Computer Physics Communications 55 (1989) 149–175
North-Holland, Amsterdam

A PROGRAM SUITE FOR THE CALCULATION OF RO-VIBRATIONAL SPECTRA OF TRIATOMIC MOLECULES

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Received 19 January 1989

A program suite for the calculation of ro-vibrational eigenfunctions of triatomic molecules is presented. The suite enables first principles calculations – starting from a set of basis functions and electronic potential energy and dipole surfaces – of the energy levels, transition frequencies and synthetic stick spectra to be made. The suite is based around the main driver program TRIATOM. This has been improved, to make more efficient use of vector processors and available memory, and generalised, to allow for different co-ordinate types (scattering, bond-length/bond-angle, radau) to be employed. Programs SELECT and ROTLEV (now ROTLEVD) have been similarly upgraded. In addition, two new programs have been written and are published here. DIPOLE calculates the line strengths and frequencies of dipole transition between the eigenfunctions produced by TRIATOM/ROTLEVD. SPECTRA calculates stick spectra based on the integrated absorption coefficients arising from the results of DIPOLE. Each member of the suite produces output which forms the direct input for subsequent members.

PROGRAM SUMMARY

Title of program: TRIATOM

Catalogue number: ABJW

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

Computer: CRAY-1; *Installation*: University of London Computer Centre

Other machines on which program was tested: Cray-XMP48, Micro Vax 3 and Convex 100

Programming language used: FORTRAN 77

High speed storage required: case dependent

Peripherals used: card reader, line printer, at least one disk file

No. of cards in program: 2934

Keywords: ro-vibrational, body-fixed, associated Laguerre polynomials, associated Legendre polynomials, Gaussian quadrature, variational, close-coupled equations, vectorised

Nature of physical problem
TRIATOM calculates the bound ro-vibrational levels of a triatomic system using the generalised body-fixed coordinates developed by Sutcliffe and Tennyson [1].

Method of solution
A basis is constructed as a product of radial (either Morse oscillator-like or spherical oscillator) functions and associated Legendre polynomials for the bending coordinate, with rotation matrices carrying the rotational motion. A secular matrix is constructed using Gaussian quadrature and diagonalised to give solutions. Input can be direct from SELECT [2]. TRIATOM provides data necessary to drive ROTLEVD [3] and DIPOLE [4].

Restrictions on the complexity of the problem
The size of matrix that can practically be diagonalised. TRIATOM 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.

Typical running time
Case dependent but dominated by matrix diagonalisation. A problem with 600 basis functions (requiring 350000 words storage) takes 9 seconds on the CRAY XMP-48.

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] B.T. Sutcliffe and J. Tennyson, Mol. Phys. 58 (1986) 1053.
[2] J. Tennyson and S. Miller, this article, second program (SELECT).
[3] J. Tennyson and S. Miller, this article, third program (ROTLEVD).
[4] J. Tennyson and S. Miller, this article, fourth program (DIPOLE).

PROGRAM SUMMARY

Title of program: SELECT

Catalogue number: ABJX

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

Computer: CRAY-1; *Installation*: University of London Computer Centre

Other machines on which program was tested: Cray-XMP48, Micro Vax 3 and Convex 100

Programming language used: FORTRAN 77

High speed storage required: case dependent

Peripherals used: card reader, line printer, one disk file

No. of cards in program: 2152

Keywords: basis set selection, first-order perturbation theory

Nature of physical problem
SELECT selects basis sets for TRIATOM [1].

Method of solution
A basis is selected either according to its quantum numbers and/or the value of its diagonal matrix element [2].

Restrictions on the complexity of the problem
The size of matrix that can be handled by TRIATOM.

Typical running time
Negligible compared to TRIATOM.

Unusual features of the program
A user supplied subroutine containing the potential energy as an analytic function (optionally a Legendre polynomial expansion) may be needed. SELECT produces a file which drives TRIATOM.

References
[1] J. Tennyson and S. Miller, this article, first program (TRIATOM).
[2] J. Tennyson, Comput. Phys. Rep. 4 (1986) 1.

PROGRAM SUMMARY

Title of program: ROTLEVD

Catalogue number: ABJY

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

Computer: CRAY-1; *Installation*: University of London Computer Centre

Other machines on which program was tested: Cray-XMP48, Micro Vax 3 and Convex 100

Programming language used: FORTRAN 77

High speed storage required: case dependent

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

No. of cards in program: 3994

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

Nature of physical problem
ROTLEVD performs the second step in a two-step variational calculation for the bound ro-vibrational levels of a triatomic system [1].

Method of solution
A basis is constructed from the solutions, optionally energy ordered [2], of the Coriolis decoupled problem. The resulting sparse matrix is then diagonalised to give the solutions.

Restrictions on the complexity of the problem
The size of matrix that can practically be diagonalised. ROTLEVD 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.

Typical running time
Highly case dependent. A test run for $J = 1$ involving a maximum of 1200 basis functions takes 15 seconds on the Cray XMP-48.

Unusual features of the program
Most data is read directly from TRIATOM [3]. ROTLEVD can provide data to drive DIPOLE [4].

References
[1] J. Tennyson and B.T. Sutcliffe, Mol. Phys. 58 (1986) 1067.
[2] B.T. Sutcliffe, J. Tennyson and S. Miller, Comput. Phys. Commun. 51 (1988) 73.
[3] J. Tennyson and S. Miller, this article, first program (TRIATOM).
[4] J. Tennyson and S. Miller, this article, fourth program (DIPOLE).

PROGRAM SUMMARY

Title of program: DIPOLE

Catalogue number: ABJZ

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

Computer: CRAY-1; *Installation*: University of London Computer Centre

Other machines on which program was tested: Cray-XMP48, Micro Vax 3 and Convex 100

Programming language used: FORTRAN 77

High speed storage required: case dependent

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

No. of cards in program: 2619

Keywords: transitions, frequencies, linestrengths, vectorised

Nature of physical problem
DIPOLE 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 using Gaussian quadrature for the primitive basis functions used in TRIATOM [2]. The wavefunctions generated by TRIATOM [2] and/or ROTLEVD [3] are then used to give transition intensities for individual pairs of states.

Restrictions on the complexity of the problem
The complexity of the problem that can be solved by TRIATOM or ROTLEVD.

Typical running time
Case dependent. A test run for $J = 0$ to $J = 1$ levels, involving a maximum of 1200 basis functions takes 15 seconds on the Cray XMP-48.

Unusual features of the program
Most data is read directly from TRIATOM [2] and/or ROTLEVD [3]. DIPOLE provides data to drive SPECTRA [4].

References
[1] S. Miller, J. Tennyson and B.T. Sutcliffe, Mol. Phys. 66 (1989) 429.
[2] J. Tennyson and S. Miller, this article, first program (TRIATOM).
[3] J. Tennyson and S. Miller, this article, third program (ROTLEVD).
[4] J. Tennyson and S. Miller, this article, fifth program (SPECTRA).

PROGRAM SUMMARY

Title of program: SPECTRA

Catalogue number: ABLA

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

Computer: CRAY-1; *Installation*: University of London Computer Centre

Other machines on which program was tested: Cray-XMP48, Micro Vax 3 and Convex 100

Programming language used: FORTRAN 77

High speed storage required: case dependent

Peripherals used: card reader, line printer, at least one disk file

No. of cards in program: 938

Keywords: synthetic spectra, absorption coefficients, Boltzmann distribution, partition function, vectorised

Nature of physical problem
SPECTRA generates synthetic, frequency ordered, stick spectra as a function of temperature. Integrated absorption coefficients can be calculated if the necessary data to calculate the partition function is supplied.

Method of solution
Transitions are sorted by frequency and weighted using Boltzmann statistics.

Restrictions on the complexity of the problem
The complexity of the problem that can be solved by TRIATOM [1] or ROTLEVD [2].

Typical running time
Case dependent, but small compared with DIPOLE.

Unusual features of the program
Most data is read directly from DIPOLE [3]. Some data from TRIATOM [2] and/or ROTLEVD [3] may also by required.

References
[1] J. Tennyson and S. Miller, this article, first program (TRIATOM).
[2] J. Tennyson and S. Miller, this article, third program (ROTLEVD).
[3] J. Tennyson and S. Miller, this article, fourth program (DIPOLE).

LONG WRITE-UP

1. Introduction

The calculation of ro-vibrational energy levels for triatomic molecules has made major strides in recent years. Such calculations have moved beyond the original goal of simply obtaining a good representation of the vibrational fundamentals and perhaps the leading rotational constants of the system [1]. Variational calculations, with no significant approximations beyond that of assuming a potential energy surface, have now been performed which stabilise over a hundred vibrational states [2] and rotational levels with total angular momenta up to 60 [3]. Conversely for electronically simple systems, such as H_3^+, calculations of accuracy competitive with that of high resolution spectroscopy have been performed for both vibrational fundamentals and overtones [4,5]. Detailed predictions of intensities for individual transitions are also available [6].

Naturally these advances have been facilitated by the increase in available computer power but they have also been achieved by the development of new methods and algorithms for solving the bound state nuclear motion problem. A number of variational approaches which rely on the use of body-fixed coordinate systems other than that suggested by Eckart [7] are now available. In particular we cite the work of Carter and Handy [8] and Bacic and Light [2].

Over a number of years Tennyson and Sutcliffe developed a secular equation approach based on scattering coordinates [9–11]. This approach was implemented in programs ATOMDIAT [12] and ATOMDIAT2 [13]. More recently these workers extended their work to a generalised body-fixed coordinate system [14] using basis set selection [15] and developed a two-step variational approach for rotationally excited states [16]. These developments were implemented in programs TRIATOM, SELECT and ROTLEV [17], respectively.

Since the above programs were published there have been a number of improvements and extensions to the methodology employed in these rovibrational calculations. The coordinates used have been further generalised [18]. Program DIPOLE has been written to allow intensities to be computed for transitions between the states calculated by TRIATOM and ROTLEV [19]. Program SPECTRA processes the output of DIPOLE to given temperature dependent, synthetic stick spectra. An energy-ordered basis set selection criterion has been implemented in ROTLEV [20].

