Legendre functions of degree k . The radial basis functions are either Morse oscillator-like functions or spherical oscillators. The Morse oscillator-like functions are defined as [23]:

$$|n\rangle = H_n(r) = \beta^{1/2} N_{n\alpha} \exp(\frac{1}{2}y) y^{(\alpha+1)/2} L_n^\alpha(y), \quad y = A \exp[-\beta(r - r_e)], \quad (5)$$

where

$$A = \frac{4D_e}{\beta}, \quad \beta = \omega_e \left(\frac{\mu}{2D_e} \right)^{1/2}, \quad \alpha = \text{integer}(A). \quad (6)$$

The parameters μ , r_e , ω_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, ω_e, D_e) are treated as variational parameters and optimised accordingly. $N_{n\alpha} L_n^\alpha$ is a normalised associated Laguerre polynomial [24].

The spherical oscillator functions are particularly useful for systems which have significant amplitude for $r_2 = 0$. These functions are defined by [25]:

$$|n\rangle = H_n(r) = 2^{1/2} \beta^{1/4} N_{n\alpha+1/2} \exp(-\frac{1}{2}y) y^{(\alpha+1)/2} L_n^{\alpha+1/2}(y), \quad y = \beta r^2, \quad (7)$$

where

$$\beta = (\mu \omega_e)^{1/2} \quad (8)$$

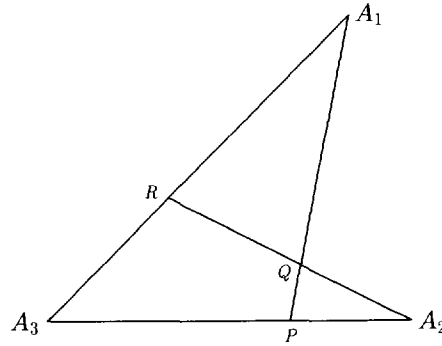


Fig. 1. Internal coordinate system of Sutcliffe and Tennyson [26]: A_i represents atom i . The coordinates are given by $r_1 = A_2 - R$, $r_2 = A_1 - P$ and $\theta = A_1 \hat{Q} A_2$. The geometric parameters are defined by $g_1 = (A_3 - P)/(A_3 - A_2)$ and $g_2 = (A_3 - R)/(A_3 - A_1)$.

and (α, ω_e) are treated as variational parameters.

It should be noted that our usual practice is to optimise the parameters for both Morse-like and spherical oscillator functions using an FBR isomorphic to the DVR in which the final calculation is to be performed. This is because optimisation is usually performed on cut-down problems for which a DVR can become unreliable because of the linkage between accuracy of integration and size of basis [1]. To this end optimisation is generally performed using the FBR³ code TRIATOM [13] or the two-dimensional (ZTWOD = T) option in the DVR¹ – FBR² code DVR1D [14].

In (1) V is the potential, and the radial kinetic energy integrals are given by

$$\langle t | \hat{h}^{(i)} | t' \rangle = \langle t | \frac{-\hbar^2}{2\mu_i r_i^2} \frac{\partial^2}{\partial r_i^2} | t' \rangle, \quad (9)$$

$$\langle t | \hat{g}^{(i)} | t' \rangle = \langle t | \frac{\hbar^2}{2\mu_i r_i^2} | t' \rangle, \quad (10)$$

where $|t\rangle = |m\rangle$ for $i = 1$ and $|t\rangle = |n\rangle$ for $i = 2$. μ_i are the appropriate reduced masses given by [26]:

$$\mu_1^{-1} = g_2^2 m_1^{-1} + m_2^{-1} + (1 - g_2)^2 m_3^{-1}, \quad \mu_2^{-1} = m_1^{-1} + g_1^2 m_2^{-1} + (1 - g_1)^2 m_3^{-1}. \quad (11)$$

where for scattering coordinates

$$g_1 = \frac{m_2}{m_2 + m_3}, \quad g_2 = 0 \quad (12)$$

and for Radau coordinates [26]:

$$g_1 = 1 - \frac{\alpha}{\alpha + \beta - \alpha\beta}, \quad g_2 = 1 - \frac{\alpha}{1 - \beta + \alpha\beta},$$

$$\alpha = \left(\frac{m_3}{m_1 + m_2 + m_3} \right)^{1/2}, \quad \beta = \frac{m_2}{m_1 + m_2}. \quad (13)$$

The relationship between the g 's and geometrically defined coordinates is given by Fig. 1.

A 1D DVR transformation for either of r_1 , r_2 or θ is defined in terms of points, η , and weights, w_η , of the N -point Gaussian quadrature associated with the orthogonal polynomials used for the FBR in that coordinate [5]:

$$T_t^\eta = (w_\eta)^{1/2} |t(\eta)\rangle, \quad (14)$$

where $|t \rangle = |m \rangle, |n \rangle, |j \rangle$ for $\eta = \alpha, \beta, \gamma$ respectively. DVR3DRJ automatically generates Gaussian quadrature schemes using routines adapted [23] from Stroud and Secrest [27].

The required composite transformation is written as a product of 1D transformations:

$$\underline{T} = T_{m,n,j}^{\alpha,\beta,\gamma} = T_m^\alpha T_n^\beta T_j^\gamma. \tag{15}$$

A three dimensional DVR is obtained by applying the transformation $\underline{T}^T \underline{H} \underline{T}$. The transformed Hamiltonian can be written at the DVR grid points as

$$\begin{aligned} {}^{(3D)}H_{\alpha,\alpha',\beta,\beta',\gamma,\gamma'} &= K_{\alpha,\alpha'}^{(1)} \delta_{\beta,\beta'} \delta_{\gamma,\gamma'} + K_{\beta,\beta'}^{(2)} \delta_{\alpha,\alpha'} \delta_{\gamma,\gamma'} + L_{\alpha,\alpha',\gamma,\gamma'}^{(1)} \delta_{\beta,\beta'} + L_{\beta,\beta',\gamma,\gamma'}^{(2)} \delta_{\alpha,\alpha'} \\ &+ (J(J+1) - k^2) M_{\alpha,\alpha',\beta,\beta'}^{(i)} \delta_{\gamma,\gamma'} + V(r_{1\alpha}, r_{2\beta}, \theta_\gamma) \delta_{\alpha,\alpha'} \delta_{\beta,\beta'} \delta_{\gamma,\gamma'}, \end{aligned} \tag{16}$$

where $i = 1$ for z embedded along r_1 and $i = 2$ for z along r_2 . In the bisector embedding the J -dependent term is replaced by:

$$\begin{aligned} &\frac{1}{8} \left(M_{\alpha,\alpha',\beta,\beta'}^{(1)} + M_{\alpha,\alpha',\beta,\beta'}^{(2)} \right) \delta_{\gamma,\gamma'} \\ &\times \left(\frac{1}{8} (J(J+1) - k^2) + \delta_{k,1} \frac{(-1)^{1-p}}{16} J(J+1) \frac{(1+\gamma)}{(1-\gamma)} \right). \end{aligned} \tag{17}$$

In (16), the potential energy operator is diagonal because of the quadrature approximation [5,28]

$$\sum_{m,n,j} \sum_{m',n',j'} T_{m,n,j}^{\alpha,\beta,\gamma} \langle m, n, j | V(r_1, r_2, \theta) | m', n', j' \rangle T_{m',n',j'}^{\alpha',\beta',\gamma'} \simeq V(r_{1\alpha}, r_{2\beta}, \theta_\gamma) \delta_{\alpha\alpha'} \delta_{\beta\beta'} \delta_{\gamma\gamma'}, \tag{18}$$

where $(r_{1\alpha}, r_{2\beta}, \theta_\gamma)$ is the value of (r_1, r_2, θ) at (α, β, γ) . A major attraction is that no integration at all is required over the potential; it is diagonal in every coordinate.

The kinetic energy terms in (15) are represented by

$$K_{\eta,\eta'}^{(i)} = \sum_{t,t'} T_t^\eta \langle t | \hat{h}^{(i)} | t' \rangle T_{t'}^{\eta'}, \tag{19}$$

$$L_{\eta,\eta',\gamma,\gamma'}^{(i)} = J_{\gamma\gamma'} \sum_{t,t'} T_t^\eta \langle t | \hat{g}^{(i)} | t' \rangle T_{t'}^{\eta'} \tag{20}$$

$$\simeq \frac{J_{\gamma\gamma'} \hbar^2}{2\mu_i r_{i\eta}^2} \delta_{\eta\eta'}, \tag{21}$$

again applying the quadrature approximation, and where

$$J_{\gamma\gamma'} = \sum_j T_j^\gamma j(j+1) T_j^{\gamma'}. \tag{22}$$

For $J > 0$, the extra term is given by

$$M_{\alpha,\alpha'}^{(1)} = \sum_{m,m'} T_m^\alpha \langle m | \hat{g}^{(1)} | m' \rangle T_{m'}^{\alpha'} \simeq \delta_{\alpha\alpha'} \frac{\hbar^2}{2\mu_1 r_{1\alpha}^2} \tag{23}$$

if $i = 1$, when it is diagonal in β , and

$$M_{\beta,\beta'}^{(2)} = \sum_{n,n'} T_n^\beta \langle n | \hat{g}^{(2)} | n' \rangle T_{n'}^{\beta'} \simeq \delta_{\beta\beta'} \frac{\hbar^2}{2\mu_2 r_{2\beta}^2} \tag{24}$$

if $i = 2$, when it is diagonal in α .

Similarly for the bisector embedding the extra angular integrals are evaluated using the quadrature approximation. It should be noted, however, that the operators which depend on $(1 - \cos \theta)^{-1}$ are singular for when $\theta = 0$. These ABB linear geometries correspond to very high energy for many AB_2 molecules, for instance water. The present code assumes that the wavefunction has zero amplitude in this region; this can actually be enforced for rotationally excited states by using the switch ZTEST in ROTLEV3B.

The calculation is generally set up as a series of diagonalisations and truncations [29,30]. Assume for the moment that the coordinate ordering θ then r_1 then r_2 is used, *ie* diagonalise on γ first and β last ($\theta \rightarrow r_1 \rightarrow r_2$). With this ordering, the 1D problems that have to be solved for each α and β are given by

$${}^{(1D)}H_{\gamma,\gamma'}^{\alpha,\beta} = L_{\alpha,\alpha,\gamma,\gamma'}^{(1)} + L_{\beta,\beta,\gamma,\gamma'}^{(2)} + V(r_{1\alpha}, r_{2\beta}, \theta_\gamma) \delta_{\gamma\gamma'}. \quad (25)$$

Amplitudes for the k^{th} level, with eigenenergy $\epsilon_k^{\alpha,\beta}$, are given at each grid point by $C_{\gamma,k}^{\alpha,\beta}$.

The solutions with $\epsilon_k^{\alpha,\beta} \leq E_{\text{max}}^{1D}$ are then selected and used to solve 2D problems for each value of β . This gives

$${}^{(2D)}H_{\alpha,\alpha',k,k'}^\beta = \epsilon_k^{\alpha,\beta} \delta_{\alpha\alpha'} \delta_{kk'} + \sum_{\gamma} C_{\gamma,k}^{\alpha,\beta} C_{\gamma,k'}^{\alpha',\beta} K_{\alpha\alpha'}^{(1)}. \quad (26)$$

Solutions for the l^{th} level, with eigenenergy ϵ_l^β are given by $C_{\alpha,l,k}^\beta$.

The solutions with $\epsilon_l^\beta \leq E_{\text{max}}^{2D}$ are then used to solve the full 3D problem of dimension N :

$${}^{(3D)}H_{\beta,\beta',l,l'} = \epsilon_l^\beta \delta_{\beta\beta'} \delta_{ll'} + \sum_{\alpha,k,k'} C_{\alpha,l,k}^\beta C_{\alpha,l',k'}^{\beta'} \sum_{\gamma} C_{\gamma,k}^{\alpha,\beta} C_{\gamma,k'}^{\alpha,\beta'} K_{\beta\beta'}^{(2)}. \quad (27)$$

Solutions of this diagonalisation are the required eigenenergies, ϵ_i , and wavefunction coefficients $C_{\beta,i,l}$.

2.1.2. Wavefunctions

Once the eigenvectors of the 3D Hamiltonian have been obtained one would usually like to use them to express a more physically meaningful quantity. This can be achieved by transforming them to yield values for the amplitude of the wavefunction at the DVR grid points. These wavefunctions can then, in principle, be put to many quantum mechanical and spectroscopic uses.

The wavefunction amplitude for the i th eigenstate at the DVR grid points is simply

$$\Psi_{\alpha\beta\gamma}^i = \sum_{lk} C_{\beta il} C_{\alpha lk}^\beta C_{\gamma k}^{\alpha\beta}. \quad (28)$$

Computationally this process is more efficiently written as

$$\Psi_{\alpha\beta\gamma}^i = \sum_l C_{\beta il} \sum_k C_{\alpha lk}^\beta C_{\gamma k}^{\alpha\beta}. \quad (29)$$

Reverse transformations to FBR are also fairly straightforward to write down. In particular ROTLEV3 and DIPOLE3 work with the angular functions represented as a basis set of associated Legendre polynomials. In these programs the wavefunction is written

$$\Psi_{\alpha\beta}^{Ji} = \sum_{jk} d_{j\alpha\beta}^{Jki} |j\rangle. \quad (30)$$

The new coefficients, $d_{j\alpha\beta}^{Jki}$, are obtained from the back transformation

$$d_{j\alpha\beta}^{Jki} = \sum_{\gamma} \Psi_{\alpha\beta\gamma}^i \omega_{\gamma}^{1/2} |j(\gamma)\rangle. \quad (31)$$

2.1.3. A problem with the quadrature approximation

The quadrature approximation can be used when evaluating the DVR transformation of FBR matrix elements of an operator that leaves the ket unchanged. Its validity is due to the unitarity of the DVR transformation matrix. We have experienced one particular failure of the quadrature approximation [16], which occurred when evaluating the r_2^{-2} integrals.