Considerable improvements have been made in the algorithm used by ROTLEV – for example obviating the need for separately calculating the Hamiltonian for the odd parity f states. Hamiltonian scratch files have been implemented in both TRIATOM and ROTLEVD leading to considerable savings in fast storage for large calculations. Increased vectorisation means the TRIATOM and ROTLEVD, the time-consuming modules in the suite, now drive a single Cray-XMP processor at over 110 and 140 Mflops (million floating point operations per second), respectively [21].

Two bugs in the published version of SELECT have been corrected. A number of extra options in all three programs have been implemented. In particular program ROTLEVD is ROTLEV augmented by subroutine DSTORE which allows the ro-vibrational wavefunction to be expressed in terms of the first variational step basis functions used by TRIATOM.

The purpose of this work is to present these versions of SELECT, TRIATOM, ROTLEVD, DIPOLE and SPECTRA as a program suite. These programs supersede the programs referenced above. They allow for the complete calculation of synthetic ro-vibrational stick spectra for any triatomic system from given potential energy and dipole surfaces.

2. Method

2.1. The ro-vibrational problem: TRIATOM

Using the generalised coordinates of Sutcliffe and Tennyson [18] defined in fig. 1, a bodyfixed Hamiltonian can be written,

$$\hat{H} = \hat{K}_V^{(1)} + \hat{K}_V^{(2)} + \hat{K}_{VR}^{(1)} + \hat{K}_{VR}^{(2)} + V(r_1, r_2, \theta), \tag{1}$$

where V is the electronic potential. Symmetrised angular basis functions for $\hat{H}$ can be written as [14]

$$|j, k\rangle = 2^{-1/2}(1+\delta_{k0})^{-1/2}\left[\Theta_{jk}(\theta)D^J_{Mk}(\alpha, \beta, \gamma) + (-1)^p\Theta_{j-k}(\theta)D^J_{M-k}(\alpha, \beta, \gamma)\right], \tag{2}$$

where D^J_{Mk} is a rotation matrix element [22] and Θ_{jk} an associated Legendre polynomial [23]. The total parity is given by $(-1)^{J+p}$ with $p = 0$ or 1 for e or f states, respectively. k is the projection of the total angular momentum, J, along the body-fixed z axis which can be chosen parallel to either r_1 or r_2. α, β, γ are the Euler angles required to rotate the space fixed axes into the body-fixed ones.

Letting $\hat{H}$ act on $|j, k\rangle$, multiplying from the left by $\langle j', k'|$ and integrating over all *angular* coordinates yields an effective Hamiltonian [14]:

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

$$\begin{aligned}\hat{K}_V^{(2)} = &-\delta_{j'j+1}\delta_{k'k}d_{jk}\frac{\hbar^2}{\mu_{12}}\left(\frac{\partial}{\partial r_1} - \frac{j+1}{r_1}\right)\left(\frac{\partial}{\partial r_2} - \frac{j+1}{r_2}\right)\\ &-\delta_{j'j-1}\delta_{k'k}d_{j-1,k}\frac{\hbar^2}{\mu_{12}}\left(\frac{\partial}{\partial r_1} + \frac{j}{r_1}\right)\left(\frac{\partial}{\partial r_2} + \frac{j}{r_2}\right),\end{aligned} \tag{4}$$

$$\hat{K}_{VR}^{(1)} = \delta_{j'j}\delta_{k'k}\frac{\hbar^2}{2\mu_1 r_1^2}\left(J(J+1) - 2k^2\right) - \delta_{j'j}\delta_{k'k\pm1}\frac{\hbar^2}{2\mu_1 r_1^2}(1+\delta_{k0}+\delta_{k'0})^{1/2}C^{\pm}_{jk}C^{\pm}_{jk}, \tag{5}$$

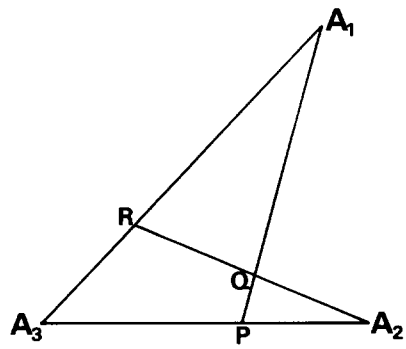

Fig. 1. Program coordinate system.

$$\hat{K}_{VR}^{(2)} = \delta_{j'j+1}\delta_{k'k\pm1}\frac{\hbar^2}{2\mu_{12}}(1+\delta_{k0}+\delta_{k'0})^{1/2}C_{Jk}^{\pm}\frac{a_{j\pm k}}{r_1}\left(\frac{j+1}{r_2}-\frac{\partial}{\partial r_2}\right)$$
$$+\delta_{j'j-1}\delta_{k'k\pm1}\frac{\hbar^2}{2\mu_{12}}(1+\delta_{k0}+\delta_{k'0})^{1/2}C_{Jk}^{\pm}\frac{b_{j\pm k}}{r_1}\left(\frac{j}{r_2}+\frac{\partial}{\partial r_2}\right). \tag{6}$$

The angular factors in the above equations are:

$$C_{Jk}^{\pm} = [J(J+1)-k(k\pm1)]^{1/2}, \tag{7}$$

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

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

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

The reduced masses are:

$$\mu_1^{-1} = g_2^2 m_1^{-1} + m_2^{-1} + (1-g_2)^2 m_3^{-1}, \tag{11}$$

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

$$\mu_2^{-1} = m_1^{-1} + g_1^2 m_2^{-1} + (1-g_1)^2 m_3^{-1}, \tag{13}$$

where g_1 and g_2 define the coordinate system used, see fig. 1.

Special case of g_1 and g_2 include scattering coordinates for which

$$g_1 = \frac{m_2}{m_2+m_3}, \qquad g_2 = 0; \tag{14}$$

bondlength–bondangle coordinates used by Carter and Handy for which the g's equal either 0 or 1, an 'geometric' coordinates with $g_1 = \frac{1}{2}$, $g_2 = 0$ which are useful for systems whose symmetry has been broken by isotopic substitution. Radau coordinates [24], and alternative set of orthogonal coordinates to scattering coordinates, are obtained with specific mass-dependent values of the g's [18]:

$$g_1 = 1-\frac{\alpha}{\alpha+\beta-\alpha\beta}, \quad g_2 = 1-\frac{\alpha}{1-\beta+\alpha\beta}, \quad \alpha = \left(\frac{m_3}{m_1+m_2+m_3}\right)^{1/2}, \quad \beta = \frac{m_1}{m_1+m_2}., \tag{15}$$

For both the Radau and scattering (Jacobi) coordinates we have used radial coordinates defined geometrically (see fig. 1) rather than the more conventional mass-weighted coordinates.

All the special cases covered above can be obtained by using the required combination of the input parameters IDIA and ISYM. Other values of the g's have also been used [18,25] and can be obtained by inputting specific values of G1 and G2. In particular we note that others set of orthogonal coordinates can be obtained by specifying G1 and G2 such that μ_{12} equals zero. This implementation does not have the full generality of the Hamiltonian developed by Sutcliffe and Tennyson [18], but other coordinate systems can be employed with only relatively minor changes to subroutine SETCON.

The $\hat{K}_{VR}$ operators given above are for the z axis embedded parallel to r_1. The appropriate operators for the other embedding are obtained by making the exchanges $r_1 \leftrightarrow r_2$ and $\mu_1 \leftrightarrow \mu_2$.

If the potential is expressed in a Legendre expansion,

$$V(r_1, r_2, \theta) = \sum_{\lambda} V_\lambda(r_1, r_2)\Theta_{\lambda,0}(\theta), \tag{16}$$

then the angular integration can also be performed analytically,

$$\langle j',\, k' \,|\, \Theta_{\lambda,0}(\theta) \,|\, j,\, k\rangle = \delta_{k'k}(-1)^k[(2j'+1)(2j+1)]^{1/2}\begin{pmatrix} j' & \lambda & j \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} j' & \lambda & j \\ -k & 0 & k\end{pmatrix}, \tag{17}$$

where the 3-j symbols in the Gaunt coefficient are conventional [22]. This method of performing the angular integration over the potential is completely general as potentials which are not naturally expanded in Legendre polynomials can be so expressed for each $(r_1,\, r_2)$ by using Gauss–Legendre quadrature. This is a computationally efficient way of forming matrix elements over the potential [26].

Having performed the integration over all angular coordinates one obtains a set of two-dimensional coupled differential equations similar to the close-coupling equations of Arthurs and Dalgarno [27]. Rather than attempting to solve these directly one can use basis functions to carry the radial as well the angular motion. Products of one-dimensional basis are generally used,

$$\psi_{mn}(r_1,\, r_2) = r_1^{-1}H_m(r_1)r_2^{-1}H_n(r_2). \tag{18}$$

In our experience the most suitable functions are a complete set based on solutions of the Morse potential [9,10]

$$|\, n\rangle = H_n(r) = \beta^{1/2}N_{n\alpha}\exp(-\tfrac{1}{2}y)\, y^{(\alpha+1)/2}L_n^{\alpha}(y), \qquad y = A\exp[-\beta(r-r_e)], \tag{19}$$

where

$$A = \frac{4D_e}{\beta}, \quad \beta = \omega_e\left(\frac{\mu}{2D_e}\right)^{1/2}, \quad \alpha = \text{integer}(A) \tag{20}$$

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 [28].

With the Morse oscillator-like functions integrals over the differential operators in the kinetic energy operators can be computed analytically [14,15]. However, it is necessary to use Gauss–Laguerre quadrature to evaluate the integrals over inverse powers of r and the potential.

An alternative set of radial basis functions, particularly useful for systems which have significant amplitudes for $r_2 = 0$, are spherical oscillator functions, defined by

$$|\, n\rangle = H_n(r) = 2^{1/2}\beta^{1/4}N_{n\alpha}\exp(-\tfrac{1}{2}y)\, y^{(\alpha+1)/2}L_n^{\alpha+1/2}(y), \qquad y = \beta r^2, \tag{21}$$

where

$$\beta = (\mu\omega_e)^{1/2} \tag{22}$$

and (α, ω_e) are treated as variational parameters. Further details about the functions can be found elsewhere [11,12,17].