In scattering coordinates, it is possible for the r_2 coordinate to be equal, or very close, to zero if this linear geometry is energetically accessible or favourable. As stated earlier, it is desirable to use the spherical oscillator functions in this case. Under these circumstances it was found [16] that the quadrature approximation had to be abandoned for the r_2^{-2} integral because of its non-polynomial behaviour as $r_2 \rightarrow 0$.

After extensive tests on the H_3^+ molecular ion [16], we found a suitable alternative was to continue to use the quadrature approximation in constructing $^{(1D)}\underline{H}$, and then construct $^{(3D)}\underline{H}$ using the full-matrix transformation of the r_2^{-2} integrals, correcting for the fact that the quadrature approximation was used in $^{(1D)}\underline{H}$. So the only change in the formulation is that now

$$^{(3D)}\tilde{H}_{\beta,\beta',l,l'} = ^{(3D)}H_{\beta,\beta',l,l'} + \sum_{\alpha,k,k'} C_{\alpha,l,k}^\beta C_{\alpha,l',k'}^{\beta'} (\tilde{M}_{\beta,\beta'}^{(2)} - M_{\beta,\beta'}^{(2)}) \sum_{\gamma,\gamma'} C_{\gamma,k}^{\alpha,\beta} C_{\gamma',k'}^{\alpha,\beta'} J_{\gamma\gamma'}, \quad (32)$$

where

$$\tilde{M}_{\beta,\beta'}^{(2)} = \sum_{n,n'} T_n^\beta \langle n | \hat{g}^{(2)} | n' \rangle T_{n'}^{\beta'}, \quad (33)$$

and $M_{\beta,\beta'}^{(2)}$ is given by the approximation (24).

Note that the FBR matrix elements above can be evaluated analytically, and are given by [23]

$$\langle n | \hat{g}^{(2)} | n' \rangle = \frac{\hbar^2 \beta}{(2\alpha + 1) \mu_2} \left(\frac{n! \Gamma(n' + \alpha + \frac{3}{2})}{n'! \Gamma(n + \alpha + \frac{3}{2})} \right)^{1/2}, \quad n \geq n'. \quad (34)$$

We have implemented a user input variable (ZQUAD2) in the program DVR3DRJ so that either of Eqs. (27) or (32) can be used.

2.1.4. Order of solution

As stated the 3D DVR Hamiltonian matrix of Eq. (16) can be solved by successive diagonalisation and truncation. In Section 2.1.1 the angle θ was dealt with first, and r_2 last. It also is possible for the problem to be solved in any of the 5 other orders. The most efficient ordering is to treat the coordinate accommodating the highest density of states last and the coordinate holding the lowest density of states coming first, although this was found to be less important in practice [9,30].

Four of the possible coordinate orders have been implemented in DVR3DRJ. The two orders where θ is considered second have been omitted; it is unlikely that such orders will offer significant savings over the case in which the order of θ and the first coordinate are swapped.

In symmetrized Radau coordinates, see below, the coordinates r_1 and r_2 are mixed and it no longer makes sense to diagonalise and truncate in these coordinates separately. Furthermore, in all the problems we have tackled with Radau coordinates, diagonalisation of θ last has been the method of choice. For this reason we have only implemented this option in DVR3DRJ for symmetrised Radau coordinates.

2.1.5. Symmetry

Scattering coordinates can exploit permutation symmetry of an AB_2 system. In a DVR-in- θ only approach this has been shown [31] to involve only a property of the so-called \underline{L} matrix. In our multidimensional DVR we have exactly the same matrix in the \underline{J} matrix of Eq. (20). Then the symmetrised \underline{J} matrix becomes

$$J_{\gamma\gamma'q} = 2 \sum_{j=0}^{N/2-1} T_{2j+q}^{\gamma'} (2j+q)(2j+q+1) T_{2j+q}^{\gamma}, \quad q = 0, 1. \quad (35)$$

It should be noted that for problems including rotational excitation, this symmetry is preserved with the body-fixed z -axis placed either along either r_2 (ZEMBED=TRUE. in the code) or r_1 (ZEMBED=FALSE.).

In Radau coordinates, the permutation symmetry of an A_2B molecule is carried by the radial coordinates. This is more complicated to treat in a DVR since it involves coupling two coordinates. In contrast to other workers [9,32], we have symmetrized our DVR by taking suitable combinations of points in r_1 and r_2 . Thus our new functions become:

$$|\alpha, \beta, q \rangle = [2(1 + \delta_{\alpha,\beta})]^{-1/2} (|\alpha, \beta \rangle + (-1)^q |\beta, \alpha \rangle), \quad \alpha \geq \beta + q, \quad q = 0, 1. \quad (36)$$

2.2. Rotation motion with standard embeddings: ROTLEV3

The rotational problem can be fully expanded in terms of a finite set of functions, generally called rotation matrices [33]. These functions are symmetrized to reflect the rotational parity of the system, given by $(-1)^{J+p}$ with $p = 0, 1$; these functions will be denoted $|J, k, p \rangle$ below. To deal satisfactorily with the transition from linear to non-linear geometries it is usual to couple these rotation matrices with the k -dependent angular functions denoted $|j \rangle$ above [26]. The FBR Hamiltonian matrix for the fully coupled vibration-rotation problem can be expressed as

$$\begin{aligned} \langle m, n, j, J, k, p | \hat{H} | m', n', j', J, k', p \rangle &= \delta_{k,k'} \langle m, n, j | \hat{H}^{J,k} | m', n', j' \rangle \\ &- (1 + \delta_{k,0} + \delta_{k',0})^{-1/2} \delta_{k',k\pm 1} \langle t | \hat{g}^{(i)} | t' \rangle \delta_{j,j'} \delta_{s,s'} C_{J,k'}^{\pm} C_{j,k'}^{\pm}, \\ k &= p, p+1, \dots, J, \quad p = 0, 1, \end{aligned} \quad (37)$$

where if the body-fixed z -axis is taken parallel to r_1 then $|t \rangle = |m \rangle$, $s = n$ and $i = 1$; and if z is along r_2 , $|t \rangle = |n \rangle$, $s = m$ and $i = 2$. The angular factors are given by

$$C_{\ell,k}^{\pm} = (\ell(\ell+1) - k(k\pm 1))^{1/2}. \quad (38)$$

Using the solutions of the first step as a basis to expand the full problem means that the first term in (37) is simply $\epsilon_h^{J,k}$ and the problem of constructing the Hamiltonian matrix reduces to the one of constructing the second term.

The quadrature approximation means that the matrix element $\langle t | \hat{g}^{(i)} | t' \rangle$ is diagonal in the DVR. Conversely the angular contribution is diagonal in the FBR. ROTLEV3 therefore transforms the DVR wavefunctions generated by DVR3DRJ to an FBR in θ by

$$\psi_{\alpha,\beta,j}^{J,k,h} = \sum_{\gamma} T_j^{\gamma} \psi_{\alpha,\beta,\gamma}^{J,k,h}. \quad (39)$$

This means that only transformations of diagonal matrix element are required, see (40) below. It should be noted that the above transformation, unlike that of the matrix elements, is one-dimensional and therefore rapid.