In terms of these basis functions, the approximation to the ℓth energy level, E_ℓ^J has a wavefunction

$$\Psi_\ell^J = \sum_k \sum_{jmn} d_{kjmn}^{J\ell}\,|\, jk\rangle\,|\, m\rangle\,|\, n\rangle. \tag{23}$$

For homonuclear diatomics the wavefunction should be either symmetric or antisymmetric with respect to interchange of the like atoms. This symmetry is naturally represented in scattering coordinates where functions with j even and odd are symmetric and antisymmetric, respectively. The wavefunction can also

be symmetrised, for the case of $J = 0$, in coordinates for which $g_1 = g_2$ – these include bondlength–bondangle ($g_1 = 0$) and Radau coordinate. Then the symmetric wavefunctions has the form

$$\Psi_\ell^0 = \sum_{jmn} d_{0jmn}^{0\ell} \, |j0\rangle 2^{-1/2} (1 + \delta_{mn})^{-1/2} (|m\rangle |n\rangle + |n\rangle |m\rangle), \quad m \geq n, \tag{24}$$

and the antisymmetric wavefunction has the form

$$\Psi_\ell^0 = \sum_{jmn} d_{0jmn}^{0\ell} \, |j0\rangle 2^{-1/2} (|m\rangle |n\rangle - |n\rangle |m\rangle), \quad m > n. \tag{25}$$

2.2. *Vibrational basis set selection: SELECT*

A number of methods of building basis sets from the functions described above have been tested with a view to obtaining the most rapid convergence for a given problem [15]. As the vibrational basis set is a product of one-dimensional basis sets for each internal coordinate, one method is simply to take all possible product functions given by terminating each series at some maximum quantum number.

A second alternative is to use a compound quantum number NQMAX to determine which functions are selected. Allowing for selective weighting of functions in different coordinates this means that function $|jk\rangle |m\rangle |n\rangle$ is included in the basis if

$$\text{NQMAX} \geq \frac{j}{d_j} + \frac{m}{d_m} + \frac{n}{d_n}. \tag{26}$$

A third alternative is to use an energy criterion in selecting the functions. In this case the diagonal matrix elements of a large set of functions are evaluated. The lowest LBASS are then selected for the final basis.

Although we have found the energy ordering criterion to be often the most efficient, all three methods have been found useful for certain systems. Furthermore, it is also possible to select a basis using a mixture of methods.

2.3. *Rotational excitation: ROTLEVD*

The theory outlined in section 2.1 is in principle sufficient for finding the ro-vibrational wavefunctions of arbitrary triatomics. However, as the size of the secular problem implied by this method grows rapidly with increasing angular momentum, J, alternative methods have been developed to deal with rotational excitation [29].

If k, the projection of J on the body-fixed z axis, is assumed to be a good quantum number, then the Hamiltonian of section 2.1 becomes

$$\hat{H}_{Jk} = \hat{K}_V^{(1)} + \hat{K}_V^{(2)} + \delta_{k'k} \hat{K}_{VR}^{(1)} + V(r_1, r_2, \theta). \tag{27}$$

Solutions of this Hamiltonian with eigenenergy ϵ_i^{Jk} can be written

$$|i, k\rangle = \sum_{jmn} c_{jmn}^{Jki} \, |jk\rangle |m\rangle |n\rangle, \tag{28}$$

in terms of the basis functions defined above. The functions $|i, k\rangle$ can then be used as a basis for the fully coupled problem.

The advantages of this procedure are two-fold. Firstly, the secular matrix obtained in the second step has a distinctive sparse structure which is well suited to iterative diagonalisation techniques [16,30].

Secondly, not all the functions $|i, k\rangle$ are needed to obtain converged results. A suitable basis set can be selected either by using the lowest NVIB functions for each k block, or by choosing the LBASS functions with the lowest eigenenergy, ϵ_i^{Jk}. Again, the energy selection criterion has proved the most efficient [20].

If the ℓth solution of the second step is written

$$\Psi_\ell^J = \sum_{ik} b_{ik}^{J\ell} |ik\rangle, \tag{29}$$

then coefficient vectors $\boldsymbol{b}^{J\ell}$ can be back transformed to yield coefficients of the wavefunction in terms of the original basis functions

$$d_{kjmn}^{J\ell} = \sum_i b_{ik}^{J\ell} c_{jmn}^{Jki}. \tag{30}$$

2.4. Transition intensities: DIPOLE

With the wavefunctions generated in the previous sections, dipole transition intensities for selected transitions can be calculated given appropriate dipole surfaces. For a triatomic lying in the x–z plane, the dipole can be expressed in a generalisation of the Legendre expansion used to express the potential [31]:

$$\mu_z(r_1, r_2, \theta) = \sum_\lambda C_{\lambda,0}(r_1, r_2)\Theta_{\lambda,0}(\theta), \tag{31}$$

$$\mu_x(r_1, r_2, \theta) = \sum_\lambda C_{\lambda,1}(r_1, r_2)\Theta_{\lambda,1}(\theta). \tag{32}$$

Such an expansion can be obtained from any dipole surface using Gauss–Legendre quadrature, providing care is taken with the sin θ factors [19].

Integrating over the dipole surface yields an expression for the transition dipole [19],

$$\begin{aligned} T_{if}^{M'M''\tau} = {} & \frac{(-1)^{M'}}{2}[(2J'+1)(2J''+1)]^{1/2}\begin{pmatrix} J' & 1 & J'' \\ -M' & \tau & M'' \end{pmatrix} \\ & \times \sum_{\nu=-1}^{+1} \sum_{\lambda=|\nu|} \sum_{k=p''}^{J'} \sum_{j''j'} a(\nu, \nu+k, \lambda)[(2j'+1)(2j''+1)]^{1/2} \\ & \times \begin{pmatrix} J' & 1 & J'' \\ -k-\nu & \nu & k \end{pmatrix}\begin{pmatrix} j' & \lambda & j'' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} j' & \lambda & j'' \\ -k-\nu & \nu & k \end{pmatrix} \\ & \times \sum_{m''n''} \sum_{m'n'} B_{\lambda,\nu}^{m'm''n'n''} \times d_{k'j'm'n'}^{J'M'p'\ell'} d_{k''j''m''n''}^{J''M''p''\ell''} \left[(-1)^{J''+J'+1} + (-1)^{p''+p'}\right], \end{aligned} \tag{33}$$

where the radial integrals, $B_{\lambda,\nu}^{m'm''n'n''}$, are again evaluated using Gauss–Laguerre quadrature and

$$a(0, n, \lambda) = 1, \quad 0 \le n \le J', \qquad a(\pm 1, 0, \lambda) = -[\lambda(\lambda+1)]^{1/2},$$

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

In practice, the individual magnetic components of the wavefunctions are not computed separately. Summing over these then gives the transition line strength:

$$S(f-i) = \tfrac{1}{4}[(2J'+1)(2J''+1)] \times \left[\sum_{\nu=-1}^{+1} \sum_{\lambda=|\nu|} \sum_{k=p''}^{J''} \sum_{j''j'} a(\nu, \nu+k, \lambda)[(2j'+1)(2j''+1)]^{1/2} \times \begin{pmatrix} J' & 1 & J'' \\ -k-\nu & \nu & k \end{pmatrix} \begin{pmatrix} j' & \lambda & j'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j' & \lambda & j'' \\ -k-\nu & \nu & k \end{pmatrix} \times \sum_{m''n''} \sum_{m'n'} B_{\lambda,\nu}^{m'm''n'n''} \times d_{k'j'm'n'}^{J'p'\ell'} d_{k''j''m''n''}^{J''p''\ell''} \left[(-1)^{J''+J'+1} + (-1)^{p''+p'} \right] \right]^2. \tag{34}$$

From this the Einstein A_{if} coefficient for spontaneous emission can be obtained:

$$A_{if} = \frac{1}{(2J_f+1)} \frac{64\pi^4 \omega_{if}^3}{3h} S(f-i). \tag{35}$$

2.5. Synthetic spectra: SPECTRA

Stick spectra for rotational and ro-vibrational transitions can be generated as a function of frequency, ω_{if}, and temperature, T, using the formula

$$I(\omega_{if}) = \frac{8\pi^3 N_A \omega_{if} g_i \exp(-E''/kT)\left[1 - \exp(hc\omega_{if}/kT)\right]}{3hcQ(T)} S(f-i), \tag{36}$$

where $Q(T)$ is the partition function of the system and $I(\omega_{if})$ is the integrated absorption coefficient in units of cm mol^{-1}. The degeneracy factor g, for a particular level is determined by nuclear spin statistics and the symmetry of the molecule.

If enough energy levels of the system are known it is possible to obtain an expression for the partition function of the system,

$$Q(T) = \sum_J \sum_i g_i \exp\left(-\frac{E_i^J}{kT}\right). \tag{37}$$

3. Program structure

Figure 2 gives the structure of the program suite showing how the various modules interconnect. The key program in TRIATOM which has to be run in all cases. Input for TRIATOM is either specified by the user or provided by SELECT which acts as a basis set preprocesser. If a two-step variational calculation is being performed the eigenvalues, eigenvectors and some matrix elements generated by TRIÁTOM are passed to ROTLEVD. The input wavefunctions for DIPOLE come from either TRIATOM or ROTLEVD. DIPOLE processes the wavefunctions in pairs and has to be run for each (J, p, symmetry) $\leftrightarrow$ (J, p, symmetry) block that is to be considered. The output from these runs is concatenated into a single file which forms the input to SPECTRA. If SPECTRA is to compute a partition function, an additional input file from TRIATOM (and ROTLEVD) containing energy levels and quantum numbers is also required.

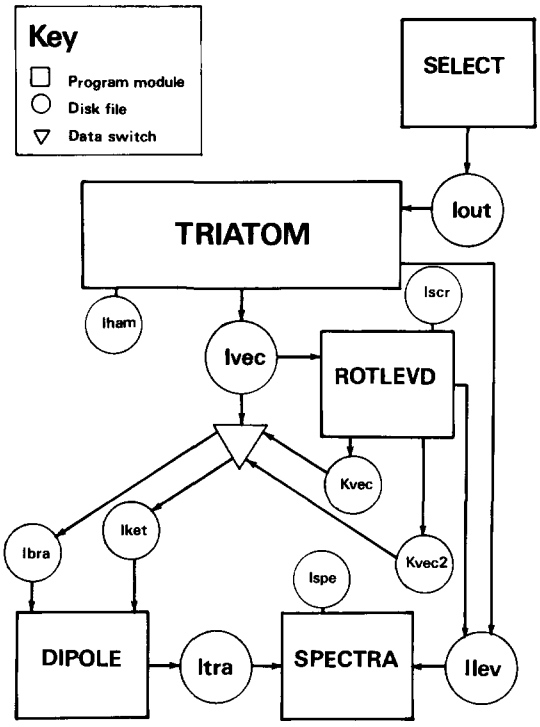

Fig. 2. Program module flow diagram.

Additional card input is needed for all modules. 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.

All the 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. Where possible, constants have been placed in data statements and generic function names have been used to ease conversion between machines with different word lengths.

All programs 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 in subroutine GTMAIN. For efficient storage management a call to a local GETMAIN or MEMORY command should be implemented.

TRIATOM can be divided into four segments which form the basis of a possible overlay structure – see fig. 3. It is convenient to consider each segment in turn as they perform physically distinct stages of the calculation.

3.1. Routines always retained in core

These comprise the main program(s) and several service routines. Subroutine ⟨6⟩ CCMAIN would be the main program if there was no dynamic array allocation (⟨i⟩ represents the ith subroutine in the program source).

⟨1⟩ MAIN reads in namelist data (stored in COMMON/OUTP/) and calls the initialising routines ⟨3⟩ INSIZE, ⟨5⟩ CORE and ⟨30⟩ GTMAIN.

⟨5⟩ CORE calculates storage requirements and sets up array pointers. Entry DYNAM calls

⟨6⟩ CCMAIN if sufficient array space is available.

⟨6⟩ CCMAIN, driver routine which calls the overlaid branches.

⟨24⟩ OUTROW, fast unformatted write.

⟨25⟩ GETROW, fast unformatted read.

⟨31⟩ TIMER, service timing routine. Should be modified to make use of machine routines as appropriate.

⟨32⟩ GTMAIN, FORTRAN version of an assembler routine which request space for the dynamic allocation of storage. The array ARRAY(NAVAIL) should be dimensioned to the limit of the storage available.

3.2. Overlay 1: data input and initialisation

Namelist data which changes the defaults set in ⟨2⟩ BLOCK DATA is read in ⟨1⟩ MAIN. Integer data which characterizes the size of the problem is read in ⟨3⟩ INSIZE, prior to array allocation. The real constants of the problem are read in ⟨7⟩ SETCON. If the basis is selected then ⟨9⟩ BASOUT reads the quantum numbers of the selected functions.

⟨3⟩ INSIZE reads the integer parameters of the problem which are then stored in COMMON /SIZE/. INSIZE includes a BACKSPACE command, which is machine dependent and may need to be removed on certain machines.

⟨4⟩ NSEC determines the size of the secular problem to be solved.

⟨7⟩ SETCON reads in the real constants of the problem, and sets up the coordinate system and the reduced masses (saved in COMMON/MASS/), and the radial basis set parameters (stored in COMMONs/SPLIT1/ and /SPLIT2/).

⟨20⟩ SETFAC uses Pascal's triangle to initialize array BINOM of binomial coefficients.

⟨21⟩ NORMS sets up arrays of pseudo-normalisation constants.

3.3. Overlay 2: radial basis functions and matrix elements

This segment sets up arrays V0, V1, R1M1, R2M1, R1M2, R2M2, HBL1, HBL2, HBL3 and HBL4 which contain all the radial matrix elements required to set up the secular matrix.

⟨8⟩ SYMOUT prints a symmetric matrix stored in lower triangular form.

⟨11⟩ KEINTS forms the analytic matrix elements (HBL1,HBL2) and (HBL3,HBL4) for the Morse-like functions.

⟨12⟩ KEINT2 forms the analytic matrix elements of (HBL2) and (R2M2) for the spherical oscillator functions.

⟨14⟩ LAGPT sets up the radial basis set(s) at the numerical integration points and forms matrix elements over the potential (V0,V1) and inverse powers of r for the Morse-like functions (R1M1,R1M2,R2M1,R2M2).

⟨15⟩ LAGUER, adaptation [9] of the Gauss–Laguerre integration points and weights routine of Stroud and Secrest [32] for large α. Note that the initial guess formulae are arbitrary and may need to be adjusted. The ith call returns the ith point and weight.

⟨16⟩ LGROOT improves the guess to the integration point [32].

⟨17⟩ LGRECR uses recurrence relations to generate orthogonal polynomials [32].

⟨26⟩ POT returns the potential in the form of eq. (16) at the specified (r_1, r_2). If ZLPOT.EQ.TRUE this routine must be user supplied, see section 4.1. If ZLPOT.EQ.FALSE then POT calls ⟨33⟩ POTV at (r_1, r_2, x_i), where x_i ($= \cos\theta$) is a Gauss–Legendre integration point.

⟨27⟩ LEGPT sets up Gauss–Legendre integration points and weights; an adaptation of subroutine JACOBI [32].

⟨28⟩ LEGEND sets up weighted normalised Legendre polynomials.
⟨29⟩ LEGS calculates Legendre polynomials.
⟨32⟩ POTV, user supplied potential subroutine, see section 4.1.

3.4. Overlay 3: angular integration and secular matrix construction

This segment constructs a basis set, performs the analytic angular integration and constructs the Hamiltonian matrix HAMIL. Note that if input is being prepared for ROTLEV (ZROT.EQ.TRUE) then ⟨6⟩ CCMAIN loops over this and the following segment.

⟨9⟩ BASOUT prints basis set labels either read in from SELECT or generated by ⟨10⟩ BASGEN.
⟨10⟩ BASGEN generates basis set labels.
⟨14⟩ MATRG performs the angular integration and forms the lower triangle of the Hamiltonian matrix.
⟨19⟩ VTOT performs the angular integration over the potential.
⟨20⟩ GAUNT calculates Gaunt coefficients, eq. (17).

3.5. Overlay 4: diagonalisation

This segment handles diagonalisation of the secular matrix.

⟨23⟩ DGCORE controls the call to the in-core diagonaliser and prints the results.
⟨24⟩ NORM, normalisation routine, not required if a diagonaliser is used which returns eigenvectors normalised to unity.
⟨33⟩ EIGSFM, this is a mock-up of an EISPACK routine of the same name [33] which calls routines ⟨34⟩–⟨44⟩ to perform the diagonalisation. These routines may be beneficially replaced by a symmetric matrix diagonalisation suite appropriate to the machine being used.

3.6. Routines for SELECT

SELECT is composed mainly of routines adapted from TRIATOM. Its structure is given by fig. 3, except that segment 4 is replaced by a call to ⟨22⟩ SORT. As only the diagonal elements of HAMIL and hence the matrix element arrays are needed by SELECT, it is unlikely that an overlay will be required for this step. The routines listed below are the only ones that are substantially different from the routines found in TRIATOM.

⟨1⟩ SELECT reads in data controlling basis set selection (stored in COMMON/SELEC/). It includes a machine dependent BACKSPACE command.
⟨8⟩ BASOUT writes out data for TRIATOM including selected basis function labels.
⟨22⟩ SORT chooses functions which satisfy selection criteria and sorts them according to increasing $|k|$ and then increasing j (a requirement for TRIATOM).

3.7. Routines for ROTLEVD

Figure 4 gives the structure of program ROTLEVD. Routines which have the same name as routines in TRIATOM serve the same purpose and will not be considered below.

⟨6⟩ VRMAIN, driver routine which would be the main program if there was no dynamic storage allocation.
⟨7⟩ SELECT determines the vibrational basis functions to be used.
⟨8⟩ WRTBAS prints the basis set labels.
⟨9⟩ WRTHAM prints the Hamiltonian matrix if requested.

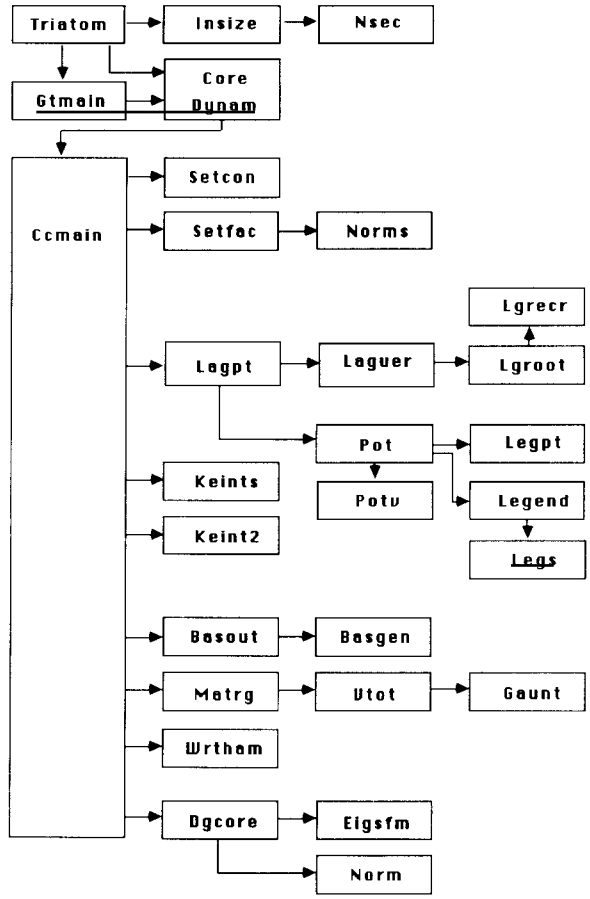

Fig. 3. Structure of program TRIATOM. Service routines TIMER, GETROW and OUTROW have been omitted.