In this new DVR²-FBR¹ representation, the Hamiltonian matrix in terms of solutions of the first step is

$$\begin{aligned} \langle h, k, p | \hat{H} | h', k', p \rangle &= \delta_{h,h'} \delta_{k,k'} \epsilon_h^{J,k} \\ &- (1 + \delta_{k,0} + \delta_{k',0})^{-1/2} \delta_{k',k\pm 1} \sum_{\alpha,\beta,j} \psi_{\alpha,\beta,j}^{J,k,h} \psi_{\alpha,\beta,j}^{J,k',h'} C_{J,k'}^{\pm} C_{j,k'}^{\pm}, M_{\alpha,\alpha,\beta,\beta}^{(i)}, \\ k &= p, p+1, \dots, J, \quad p = 0, 1. \end{aligned} \quad (40)$$

For a given J , DVR3DRJ solves the $J + 1$ unique Coriolis decoupled “vibrational” problems. ROTLEV3 selects the IBASS lowest energy solutions of these calculations [34] as a basis for the full problem. The angular coordinate of these solutions is transformed back to an FBR and the Hamiltonian constructed. Because of its sparse nature, only the diagonal elements and $(k, k + 1)$ off-diagonal blocks are computed and stored. Usually the matrix is diagonalised iteratively, a procedure which has proved very successful for programs ROTLEVD [13] and ROTLEV2 [14]. An option to diagonalise in core has also been provided as this has proved more efficient for case where very many levels are required [36]. As has been previously noted [35], the $p = 1$ matrix is simply a submatrix of the $p = 0$ problem with the $k = 0$ rows and columns deleted. This matrix thus need not be recalculated (option KMIN=2).

2.3. Rotation motion with a bisector embedding: ROTLEV3B

Unlike ROTLEV3, ROTLEV3B works uses a DVR for all three coordinates. In this representation, the Hamiltonian matrix in terms of solutions of the first step is

$$\begin{aligned} < h, k, p, q | \hat{H} | h', k', p, q' > = \delta_{h,h'} \delta_{k,k'} \epsilon_h^{J,k} \\ & - (1 + \delta_{k,0} + \delta_{k',0})^{-1/2} \delta_{k',k \pm 1} \delta_{q',1-q} C_{J,k}^{\pm} \sum_{\alpha,\beta,\gamma,\gamma'} \psi_{\alpha,\beta,\gamma}^{J,k,h} \psi_{\alpha,\beta,\gamma'}^{J,k',h'} \left(M_{\alpha,\alpha,\beta,\beta}^{(1)} - M_{\alpha,\alpha,\beta,\beta}^{(2)} \right) J_{k \pm 1,k,\gamma,\gamma'}^{(1)} \\ & - (1 + \delta_{k,0} + \delta_{k',0})^{-1/2} \delta_{k',k \pm 2} \delta_{q',q} C_{J,k \pm 1}^{\pm} C_{J,k}^{\pm} \\ & \times \sum_{\alpha,\beta,\gamma} \psi_{\alpha,\beta,\gamma}^{J,k,h} \psi_{\alpha,\beta,\gamma}^{J,k',h'} \left(\frac{1 + \gamma}{1 - \gamma} \right) \left(M_{\alpha,\alpha,\beta,\beta}^{(1)} + M_{\alpha,\alpha,\beta,\beta}^{(2)} \right) J_{k \pm 2,k,\gamma,\gamma'}^{(2)}, \\ & k = p, p + 1, \dots, J, \quad p = 0, 1. \end{aligned} \tag{41}$$

In (41), the angular integrals are obtained by quadrature in terms of basis functions and then transformed:

$$J_{k',k,\gamma,\gamma'}^{(1)} = \sum_{j,j'} T_j^{\gamma(k)} \left(\delta_{j,j'} + \left(\frac{k + k'}{2} \right) < j, k | \frac{(1 + \cos \theta)}{\sin \theta} | j', k' > \right) T_{j'}^{\gamma'(k')}, \tag{42}$$

$$J_{k',k,\gamma,\gamma'}^{(2)} = \sum_{j,j'} T_j^{\gamma(k)} \left(\delta_{j,j'} + < j, k | \frac{(1 + \cos \theta)}{(1 - \cos \theta)} | j', k' > \right) T_{j'}^{\gamma'(k')}, \tag{43}$$

where the notation $\gamma(k)$ has been used to emphasis that the DVR points for the bra and ket are based on the Gaussian quadrature points of associated Legendre functions of different degrees.

2.4. Dipole transition moments: DIPOLE3

Lynas-Gray et al. [12] adapted Miller et al. ’s [37] formalism for calculating dipole transition strengths between ro-vibrational levels which use only rigorous selection rules. In the radial DVR, angular FBR scheme referred to as DVR²FBR¹ above, the formula for the transition linestrengths, $S(f - i)$, is

$$\begin{aligned} S(f - i) &= \frac{1}{4} [(2J' + 1)(2J'' + 1)] \\ & \times \left[\sum_{\nu=-1}^{+1} \sum_{\lambda=|\nu|}^{J''} \sum_{k=p''}^{J''} \sum_{j''j'} a(\nu, \nu + k, \lambda) [(2j' + 1)(2j'' + 1)]^{1/2} \right. \\ & \left. \times \begin{pmatrix} J' & 1 & J'' \\ -k - \nu & \nu & k \end{pmatrix} \begin{pmatrix} j' & \lambda & j'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j' & \lambda & j'' \\ -k - \nu & \nu & k \end{pmatrix} \right] \end{aligned}$$

$$\times \sum_{\alpha\beta} d_{j'\alpha\beta}^{j'k'i'} d_{j''\alpha\beta}^{j''k''i''} C_{\lambda,\nu}(\alpha, \beta) [(-1)^{J''+J'+1} + (-1)^{p''+p'}] \Bigg]^2, \quad (44)$$

where

$$\begin{aligned} a(0, n, \lambda) &= 1, \quad 0 \leq n \leq J', & a(\pm 1, 0, \lambda) &= -[\lambda(\lambda + 1)]^{1/2}, \\ a(\pm 1, n, \lambda) &= -[\lambda(\lambda + 1)/2]^{1/2}, \quad 0 < n \leq J', \\ a(\nu, n, \lambda) &= 0, \quad n < 0, n > J', \quad \nu = 0, \pm 1. \end{aligned}$$

For a triatomic lying in the $x-z$ plane, the dipole surface can be expressed in a generalisation of the Legendre expansion used to express the potential

$$\mu_z(r_1, r_2, \theta) = \sum_{\lambda} C_{\lambda,0}(r_1, r_2) P_{\lambda,0}(\theta), \quad (45)$$

$$\mu_x(r_1, r_2, \theta) = \sum_{\lambda} C_{\lambda,1}(r_1, r_2) P_{\lambda,1}(\theta). \quad (46)$$

Such an expansion can be obtained from any dipole surface using Gauss–Legendre quadrature, providing care is taken with the $\sin \theta$ factors [37].