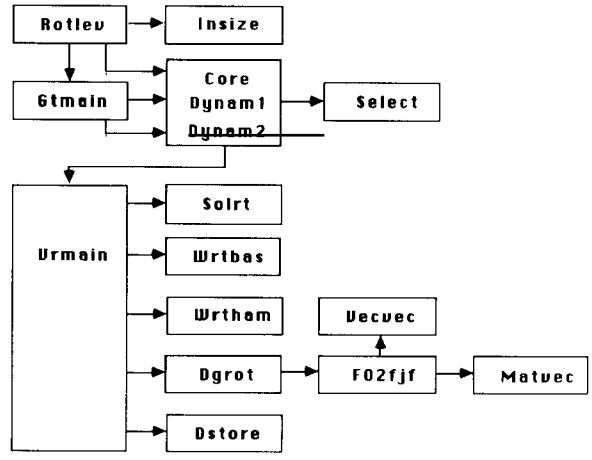

Fig. 4. Structure of program ROTLEVD. Service routines as in TRIATOM, plus MXMB and RDIVEC have been omitted.

⟨10⟩ SOLRT reads matrix elements, eigenvalues and eigenvectors from TRIATOM. Constructs the diagonal (array DIAG) and non-zero off-diagonal (OFFDG) matrices [30].

⟨11⟩ DGROT sets up the diagonalisation including shifting the diagonal elements so the highest is zero, which ensures that ⟨18⟩ F02FJF returns the lowest eigenvalues. DGROT contains a machine dependent BACKSPACE command.

⟨12⟩ DSTORE transform the eigenvectors back to the vibrational basis, see eq. (29).

⟨14⟩ RDIVEC reads the header from stream IVEC.

⟨16⟩ VECVEC, dot product for ⟨18⟩ F02FJF.

⟨17⟩ MATVEC performs the vector matrix multiplication required by ⟨17⟩ F02FJF taking advantages of the structure of the Hamiltonian.

⟨18⟩ F02FJF–⟨46⟩G05CAF are a NAG Library [34] subroutine suite for diagonalising sparse matrices, based on the algorithm of Nikolai [35]. The implementation given here is appropriate for IBM machines and it is recommended that users replace this by a local implementation where possible.

⟨48⟩ MXMB, fast vector matrix multiplier. This routine uses the bulk of the CPU time [21] and thus may need optimising for the architecture of any particular machine.

3.8. Routines for DIPOLE

Figure 5 gives the structure of program DIPOLE. Many of the routines used in DIPOLE are the same, or very similar, to those used in TRIATOM for the evaluation of the integrals over the potential energy surface, the main difference being that the dipole moment operator is a vector. In addition, the fact that

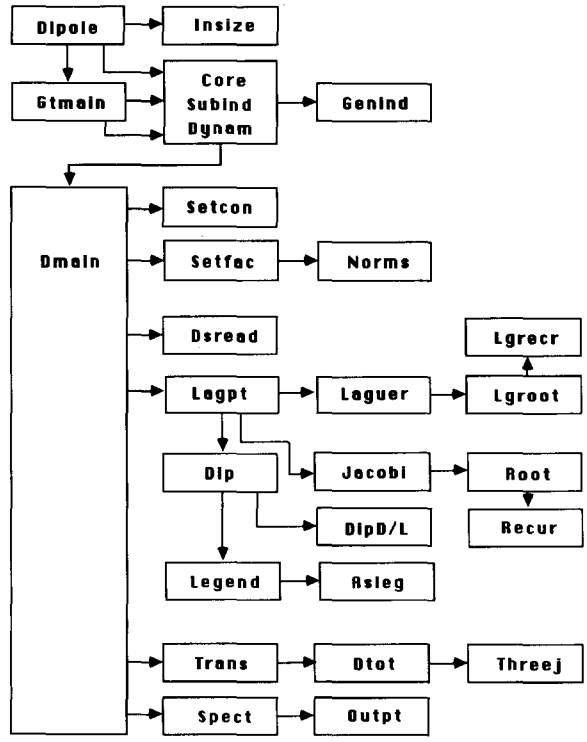

Fig. 5. Structure of program DIPOLE. Service routines have been omitted.

the ket and bra states considered are generated in separate TRIATOM/ROTLEVD jobs means that extra checks on compatibility are carried out in subroutine INSIZE (⟨3⟩). Subroutines RDIVEC and MXMB, described in ROTLEVD, are also used. The new routines are:

⟨6⟩ GENIND generates the indices used to evaluate the integrals from the basis function labels supplied from TRIATOM/ROTLEVD.

⟨7⟩ DMAIN, the main driver routine, responsible for correctly aligning the k-components of the bra and ket and the z- and x-components of the dipole.

⟨16⟩ DIP, analogous to POT in TRIATOM for ZLPOT false. Uses Gauss–Jacobi integration to evaluate the angular expansion.

⟨18⟩ ASLEG generates Associated Legendre polynomials $P_l^m(\cos\theta)$ with a factor of $\sin^{2m}\theta$ removed.

⟨19⟩ JACOBI sets up Gauss–Jacobi points and weights [29].

⟨20⟩ ROOT improves the guess to the integration point.

⟨21⟩ RECUR uses recurrence relations to generate orthogonal polynomials.

⟨22⟩ TRANS calculates the transition moment stepwise over the bra and ket using the basis function indices generated by GENIND.

⟨23⟩ DTOT performs the angular integration over the dipole.

⟨24⟩ THREEJ calculates the 3-j symbols used in DTOT.

⟨25⟩ DSREAD reads in the vector coefficients (for bra and ket).

⟨29⟩ SPECT calculates transition frequencies, line strengths and Einstein A-coefficients.

⟨30⟩ OUTPT writes the above data to stream ITRA. It includes a machine dependent BACKSPACE command.

⟨31⟩ DPRINT prints out the dipole matrix elements produced by LAGPT (for debugging purposes).

⟨33⟩ DIPD contains the unexpanded dipole surface (if ZLPOT is false).

⟨34⟩ DIPL contains the dipole surface expanded in Associated Legendre polynomials (if ZLPOT is true).

3.9. Routines for SPECTRA

The structure of program SPECTRA is very straightforward and a diagram is not given. It uses routines to allocate memory and input data with the same names as those in TRIATOM. These have identical or near identical structures to the TRIATOM routines. Routines unique to SPECTRA are as follows:

⟨1⟩ SPECT reads program data needed to set up core.

⟨2⟩ SPMAIN is the main driving routine.

⟨3⟩ SORTSP sorts out the transitions on ascending frequency.

⟨4⟩ PFCALC calculates the partition function at the appropriate temperature.

⟨5⟩ SPECTM calculates the absolute and relative intensities of transitions specified in the range required.

4. Program use

4.1. The potential and dipole subroutines

Both TRIATOM and SELECT require a user supplied potential energy subroutine. There are two ways of supplying the potential. If it is specified as a Legendre expansion, eq. (15), 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 |IDIA| = 2, only even V_λ are needed. If NCOORD = 1, R1 and VL are dummies. If NCOORD = 2, R1 contains the rigid diatom bondlength r_e. If NCOORD > 1 then V_λ 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 gives by R1 = r_1, R2 = r_2 (both in Bohr) and XCOS = cos θ.

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 = ν = 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 ν = 1, D0 is not required. If |IDIA| = 2, only terms with λ even are required.

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 NUth 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 θ where NU = 0 corresponds to μ_z and NU = 1 to μ_x.

TRIATOM, SELECT and DIPOLE include COMMON/MASS/XMASS(3),G1,G2 to enable users to write flexible potential subroutines which allow for changes in coordinates or isotopic substitution. (See, for example, the version of POTV supplied.) In DIPOLE, ZEMBED is passed in COMMON/LOGIC/, allowing proper account of the embedding to be taken.

4.2. Input for TRIATOM

TRIATOM requires 8 lines of input for *all* runs, extra lines are required if the basis set is selected. Lines giving data not required or for which the defaults [given below in parenthesis] are sufficient should be left blank. Triatom input can optionally all be generated by SELECT.

Line 1: NAMELIST/PRT/

ZPHAM[F]	= T requests printing of the Hamiltonian matrix.
ZPRAD[F]	= T requests printing of the radial matrix elements.
ZPMIN[F]	= T requests only minimal printing.
ZPVEC[F]	= T requests printing of the eigenvectors.
ZDIAG[T]	= T requests diagonalisation of Hamiltonian matrix.
ZROT[F]	= T, TRIATOM to perform first step in a two-step variational calculation.
ZLADD[F]	= T, maximum j in angular basis (LMAX) incremented with (J, k);
	= F, maximum j fixed (only used if ZROT = T).
ZEMBED[T]	= T, z axis embedded along r_2;
	= F, z axis embedded along r_1.
ZMORSE[T]	= T, use Morse oscillator-like functions for r_2 coordinate;
	= F, use spherical oscillator functions (only allowed if IDIA > 0).
ZLPOT[F]	= T, potential supplied in POT;
	= F, potential supplied in POTV.

ZVEC[F] = T, data for ROTLEVD or DIPOLE to be written to stream IVEC.
IVEC[4] stream for ROTLEVD or DIPOLE data.
ZPFUN[F] = T, eigenvalues concatenated on stream ILEV. Warning, the first eigenvalues on this file must be for J = 0, j even.
ILEV[4] stream for eigenvalue data.
IHAM[10] stream for Hamiltonian matrix.

Line 2: NCOORD (I5)
NCOORD[3] the number of vibrational coordinates of the problem:
= 1 for a diatomic (is useful for basis set optimisation);
= 2 for an atom rigid diatom system (not valid for |ISYM| = 2);
= 3 for a full triatomic.

Line 3: NPNT2,NMAX2,JROT,NEVAL,LMAX,LPOT,IDIA,KMIN,NPNT1,NMAX1,ISYM,NBASS, NRAD(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] |JROT| is the total angular momentum quantum number of the system:
> 0, the off-diagonal Coriolis terms are included;
< 0, they are neglected and k (KMIN) is treated as a good quantum number;
= 0 or NCOORD = 1, there are no Coriolis terms.
NEVAL[0] number of eigenvalues and eigenvectors required.
If NCOORD = 1, the rest of the line is ignored.
LMAX order of the highest associated Legendre polynomials in the basis.
If IDIA = 2, the parity of the angular basis is given by the parity of LMAX.
LPOT[2*LMAX2], highest value of λ in the Legendre expansion of the potential . If ZLPOT = T, LPOT must be consistent with subroutine POT. If ZLPOT = F, ((LPOT + 2)/2)*2 point Gauss–Legendre integration is used for the θ-coordinate.
IDIA = −1 for generalised coordinates;
= 0 for Radau or other orthogonal coordinates;
= 1 for scattering coordinates with a hetronuclear diatomic;
= 2 for scattering coordinates with a homonuclear diatomic;
= −2 for midpoint coordinates with a symmetric potential (eg. where the symmetry has been broken by isotopic substitution).
KMIN = k for JROT < 0;
= $(1 - p)$ for JROT > 0 (including ZROT = T).
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.
ISYM[0] ≠ 0 for bondlength-bondangle coordinates ($g_1 = g_2 = 0$) or other symmetric cases ($g_1 = g_2$);
= 1 for hetronuclear case;
= 2 for symmetric AB_2 case;
= −2 for anti-symmetric AB_2 case.
|ISYM| = 2 cannot be used with JROT > 0 or ZROT = T.
NBASS[0] number of basis functions in the secular problem:
= 0 determined internally;
> 0 basis preselected and to be read in (see card 9).

NRAD[0] largest number of radial functions in any block:
if NBASS = 0, set internally as (NMAX1 + 1)*(NMAX2 + 1);
if NBASS > 0, must be specified.

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

Line 5: (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.

Line 6: G1,G2 (2F20.0)
Parameters g_1 and g_2 determine the coordinate system used if IDIA = −1 or IDIA = 0 and ISYM = 1. Otherwise this line is ignored and:
if IDIA > 0, G1 = $m_2/(m_2 + m_3)$, G2 = 0;
if IDIA = −2, G1 = $\frac{1}{2}$, G2 = 0;
if IDIA = 0 and ISYM = ±2, G1 = G2 = $1 + s - (s^2 + 2s)^{1/2}$, where $s = m_3/m_2$;
if ISYM = ±2 then $G_2 = G_1$.

Line 7: RE1,DISS1,WE1 (3F20.0)
If NCOORD = 1, this line 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 = ω_e are Morse parameters for the r_1 coordinate.

Line 8: RE2,DISS2,WE2 (3F20.0)
If |ISYM| = 2, this line is read but ignored.
If ZMORSE = T, RE2 = r_e, DISS2 = D_e and WE2 = ω_e are Morse parameters for the r_2 coordinate.
If ZMORSE = F, RE2 is ignored; DISS2 = β and WE2 = ω_e are spherical oscillator parameters for the r_2 coordinate.

Line 9 onwards: (IK(I,IL(I),IM(I),IN(I),I = 1,NBASS) (36I2)
If NBASS = 0, not read.
If NBASS > 0, basis set labels as generated by SELECT:
IK(I) = k, IL(I) = j, IM(I) = $m + 1$ and IN(I) = $n + 1$
for the Ith basis function.

4.3. Input for SELECT

Line 1: LBASS, NQMAX,NQJ,NQM,NQN,IFLAG,IOUT (7I5)
LBASS[0] select the LBASS lowest basis functions ordered by their diagonal elements.
NQMAX[0] = N_{max}, maximum total quantum number for a basis function.
NQJ[1] = d_j, weight of $P_{jk}(\theta)$ in determining NQMAX.
NQM[1] = d_m, weight of $H_m(r_1)$ in determining NQMAX.
NQN[1] = d_n, weight of $H_n(r_2)$ in determining NQMAX.
IFLAG[0] ≠ 0: select basis for different (J, k) or symmetry than the full calculation.
IOUT[7] output stream for TRIATOM data file.

Lines 2–9 These are the same as lines 1–8 of the TRIATOM input, except:
If IFLAG > 0, then TRIATOM card 3 is repeated: first to characterise the basis for the selection run, second to characterise the TRIATOM run.
If NQMAX > 0, then NMAX1 and NMAX2 default to NQM * NQMAX and NQN * NQMAX, respectively.

4.4. Input for ROTLEVD

Most of the data for ROTLEVD, which must have been prepared previously by TRIATOM, is read from stream IVEC. Three lines of data are read in.

Line 1: NAMELIST/PRT/
TOLER[0.0D0] tolerance for convergence of the eigenvalues, zero gives machine accuracy.
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.
ZVEC[F] = T, eigenvalue and eigenvector data to be written to disk file. (= T forced if ZTRAN = T).
JVEC[3] stream for first set of eigenvalue and eigenvector output.
JVEC2[7] stream for second set of eigenvalue and eigenvector output (KMIN = 2).
ZTRAN[F] = T, eigenvectors transformed back to original basis.
KVEC[8] stream for first set of transformed eigenvector output.
KVECZ[9] stream for second set of transformed eigenvector output (KMIN = 2).
ISCR[1] stream for scratch file storing array OFFDG.
IRES[0] restart flag:
= 1, full restart (stream ISCR must be supplied);
= 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.

Line 2: NVIB,NEVAL,KMIN,IBASS,NEVAL2 (5I5)
NVIB number of vibrational levels from TRIATOM for each k to be read, and perhaps selected from, in the second variational step.
NEVAL[10] the number of eigenvalues required from the first diagonalisation.
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 from the second diagonalisation.

Line 3: TITLE (9A8)
A 72 character title.

4.5. Line input for DIPOLE

DIPOLE processes batches of transitions between states defined by the the bra and ket input files. These files are produced either by TRIATOM – stream IVEC – or ROTLEVD – stream JVEC or JVEC2. They contain most of the data necessary to characterise the run. This data must be consistent which means that runs creating the bra and ket files must have identical input for lines 5–9 in TRIATOM, otherwise an error condition will result. To generate transitions with $\Delta J = 0$, $\Delta p = 0$, the same input files should be used for the bra and ket. In this case the diagonal transition dipoles are simply the vibrational averaged dipoles of the relevant state.

The user must supply the following three lines of input:

Line 1: NAMELIST/PRT/

ZLPOT[F] = T, the dipole surfaces supplied in DIPL;
= F, the dipole surfaces supplied in DIPD.

ZPRINT[F] = T supplies extra print out for debugging purposes.

ZTRA[F] = T writes data for SPECTRA to stream IOUT.

ZSTART[F] = T to initiate the output file for the data for SPECTRA;
= F, data is written to the end of existing file on stream ITRA.

IKET[11] input stream from TRIATOM/ROTLEVD for the ket.

IBRA[12] input stream for the bra.

ITRA[13] output stream to SPECTRA (if ZTRA = T).

Line 2: TITLE (9A8)
A 72 character title.

Line 3: LPOT,NPNT1,NPNT2,NV1,NV2 (5I5)

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 + 2)/2)*2) point Gauss–Legendre integration is used for the θ coordinate.

NPNT1[2*NMAX1 + 1], order of Gaussian quadrature in the r_1 coordinate.

NPNT2[2*NMAX2 + 1], order of Gaussian quadrature in the r_2 coordinate.

NV1[all] number of ket eigenfunctions considered.

NV2[all] number of bra eigenfunctions considered.

Input and output on streams IKET, IBRA and ITRA are in atomic units. The data printed at the end of DIPOLE are given in wavenumbers and Debye.

4.6. Line input for SPECTRA

SPECTRA takes most of its input from stream ITRA generated by DIPOLE. Data for generating partition functions may optionally be provided by TRIATOM/ROTLEVD stream ILEV. The user must supply at least 4 (3 if ZSPE = F or ZSORT = F) cards in input, cards 5 and 6 can be repeated to generate spectra from the same transitions for different conditions.

Line 1: NAMELIST/PRT/

ZOUT[F] = T, print sorted transition frequencies and line strengths.
ZOUT is set automatically to T if ZSPE is F.

ZSORT[T] = T, sort transition data and write it to stream ISPE;
= F, sorted transition data is to be read from stream ISPE.
ZSPE[T] = F, if the program is to stop after sorting only.
ZPFUN[T] = T, calculate the partition function from data on stream ILEV;
= F, the partition function is not calculated but set to 1.0
ITRA[13] input stream from DIPOLE containing the transitions of interest.
ILEV[14] input stream for the energy levels appropriate for the partition function.
The first eigenenergy on ILEV must be the ground state for $J = 0$, (j = even).
This is the zero energy of the problem.
ISPE[15] stream for the sorted transitions.

Line 2: TITLE (9A8)
A 72 character title.

Line 3: NAMELIST/SOR/
If ZSORT = F this line should not be supplied.
EMIN[−1.0D27], minimum value of the ket energy E'' in cm^{-1} for which data is to be printed.
EMAX[+1.0D27], maximum value of the ket energy E'' in cm^{-1} for which data is to be printed.
JMAX[all] maximum value of J'', the ket angular momentum, for which data is to be printed.
SMIN[0.0] lowest relative linestrength to be printed out.

Line4: GE,GO (2D10.0)
GE[1.0D0] nuclear-spin times symmetry-degeneracy factors for homonuclear diatomic-containing molecules for the j even states.
GO[1.0D0] nuclear-spin times symmetry-degeneracy factors for homonuclear diatomic-containing molecules for the j odd states.

Line 5: TEMP,XMIN,WMIN,WMAX (4D10.0)
TEMP temperature in K.
XMIN lowest relative intensity to be printed out.
WMIN[0.0] minimum transition frequency required in cm^{-1}.
WMAX[1.0D27], maximum transition frequency required in cm^{-1}.

Line 6: NAMELIST/SPE/
EMIN[−1.0D27], minimum value of the ket energy E'' in cm^{-1} for which data is to be printed.
EMAX[+1.0D27], maximum value of the ket energy E'' in cm^{-1} for which data is to be printed.
JMAX[all] maximum value of J'', the ket angular momentum, for which data is to be printed.