3. Program structure

Card input is needed for all modules. The modules 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 data flow through the modules is given in Fig. 2. The role of the individual subroutines is described in comment cards included in the source programs. All modules use 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 version supplied) in subroutine GTMAIN. For efficient storage management a call to a local GETMAIN, MEMORY or HPALLOC command should be implemented. Similarly a routine TIMER is provided which will return timings for program sections if a call to a machine dependent timer such as ETIME or SECOND is implemented, otherwise zero time use is recorded.

Certain disk files (ILEV in DVR3DRJ, ROTLEV3 and ROTLEV3B, ITRA in DIPOLE3) may be read to the end and then written to. Unfortunately whether it is necessary to BACKSPACE the file between the reads and the writes depends on the machine being used. The present implementation **does** BACKSPACE and it may be necessary to remove these statements, on certain machines such as VAXes. The occurrences are all clearly labelled in the sources of the programs.

3.1. DVR3DRJ

For large runs, the CPU time requirement of DVR3DRJ is usually dominated by the diagonalisation of the final 3D Hamiltonian matrix HAM3. The required diagonaliser has to compute all eigenvalues and eigenvectors of a real symmetric matrix. The present implementation uses subroutine EGVQR [38] to mimic NAG routine F02ABF [39]. All of the intermediate diagonalisations of the various HAM1 and HAM2 matrices also use this routine. 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.

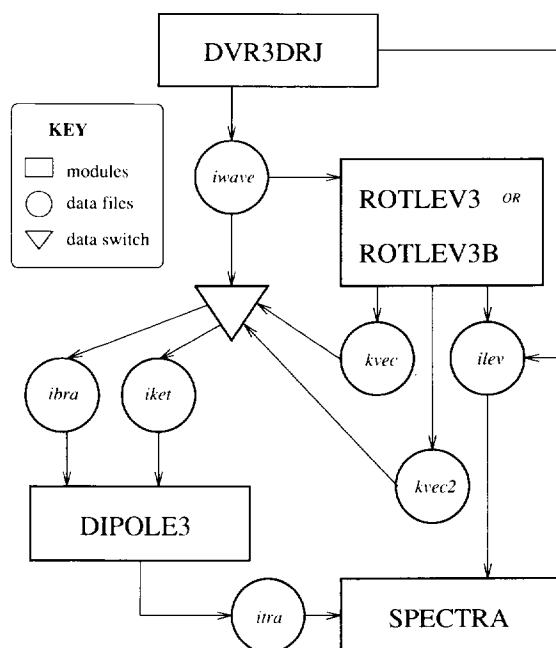


Fig. 2. Structure and data flow for the DVR3D program suite. Program SPECTRA is contained in Ref. [13]. Scratch disk files used by individual modules are not shown.

3.2. ROTLEV3 and ROTLEV3B

These routines have rather different performance characteristics with ROTLEV3B being considerably more time consuming [10,19,40]. However the execution time for both programs is dominated by two processes, transformation and diagonalisation [41]. In transforming the matrix elements subroutine MXMB, a fast vector-matrix multiplier, uses the bulk of the CPU time. Iterative diagonalisation is performed using NAG Library routine FOJFJF [39] and associated subroutines. (The implementation given here is appropriate for IBM mainframes and it is recommended that users replace this by a local implementation where possible.) This diagonaliser uses the algorithm of Nikolai [42] and again timing is dominated by the vector matrix multiplies performed by MXMB. Greatly enhanced performance for both modules can be obtained by optimizing MXMB for the architecture of the user's computer. In core diagonalisation option is provided by EGVQR mimicing NAG routine F02ABF as discussed for DVR3DRJ.

When using ROTLEV3B for rotational states with $J > 1$, it is *essential* that the vibrational wavefunctions output file IWAVE is input on *both* streams IVEC and IVEC2, which *must* correspond to separate files. This duplication is required to prevent excessive repositioning of the input file.

3.3. DIPOLE3

DIPOLE3 also uses the fast matrix multiply routine MXMB to perform transformations. It can therefore be replaced at the same time as that for ROTLEV3 or ROTLEV3B. However the nature of the DVR is such that we anticipate that DIPOLE3 should not be a major consumer of CPU time compared to the earlier modules.

4. Program use

4.1. The potential and dipole subroutines

DVR3DRJ requires a user supplied potential energy subroutine. There are two ways of supplying the potential. If it is specified as a Legendre expansion,

$$V(r_1, r_2, \theta) = \sum_{\lambda} V_{\lambda}(r_1, r_2) P_{\lambda}(\theta) \quad (47)$$

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

SUBROUTINE POT(V0,VL,R1,R2)

which returns V0 = $V_0(r_1, r_2)$ and VL(λ) = $V_{\lambda}(r_1, r_2)$ in Hartree for R1 = r_1 and R2 = r_2 in Bohr. If NCOORD=2, R1 contains the rigid diatom bondlength r_e . 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 = $\cos \theta$.

DVR3DRJ includes COMMON /MASS/ XMASS(3),G1,G2 where XMASS contains the atomic masses in atomic mass units, 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.

DIPOLE requires a subroutine defining the dipole surfaces. If ZLPOT = .TRUE. and the surfaces are supplied as a Legendre expansion, Eqs. (20) and (21), then

SUBROUTINE DIPL(D0,DL,R1,R2,NU)

must be supplied, where for R1 = r_1 , R2 = r_2 (in Bohr) and NU = $\nu = 0$ or 1, the routine returns D0 = $C_{0,\nu}(r_1, r_2)$ and DL = $C_{\lambda,\nu}(r_1, r_2)$ in atomic units. If $\nu = 1$, D0 is not required. If IDIA = 2, only terms with λ even are required. In the present version of the codes the LiCN dipole surfaces of Brocks et al. [43] is provided in DIPL. These surfaces use scattering coordinates with the CN bond frozen.

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

SUBROUTINE DIPD(DIPC,R1,R2,XCOS,NU)

must be supplied. DIPD returns the NU-th component of the dipole in atomic units (1 a.u. = 2.5417662 Debye) at point R1 = r_1 , R2 = r_2 (both in Bohr) and XCOS = $\cos \theta$ where NU = 0 corresponds to μ_z and NU = 1 μ_x .

DIPOLE3 includes COMMON /MASS/ XMASS(3),G1,G2,ZEMBED,ZBISC where XMASS contains the atomic masses, G1= g_1 , G2= g_2 , ZEMBED is the axis embedding parameter defined below and ZBISC=.TRUE. for the bisector embedding case and .FALSE. otherwise. This enables users to write dipole subroutines which allow for changes in coordinates, embeddings or isotopic substitution, see for example the version of subroutine DIPD provided.

4.2. Input for DVR3DRJ

DVR3DRJ 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.
 ZP1D [F] = T requests printing of the results of 1D calculations.
 ZP2D [F] = T requests printing of the results of 2D calculations.