Lines 5 and 6 are repeated for each set of spectral conditions required.

4.7. Test input

A test run of the full SELECT, TRIATOM, ROTLEVD, DIPOLE and SPECTRA suite for the H_2S molecule has been prepared using the potential and dipole surfaces of Senekowitsch et al. [36]. These surfaces were recently used to benchmark the codes presented here [37]. The example input file given below calculates the energy levels and allowed transitions for the molecule for $J = 0$ and 1, for the ground state, ν_2, $2\nu_2$, ν_1 and ν_3 vibrational manifolds. The spectrum is calculated for a temperature of 10 K.

The input file is designed to run on the Cray-XMP 48 at RAL, which uses a IBM 3900 as a "front end". The job control language sequence, written in Cray JCL, is numbered M. Input data, which is not machine dependent, is numbered *N.

Datasets which contain the program modules are FETCHed from the front end, compiled using CFT and run using LDR. If a program is to be run more than once, the absolute binary, AB, is given a name and it can be run again simply by repeating that name (e.g. lines 13 and 23 for TRIATOM). Input and output streams are ASSIGNed so that data generated in one module can be passed to another. Files are RELEASEd as soon as possible in order to cut down the amount of on-line disk space used by the job.

Program SELECT is run for the $J = 0$ run in line 7. The program reads lines *1 to *9 (see sections 4.2 and 4.3 for details). Line *1 indicates that the lowest 400 basis functions are required to be passed to the full calculation to be carried out in program TRIATOM. All the output from this SELECT run is to be passed to TRIATOM on stream 7. TRIATOM is then run from line 13. The eigenvectors generated are stored on stream 11, the value given to IVEC in line *2. With ZPFUN = .TRUE. (line *2), the energy levels are stored on stream 14 (the default).

For the $J = 1$ runs, SELECT is run from line 21. It reads data from lines *10 to *19. Note that this time the value of IFLAG is set at 1, indicating that the parameters for which the basis functions are SELECTed are different from the final run. In this case, we are SELECTing basis functions for $J = 0$ to use for a $J = 1$ calculation. Line *14 is therefore a repeat of *13, with the value of J changed from 0 to 1. (See section 4.3.)

TRIATOM is run again from line 23. In this example, this module only completes the non-Coriolis coupled part of the calculation, since ZROT = .TRUE. (line 11), producing the 200 lowest levels for each value of $k(= 0,1)$.

The full, Coriolis-coupled calculation is run using ROTLEVD from line 31. ROTLEVD reads lines *20 to *22 (see section 4.4), and the eigenvectors for the e (basis functions with $k = 0$, 1, parity $p = 0$) and f (basis functions with $k = 1$ only, parity $p = 1$) symmetry states are stored on streams 8 and 9, respectively.

Dipole transitions for $J = 0$ to $J = 1e$ states are computed using DIPOLE from line 37. For this run, DIPOLE reads lines *23 to *25 (see section 4.5). Since this is the first time the module is run. ZSTART = .TRUE., (line *23). The transitions are stored on ITRA, stream 13.

To compute the $J = 1e$ to $J = 1f$ transitions, DIPOLE is run again from line 42, reading lines *26 to *28. The transitions are written onto stream 13, after those for the previous DIPOLE computation.

Finally, the spectrum of the computed transitions is computed using SPECTRA, run from line 47. SPECTRA reads the last six lines of data, line *29 to *34, computing just the one spectrum for $T = 10$ K.

4.8. Sample output

A much truncated sample output is given in the test run output at the end of this paper, produced by running the test input given above. The output shows all the major features of the suite: SELECTion criteria, the use of TRIATOM to calculate non-Coriolis intermediate basis functions for ROTLEVD, DIPOLE transitions, and SPECTRA output.

Full outputs from the above test input maybe obtained from the authors on request.

4.9. Machine dependency

There is one operation only contained within this program suite which is genuinely machine dependent. That is the use of the BACKSPACE command within the FORTRAN code (subroutines which have this command are noted in section 3).

The command is needed when reading files to the end prior to writing additional data. Cray computers read the file to the end, including the end-of-file marker. It is therefore necessary *within the FORTRAN*

program itself to BACKSPACE the file before the next set of data can be written onto it. For FORTRAN implementations on many computers, including Vax and Convex machines, however this is not the case and the appropriate line(s) should be "commented out".

Acknowledgement

We would like to thank Dr. Brian Sutcliffe for helpful discussions during the course of this work and NAG for permission to publish their routines. We would also like to thank Joerg Senekowitsch for permission to use his H_2S surfaces prior to publication.

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TEST RUN INPUT

```
JOB,US=SM7,JN=H2STEST,T=250,MFL=500000.                                  #1
ACCOUNT,AC=CRAY29,UPW=ZUGSWANG                                           #2
FETCH,DN=SELH2S,TEXT='FN=SELECT,FT=CPC,TID=SM7'.                         #3
FETCH,DN=TRIH2S,TEXT='FN=TRIATOM,FT=CPC,TID=SM7'.                        #4
ASSIGN,DN=DATA,A=FT07.                                                   #5
CFT,I=SELH2S,OFF=P,L=0.                                                  #6
LDR,AB=SELECT.                                                           #7
REWIND,DN=DATA.                                                          #8
ASSIGN,DN=DATA,A=FT05.                                                   #9
ASSIGN,DN=H2SOE,A=FT11.                                                  #10
ASSIGN,DN=H2SILEV,A=FT14.                                                #11
CFT,I=TRIH2S,OFF=P,L=0.                                                  #12
LDR,AB=TRIATOM.                                                          #13
REWIND,DN=H2SOE.                                                         #14
REWIND,DN=H2SILEV.                                                       #15
RELEASE,DN=SELH2S.                                                       #16
RELEASE,DN=TRIH2S.                                                       #17
RELEASE,DN=DATA.                                                         #18
ASSIGN,DN=$IN,A=FT05.                                                    #19
ASSIGN,DN=DATA,A=FT07.                                                   #20
SELECT.                                                                  #21
REWIND,DN=DATA.                                                          #22
ASSIGN,DN=DATA,A=FT05.                                                   #23
TRIATOM.                                                                 #24
RELEASE,DN=DATA.                                                         #25
ASSIGN,DN=$IN,A=FT05.                                                    #26
ASSIGN,DN=H2S1EE,A=FT08.                                                 #27
ASSIGN,DN=H2S1EF,A=FT09.                                                 #28
FETCH,DN=ROTH2S,TEXT='FN=ROTLEVD,FT=CPC,TID=SM7'.                        #29
CFT,I=ROTH2S,OFF=P,L=0.                                                  #30
LDR.                                                                     #31
REWIND,DN=H2SILEV.                                                       #32
REWIND,DN=H2S1EE.                                                        #33
REWIND,DN=H2S1EF.                                                        #34
ASSIGN,DN=H2STRAN,A=FT13.                                                #35
FETCH,DN=DIPH2S,TEXT='FN=DIPOLE,FT=CPC,TID=SM7'.                         #36
CFT,I=DIPH2S,OFF=P,L=0.                                                  #37
LDR,AB=DIPOLE.                                                           #38
REWIND,DN=H2S1EE.                                                        #39
REWIND,DN=H2STRAN.                                                       #40
RELEASE,DN=DIPH2S.                                                       #41
DIPOLE.                                                                  #42
RELEASE, DN=H2SOE:H2S1EE:H2S1EF.                                         #43
REWIND,DN=H2STRAN.                                                       #44
FETCH,DN=SPEH2S,TEXT='FN=SPECTRA,FT=CPC,TID=SM7'.                        #45
CFT,I=SPEH2S,OFF=P,L=0.                                                  #46
LDR.                                                                     #47
/EOF
  400                                                                    *1
 &PRT ZPMIN=.TRUE., ZVEC=.TRUE., ZPFUN=.TRUE., IVEC=11, &END             *2
   3                                                                     *3
  13    7    0    5   24   50   -1    0   13    7    1                  *4
H2S: J=0 USING BONDLENGTH-BONDANGLE COORDINATES                          *5
     1.007825            1.007825            31.972071                 *6
                                                                         *7
       2.75                0.1                 0.01                    *8
       2.75                0.1                 0.01                    *9
  400                        1                                         *10
 &PRT ZPMIN=.TRUE., ZROT=.TRUE., ZVEC=.TRUE., &END                       *11
   3                                                                     *12
  13    7    0   20   24   50   -1    0   13    7    1                  *13
  13    7    1  200   24   50   -1    1   13    7    1                  *14
H2S: J=1 USING BONDLENGTH-BONDANGLE COORDINATES                          *15
     1.007825            1.007825            31.972071                 *16
                                                                         *17
       2.75                0.1                 0.01                    *18
       2.75                0.1                 0.01                    *19
 &PRT TOLER=1.0D-4, ZTRAN=.TRUE., ZPFUN=.TRUE., &END                     *20
  200   10    2  350    5                                               *21
 H2S J=1, BLBA CO-ORDINATES                                              *22
 &PRT ZSTART=.TRUE., ZTRA=.TRUE., IBRA=8, &END                           *23
H2S OE TO 1E TRANSITIONS; GENERAL G1,G2; BLBA COORDS.                    *24
   50                                                                    *25
 &PRT ZTRA=.TRUE., IKET=8, IBRA=9, &END                                  *26
H2S 1E TO 1F TRANSITIONS; GENERAL G1,G2; BLBA COORDS.                    *27
   50                                                                    *28
 &PRT ZOUT = .TRUE., &END                                                *29
 H2S SPECTRUM FOR J=0 AND 1 LEVELS.
 &SOR &END                                                               *31
 1.0          1.0                                                        *32
 10.00     0.00001    0.0       10000.0                                 *33
 &SPE EMIN=-1.0, EMAX=10000.0, JMAX=1, &END                              *34
/EOD
```