- 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 dimension selected using an energy cut-off given by EMAX2.
= F final dimension determined by MAX3D (MAX3D2).
- ZWBLK[T] = T only include W -matrix in final step.
= F include diagonal portion in first step, see [31].
- ZROT[F] = T DVR3DRJ to perform first step in a two-step variational calculation.
- ZEMBED[T] Used only if $J > 0$ and IDIA > -2 .
= T z axis embedded along r_2 ;
= F z axis embedded along r_1 .
- ZLIN [F] = T forces suppression of functions at last DVR point (IDIA = -2 only).
- ZMORS1[T] = T use Morse oscillator-like functions for r_1 coordinate;
= F use spherical oscillator functions.
- ZMORS2[T] = T use Morse oscillator-like functions for r_2 coordinate;
= F use spherical oscillator functions.
- ZLPOT[F] = T potential supplied in POT;
= F potential supplied in POTV.
- ZTWOD[F] = T perform 2D calculation only at specified grid point.
- ZVEC[F] = T store the eigenvectors from all the parts of the calculation (1D,2D and 3D) on stream IOUT2. Further information relating to this (arrays IV1 and IV2) is stored on stream IOUT1.
- ZALL[F] = T requests **no** truncation of the intermediate solution.
- ZTHETA[T] = T let θ be first in the order of solution;
= F let θ be last in the order of solution.
- ZR2R1[T] = T let r_2 come before r_1 in the order of solution;
= F let r_1 come before r_2 in the order of solution.
- ZTRAN[F] = T perform the transformation of the solution coefficients to the expression for the wavefunction amplitudes at the grid points, eq (29).
Store the data on stream IWAVE. ZTRAN = T automatically sets ZVEC = T.
- ZQUAD2[T] = T use the DVR quadrature approximation for the integrals of the r_2^{-2} matrix, and hence make its DVR transformation diagonal.
= F evaluate the r_2^{-2} integrals fully and perform the DVR transformation on them.
Note that ZQUAD2 = F is only implemented for ZMORS2 = F and for ZTHETA = T.
- ZDIAG[T] = F do not do final diagonalisation, instead the final Hamiltonian matrix is written on units IDIAG1[20] and IDIAG2[21]. For further details see the source code.
- ZPFUN[F] = T eigenvalues concatenated on stream ILEV.
Warning, the first eigenvalues on this file must be for JROT=0, IPAR=0.
- ILEV[14] output stream for eigenvalue data (formatted).
- IEIGS1[7] stream for eigenvalues of the 1D solutions.
- IVECS1[3] stream for eigenvectors of the 1D solutions.
- IEIGS2[2] stream for eigenvalues of the 2D solutions.
- IVECS2[4] stream for eigenvectors of the 2D solutions.
- IVINT[17] scratch file used for storing intermediate vectors in building the final Hamiltonian.
- IBAND[15] scratch file used for storing bands of the final Hamiltonian.
- INTVEC[16] scratch file for intermediate storage of the 2D vectors.

IOUT1[24] stream for arrays IV1 and IV2, which record the sizes of the truncated vectors.
Used when ZVEC = T.
IOUT2[25] stream for the 1D, 2D and 3D vectors for use when ZVEC = T.
IWAVE[26] stores the wavefunction amplitudes at the grid points when ZTRAN = T.

Card 2: NCOORD (I5)

NCOORD[3] the number of vibrational coordinates of the problem:
= 2 for an atom – rigid diatom system,
= 3 for a full triatomic.

**Card 3: NPNT2,JROT,NEVAL,NALF,MAX2D,MAX3D,IDIA,
KMIN,NPNT1,IPAR,MAX3D2,MAX1DV (12I5)**

NPNT2 number of DVR points in r_2 from Gauss–(associated) Laguerre quadrature.
JROT[0] total angular momentum quantum number of the system, J .
NEVAL[10] number of eigenvalues and eigenvectors required.
NALF number of DVR points in θ from Gauss–(associated) Legendre quadrature.
MAX2D maximum dimension of the largest intermediate 2D Hamiltonian,
(ignored if IDIA = -2).
MAX3D maximum dimension of the final Hamiltonian.
If ZCUT = F, it is the actual number of functions selected,
if ZCUT = T, MAX3D must be \geq than the number of functions selected using EMAX2.
IDIA = 1 for scattering coordinates with a heteronuclear diatomic,
= 2 for scattering coordinates with a homonuclear diatomic.
= -1 for Radau coordinates with a heteronuclear diatomic,
= -2 for Radau coordinates with a homonuclear diatomic.
KMIN[0] = k for JROT > 0 and ZROT = F,
= $(1 - p)$ for JROT > 0 and ZROT = T.
Note: if KMIN = 2 in ROTLEV3, KMIN must be 1 in DVR3DRJ.
= 2 for JROT > 0 and ZROT = T and IDIA = -2 if both $p = 0$ and 1 to be done.
NPNT1 number of DVR points in r_1 from Gauss–(associated) Laguerre quadrature,
(ignored if IDIA = -2).
IPAR[0] parity of basis homonuclear diatomic ($|IDIA| = 2$) case:
IPAR=0 for even parity and = 1 for odd.
MAX3D2[MAX3D] maximum dimension of odd parity final Hamiltonians.
(IDIA = -2, ZROT=T only).
MAX1DV[MAX2D*NALF] maximum number of 1D vectors saved (IDIA = -2 only).

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.

Card 7: EMAX1, EMAX2 (2F20.0)

EMAX1 is the first cut-off energy in cm^{-1} with the same energy zero as the potential. This determines the truncation of the 1D solutions (IDIA > -2 only).
 EMAX2 is the second cut-off energy in cm^{-1} with the same energy zero as the potential. This controls the truncation of the 2D solutions (ie. the size of the final basis). If ZCUT = F it is ignored and the size of the final Hamiltonian is MAX3D.

Card 8: RE1,DISS1,WE1 (3F20.0)

If NCOORD = 2, RE1 is the fixed diatomic bondlength, DISS1 and WE1 ignored.
 If NCOORD = 3, RE1 = r_e , DISS1 = D_e and WE1 = ω_e
 are Morse parameters for the r_1 coordinate when ZMORS1 = T, and are
 spherical oscillator parameters when ZMORS1 = F.

Card 9: RE2,DISS2,WE2 (3F20.0)

If ZMORS2 = T, RE2 = r_e , DISS2 = D_e and WE2 = ω_e
 are Morse parameters for the r_2 coordinate.
 If ZMORS2 = F, RE2 is ignored; DISS2 = α and WE2 = ω_e
 are spherical oscillator parameters for the r_2 coordinate.
 If IDIA = -2 card read but ignored.

Card 10: EZERO [0.0] (F20.0)

The ground state of the system in cm^{-1} relative to the energy zero.
 Only read when IDIA= ± 2 , IPAR=1 and JROT=0.

4.3. Card input for ROTLEV3

Most of the data for ROTLEV3, which must have been prepared previously by DVR3DRJ run with IDIA > -2, is read from stream IWAVE. 3 or 4 lines of data are read from cards.

Card 1: NAMELIST/PRT/

TOLER[0.0D0] tolerance for convergence of the eigenvalues by F02FJF, zero gives machine accuracy.
 1.0D-4 is usually sufficient for most applications. (Ignored if ZDCORE = T.)
 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.
 ZPTRA[F] = T requests printing of the transformed vectors.
 IWAVE[26] stream for input data from DVR3DRJ (unformatted).
 ZVEC[F] = T eigenvalue and eigenvector data to be written to disk file.
 (= T forced if ZTRAN = T).
 IVEC[4] scratch file for the transformed input vectors (unformatted).
 JVEC[3] stream for first set of eigenvalue/vector output (unformatted).
 JVEC2[2] stream for second set of eigenvalue/vector output (unformatted), KMIN=2 only.
 ZTRAN[F] = T eigenvector transformed back to original basis.
 KVEC[8] stream for first set of transformed eigenvector output (unformatted).
 KVEC2[9] stream for second set of transformed eigenvector output (unformatted), KMIN=2 only.
 ISCR[1] stream for scratch file storing Hamiltonian matrix (unformatted).
 IVEC[4] stream for scratch file storing DVR3DRJ vectors transformed to an FBR in θ

(unformatted). Used only if ZTRAN = T.
 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 $J = 0$, j even) be already present.
 ILEV[14] stream for eigenvalue data (formatted).
 ZDIAG[T] = F do not diagonalise the Hamiltonian matrix.
 ZDCORE[F] = T diagonalisation performed in core using NAG routine F02ABF,
 = F diagonalisation performed iteratively using NAG Routine F02FJF.

Card 2: NVIB,NEVAL,KMIN,IBASS,NEVAL2 (5I5)

NVIB number of vibrational levels from DVR3DRJ 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.

Card 3: TITLE (9A8)

A 72 character title.

Card 4: EZERO [0.0] (F20.0)

The ground state of the system in cm^{-1} relative to the energy zero.

4.4. Card input for ROTLEV3B

Most of the data for ROTLEV3B, which must have been prepared previously by DVR3DRJ run with IDIA = -2, is read from streams IVEC and IVEC2. 3 or 4 lines of data are read from cards.

Card 1: NAMELIST/PRT/

TOLER[0.0D0] tolerance for convergence of the eigenvalues by F02FJF, zero gives machine accuracy. 1.0D-4 is usually sufficient for most applications. (Ignored if ZDCORE = T.)
 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.
 ZPTRAF[F] = T requests printing of the transformed vectors.
 IVEC[26] stream for input data from DVR3DRJ (unformatted).
 IVEC2[4] second stream for input data from DVR3DRJ (unformatted); this file is simply a copy of that on stream IVEC.
 ZVEC[F] = T eigenvalue and eigenvector data to be written to disk file. (= T forced if ZTRAN = T).

IVEC[4] scratch file for the transformed input vectors (unformatted).
 JVEC[3] stream for first set of eigenvalue/vector output (unformatted).
 JVEC2[2] stream for second set of eigenvalue/vector output (unformatted), KMIN=2 only.
 ZTRAN[F] = T eigenvector transformed back to original basis.
 KVEC[8] stream for first set of transformed eigenvector output (unformatted).
 KVEC2[9] stream for second set of transformed eigenvector output (unformatted), KMIN=2 only.
 ISCR[1] stream for scratch file storing array OFFDG (unformatted).
 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 $J = 0$, j even) be already present.
 ILEV[14] stream for eigenvalue data (formatted).
 ZDIAG[T] = F do not diagonalise the Hamiltonian matrix.
 ZDCORE[F] = T diagonalisation performed in core using NAG routine F02ABF,
 = F diagonalisation performed iteratively using NAG Routine F02FJF.

Card 2: NVIB,NEVAL,KMIN,IBASS,NEVAL2,NPNT (5I5)

NVIB number of vibrational levels from DVR3DRJ 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.

Card 3: TITLE (9A8)

A 72 character title.

Card 4: EZERO [0.0] (F20.0)

The ground state of the system in cm^{-1} relative to the energy zero.

5. Card input for DIPOLE3

DIPOLE3 takes most of its input from the output streams IWAVE (from DVR3DRJ) or KVEC and KVEC2 (from ROTLEV3 or ROTLEV3B). It has the option to produce output files for SPECTRA [13] to calculate simulated spectra at a given temperature. The user must supply the following three lines of input on card:

Card 1: NAMELIST/PRT/

ZLPOT[F] = T, the dipole surfaces supplied DIPL (not allowed if $J' = J'' = 0$);
 = F, the dipole surfaces supplied in DIPD.
 ZPRINT[F] = T supplies extra print out for debugging purposes.
 ZTRA[T] = T writes data for SPECTRA to stream ITRA.
 ZSTART[F] = T initiates the output file for the data for SPECTRA.

= F writes data to the end of existing file on stream ITRA.
 IKET[11] input stream from DVR3DRJ/ROTLEV3/ROTLEV3B for the ket (unformatted).
 IBRA[12] input stream for the bra (unformatted).
 ITRA[13] output stream to SPECTRA (if ZTRA= T) (unformatted).

Card 2: TITLE (9A8)

A 72 character title.

Card 3: LPOT, NV1, NV2 (3I5)

LPOT highest value of λ in the Legendre expansion of the dipole.
 If ZLPOT = T, LPOT must be consistent with Subroutine DIPL.
 If ZLPOT = F, LPOT+1+MOD(LPOT,2) point Gauss–Legendre integration is used for the θ coordinate.
 NV1[all] number of ket eigenfunctions considered.
 NV2[all] number of bra eigenfunctions considered.

Card 4: EZERO [0.0] (F20.0)

The ground state of the system in cm^{-1} relative to the energy zero.

Input and output on streams IKET, IBRA and ITRA are in atomic units. The data printed at the end of DIPOLE is given in wavenumbers, Debye for the transition dipoles and s^{-1} for the Einstein A coefficients.

6. Test run output

Test decks which run DVR3DRJ, ROTLEV3 and DIPOLE3 in scattering coordinates, and DVR3DRJ, ROTLEV3B and DIPOLE3 in Radau coordinates are provided. Both use the H_2S potential energy and dipole surfaces of Senekowitch et al. [44]. The run mimics the benchmark calculations on H_2S performed by Carter et al. [45] although the size of the calculations have been reduced in the test data.

The LiCN (CN frozen) scattering coordinate surface of Essers et al. [46] is supplied in subroutine POT.

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TEST RUN OUTPUT

PROGRAM DVR3D (VERSION OF 15 Feb 1994)

FULL TRIATOMIC VIBRATIONAL PROBLEM WITH

15 RADIAL R1 DVR POINTS USED,
 15 RADIAL R2 DVR POINTS USED,
 30 ANGULAR DVR POINTS USED, WITH
 5 LOWEST EIGENVECTORS CHOSEN FROM
 UP TO 400 DIMENSION SECULAR PROBLEM

CALCULATION PERFORMED IN RADAU COORDINATES
 DIATOMIC ASSUMED HETRONUCLEAR

J = 0 ROTATIONAL STATE

LOWEST 5 EIGENVALUES IN WAVENUMBERS:

.329745809331D+04 .448789773114D+04 .566947433880D+04
 .591781373825D+04 .592843571876D+04

PROGRAM DVR3D (VERSION OF 15 Feb 1994)

*** VIBRATIONAL PART OF ROT-VIB CALCULATION ***

J = 1 ROTATIONAL STATE
 WITH SYMMETRIC $|J_k\rangle + |J-k\rangle$ FUNCTIONS IN BASIS
 HALF TO BE KEPT CONSTANT WITH K

Z AXIS EMBEDDED ALONG THE R2 COORDINATE

Solutions with J = 1 k = 0

LOWEST 150 EIGENVALUES IN WAVENUMBERS:

.331637793726D+04 .450672162727D+04 .568820356822D+04
 .593644952661D+04 .594708729851D+04

Solutions with J = 1 k = 1

LOWEST 150 EIGENVALUES IN WAVENUMBERS:

.331678839011D+04 .450779162566D+04 .568997423440D+04
 .593686275896D+04 .594747089533D+04

PROGRAM ROTLEV3 (VERSION OF 20 Sept 1993):

ROTATIONAL PART OF ROT-VIB CALCULATION WITH:
 150 LOWEST VIBRATIONAL EIGENVECTORS SUPPLIED FROM
 6750 DIMENSION VIBRATION SECULAR PROBLEM
 150 LOWEST VIBRATIONAL EIGENVECTORS ACTUALLY USED
 10 LOWEST ROTATIONAL EIGENVECTORS REQUIRED FOR
 250 DIMENSION ROTATION SECULAR PROBLEM
 WITH BASIS SELECTED BY ENERGY ORDERING

J = 1 ROTATIONAL STATE, 250 BASIS FUNCTIONS
 E PARITY, SYMMETRIC $|JK\rangle + |J-K\rangle$ FUNCTIONS IN BASIS

Lowest 10 eigenvalues in wavenumbers relative to EZERO = .00000000000D+00

3311.14871 3312.53495 4501.72235 4503.28143 5683.44699 5685.19336
 5931.30794 5932.66189 5941.99438 5943.24842

Program DIPOLE3 (Version of 5 Oct 1993):

IE1	IE2	FREQUENCY	DIPOLE	S (F-I)	A-COEFFICIENT
1	1	13.691	.292619E-06	.856257E-13	.229696E-16
1	2	15.077	.982706E+00	.965710E+00	.345987E-03
1	3	1204.264	.485082E-08	.235304E-16	.429611E-14
1	4	1205.823	.159378E-01	.254015E-03	.465576E-01
1	5	2385.989	.240138E-07	.576664E-15	.818858E-12
1	6	2387.735	.375987E-02	.141366E-04	.201180E-01
1	7	2633.850	.248060E-07	.615336E-15	.117535E-11
1	8	2635.204	.778899E-02	.606683E-04	.116061E+00
1	9	2644.536	.637562E-02	.406485E-04	.785911E-01
1	10	2645.790	.485376E-06	.235590E-12	.456146E-09

TEST OUTPUT: test run 2

PROGRAM DVR3D (VERSION OF 15 Feb 1994)

FULL TRIATOMIC VIBRATIONAL PROBLEM WITH

15 RADIAL R1 DVR POINTS USED,
 15 RADIAL R2 DVR POINTS USED,
 30 ANGULAR DVR POINTS USED, WITH
 5 LOWEST EIGENVECTORS CHOSEN FROM
 UP TO 400 DIMENSION SECULAR PROBLEM

CALCULATION PERFORMED IN RADAU COORDINATES
 DIATOMIC ASSUMED HOMONUCLEAR
 EVEN PARITY FUNCTIONS IN BASIS SET

J = 0 ROTATIONAL STATE

LOWEST 5 EIGENVALUES IN WAVENUMBERS:

.329745809310D+04 .448789772988D+04 .566947433265D+04
 .591781373297D+04 .684093190174D+04

PROGRAM DVR3D (VERSION OF 15 Feb 1994)

ODD PARITY FUNCTIONS IN BASIS SET

*** VIBRATIONAL PART OF ROT-VIB CALCULATION ***

J = 1 ROTATIONAL STATE
 WITH SYMMETRIC |Jk> + |J-k> FUNCTIONS IN BASIS
 HALF TO BE KEPT CONSTANT WITH K

Z AXIS EMBEDDED ALONG THE BISCETOR OF R1 AND R2

Solutions with J = 1 k = 0

ODD PARITY SOLUTIONS

LOWEST 150 EIGENVALUES IN WAVENUMBERS:

.594198547969D+04 .711099373420D+04 .827135085104D+04
 .846626788722D+04 .942178895599D+04

Solutions with J = 1 k = 1

EVEN PARITY SOLUTIONS

LOWEST 150 EIGENVALUES IN WAVENUMBERS:

```
.331254547094D+04      .450332923592D+04      .568527866110D+04
.593267604633D+04      .685714348803D+04
```

PROGRAM ROTLEV3B (Version of 16 Oct 1993):

```
ROTATIONAL PART OF ROT-VIB CALCULATION WITH:
 150  LOWEST VIBRATIONAL EIGENVECTORS SUPPLIED FROM
3600  DIMENSION VIBRATION SECULAR PROBLEM WITH
 30   ANGULAR DVR POINTS.
 150  LOWEST VIBRATIONAL EIGENVECTORS ACTUALLY USED
 30   POINT GAUSS-ASSOCIATED LEGENDRE INTEGRATION
 10   LOWEST ROTATIONAL EIGENVECTORS REQUIRED FOR
 250  DIMENSION ROTATION SECULAR PROBLEM
      WITH BASIS SELECTED BY ENERGY ORDERING
```

```
J = 1  ROTATIONAL STATE,      250  BASIS FUNCTIONS
      E PARITY, SYMMETRIC |JK> + |J-K> FUNCTIONS IN BASIS
      ODD PARITY RADIAL FUNCTIONS IN BASIS SET
```

Lowest 10 eigenvalues in wavenumbers relative to EZERO = .000000000000D+00

```
.331253493462D+04      .450328143178D+04      .568519334821D+04
.593266187687D+04      .594199436081D+04
.685702058748D+04      .710716155569D+04      .711096720308D+04
.801764350854D+04      .827128236132D+04
```

Program DIPOLE3 (Version of 5 Oct 1993):

IE1	IE2	FREQUENCY	DIPOLE	S(F-I)	A-COEFFICIENT
1	1	15.077	.982706E+00	.965711E+00	.345986E-03
1	2	1205.823	.159378E-01	.254015E-03	.465576E-01
1	3	2387.735	.375912E-02	.141310E-04	.201099E-01
1	4	2635.204	.778895E-02	.606677E-04	.116060E+00
1	5	2644.536	.637520E-02	.406431E-04	.785808E-01
1	6	3559.562	.102949E-02	.105986E-05	.499710E-02
1	7	3809.703	.653728E-02	.427361E-04	.247029E+00
1	8	3813.509	.886475E-02	.785837E-04	.455604E+00
1	9	4720.185	.229564E-03	.526996E-07	.579383E-03
1	10	4973.824	.963142E-03	.927643E-06	.119325E-01