TEST RUN OUTPUT

```
     PROGRAM SELECT (VERSION OF FEB 12, 1989)

     BASIS SET SELECTION PROGRAM:
     8 LINES OF INPUT DATA TRANSFERED TO STREAM  7

     SELECTION CRITERIA:
     LOWEST  400 BASIS FUNCTIONS CHOSEN

     FULL TRIATOMIC VIBRATIONAL PROBLEM WITH

       13   POINT NUMERICAL INTEGRATION FOR
        7   TH ORDER R1 RADIAL BASIS FUNCTIONS
       13   POINT NUMERICAL INTEGRATION FOR
        7   TH ORDER R2 RADIAL BASIS FUNCTIONS
       24   TH ORDER ANGULAR BASIS FUNCTIONS
       50   TERMS IN THE POTENTIAL EXPANSION
     1600   CANDIDATE BASIS FUNCTIONS

     TITLE: H2S: J=0 USING BONDLENGTH-BONDANGLE COORDINATES

     LOWEST  400 FUNCTIONS SELECTED FROM    0.5129180405E-01 HARTREE TO    0.1332150739E+00 HARTREE

      BASIS SET LIMITS RESET:
     LMAX  WAS   24 RESET TO   24
     NMAX1 WAS    7 RESET TO    6
     NMAX2 WAS    7 RESET TO    6
     NBASS WAS 1600 RESET TO  400

     PROGRAM TRIATOM (VERSION OF DEC 8, 1988)

LOWEST   5 EIGENVALUES IN WAVENUMBERS

 0.329745990315E+04      0.448790120742E+04      0.566949192399E+04      0.591788890978E+04      0.592844088439E+04

     TITLE: H2S: J=1 USING BONDLENGTH-BONDANGLE COORDINATES

     ***  VIBRATIONAL PART OF ROT-VIB CALCULATION  ***
                  J =  1  K =  0
     ***  OPTION TO NEGLECT CORIOLIS INTERACTIONS  ***

LOWEST 200 EIGENVALUES IN WAVENUMBERS

 0.331642053156E+04      0.450676728552E+04      0.568826443613E+04      0.593656353963E+04      0.594713004646E+04

     ***  VIBRATIONAL PART OF ROT-VIB CALCULATION  ***
                  J =  1  K =  1
     ***  OPTION TO NEGLECT CORIOLIS INTERACTIONS  ***

LOWEST 200 EIGENVALUES IN WAVENUMBERS

 0.331679093974E+04      0.450779599475E+04      0.568999053004E+04      0.593694210142E+04      0.594748093466E+04

     PROGRAM ROTLEVD (VERSION OF DEC 12, 1989):

     ROTATIONAL PART OF ROT-VIB CALCULATION  WITH:
      200   LOWEST VIBRATIONAL EIGENVECTORS SUPPLIED FROM
      400   DIMENSION VIBRATION SECULAR PROBLEM
      200   LOWEST VIBRATIONAL EIGENVECTORS ACTUALLY USED
       10   LOWEST ROTATIONAL EIGENVECTORS REQUIRED FOR
      350   DIMENSION ROTATION SECULAR PROBLEM

           WITH BASIS SELECTED BY ENERGY ORDERING

     J =  1 ROTATIONAL STATE,    350 BASIS FUNCTIONS
           E PARITY, SYMMETRIC |JK> + |J-K> FUNCTIONS IN BASIS

LOWEST  10 EIGENVALUES IN WAVENUMBERS

 0.331115089162E+04      0.331253715324E+04      0.450172631309E+04      0.450328597011E+04      0.568346814977E+04

 0.568521052154E+04      0.593138625751E+04      0.593273977642E+04      0.594200224037E+04      0.594325623163E+04

     J =  1 ROTATIONAL STATE,    173 BASIS FUNCTIONS
           F PARITY, ANTI-SYMMETRIC |JK> - |J-K> FUNCTIONS IN BASIS

LOWEST   5 EIGENVALUES IN WAVENUMBERS

 0.331679093974E+04      0.450779599475E+04      0.568999053004E+04      0.593694210142E+04      0.594748093466E+04
```

```
 PROGRAM DIPOLE (VERSION OF FEB 12, 1989):

 H2S OE TO 1E TRANSITIONS; GENERAL G1,G2; BLBA COORDS.

 DIATOMIC PARAMETER IDIA  =  -1
 PARITY OF KET ANGULAR BASIS  0
 NUMBER OF CO-ORDINATES   =   3
 SYMMETRY PARAMETER ISYM  =   1
 Z AXIS EMBEDDED ALONG R2 CO-ORDINATE
 MORSE FUNCTIONS IN RADIAL BASIS SET
 NUMBER OF TERMS IN THE DIPOLE EXPANSION =   50

     PARAMETERS PASSED TO DIPOLE FOR THE KET & THE BRA

 TOTAL NUMBER OF BASIS FUNCTIONS     =   400     766
 NUMBER OF R1 RADIAL FUNCTIONS       =     7       7
 NUMBER OF R2 RADIAL FUNCTIONS       =     7       7
 NUMBER OF ANGULAR FUNCTIONS         =    24      24
 TOTAL ANGULAR MOMENTUM (ABS VAL)    =     0       1
 ANGULAR MOMENTUM (-VE = NO COR.)    =     0       1
 KMIN= 1-P, WHERE J + P IS PARITY,   =     1       1
 TOTAL VIB-ROT FUNCTIONS AVAILABLE   =     5      10
 VIB-ROT FUNCTIONS TAKEN (0 = ALL)   =     0       0

  ************************************************

 PRINT OUT OF DIPOLE TRANSITION MOMENTS AND S(F-1)

     FREQUENCIES IN WAVENUMBERS
     TRANSITION MOMENTS IN DEBYE (2.54174A.U.)
     S(F-I) IN DEBYE**2
     EINSTEIN A-COEFFICIENT IN SEC-1

 ************************************************

IE1 IE2   KET ENERGY    BRA ENERGY    FREQUENCY  Z TRANSITION    X TRANSITION      DIPOLE        S(F-I)       A-COEFFICIENT
  1   1     3297.460      3311.151       13.691  -0.487134E+00   0.486871E+00  0.263136E-03  0.692406E-07  0.185757E-10
  1   2     3297.460      3312.537       15.077  -0.471017E+00  -0.511689E+00  0.982706E+00  0.965711E+00  0.346014E-03
  1   3     3297.460      4501.726     1204.266  -0.419269E-02   0.418815E-02  0.454388E-05  0.206469E-10  0.376966E-08
  1   4     3297.460      4503.286     1205.826   0.540274E-01  -0.699653E-01  0.159379E-01  0.254018E-03  0.465584E-01
  1   5     3297.460      5683.468     2386.008   0.365639E-02  -0.365501E-02  0.137762E-05  0.189783E-11  0.269497E-08
  1   6     3297.460      5685.211     2387.751  -0.989474E-03  -0.277054E-02  0.376001E-02  0.141377E-04  0.201199E-01
  1   7     3297.460      5931.386     2633.926   0.411693E-02  -0.410374E-02  0.131915E-04  0.174017E-09  0.332416E-06
  1   8     3297.460      5932.740     2635.280   0.328377E-02   0.450678E-02  0.779055E-02  0.606927E-04  0.116117E+00
  1   9     3297.460      5942.002     2644.542  -0.297920E-02  -0.339696E-02  0.637616E-02  0.406554E-04  0.786050E-01
  1  10     3297.460      5943.256     2645.796   0.454725E-02  -0.456231E-02  0.150633E-04  0.226904E-09  0.439331E-06

 H2S 1E TO 1F TRANSITIONS; GENERAL G1,G2; BLBA COORDS.

IE1 IE2   KET ENERGY    BRA ENERGY    FREQUENCY  Z TRANSITION    X TRANSITION      DIPOLE        S(F-I)       A-COEFFICIENT
  1   1     3311.151      3316.791        5.640  -0.576754E+00  -0.626842E+00  0.120360E+01  0.144864E+01  0.271701E-04
  1   2     3311.151      4507.796     1196.645  -0.661830E-01   0.856606E-01  0.194776E-01  0.379378E-03  0.679594E-01
  1   3     3311.151      5689.991     2378.840  -0.124482E-02  -0.342071E-02  0.466553E-02  0.217672E-04  0.306322E-01
  1   4     3311.151      5936.942     2625.791   0.379722E-02   0.525634E-02  0.905356E-02  0.819670E-04  0.155132E+00
  1   5     3311.151      5947.481     2636.330  -0.557479E-02   0.557689E-02  0.210382E-05  0.442607E-11  0.847809E-08

 PROGRAM SPECTRUM (VERSION OF FEB 9, 1989)

  TEMPERATURE SET TO:     10.00K

  MINIMUM RELATIVE INTENSITY REQUIRED =  0.100000E-04
  FREQUENCY RANGE FROM      0.000CM-1 TO  10000.000CM-1
 PARTITION FUNCTION Q =    0.194711E+01
 ESTIMATED ERROR IN Q =    0.716357E+01 %
 MAXIMUM ABSORPTION COEFFICIENT =     0.383042E+08

    100 TRANSITIONS WITHIN SPECTRAL RANGE
     18 TRANSITIONS INCLUDED
     82 TRANSITIONS NEGLECTED

 IPAR   J2  P2  I2   J1  P1  I1       E2          E1          FREQ       S(F-I)      ABS I(W)     REL I(W)      A(IF)
    1    1   1   1    1   0   1    19.331      13.691       5.640  0.145E+01  0.188E+07  0.491E-01  0.272E-04
    1    1   0   2    0   0   1    15.077       0.000      15.077  0.966E+00  0.383E+08  0.100E+01  0.346E-03
    1    0   0   2    1   0   2  1190.441      15.077    1175.364  0.183E-03  0.731E+05  0.191E-02  0.934E-01
    1    1   0   3    1   1   1  1204.266      19.331    1184.935  0.276E-03  0.602E+05  0.157E-02  0.480E-01
    1    1   1   2    1   0   1  1210.336      13.691    1196.645  0.379E-03  0.188E+06  0.491E-02  0.680E-01
    1    1   0   4    0   0   1  1205.826       0.000    1205.826  0.254E-03  0.910E+06  0.238E-01  0.466E-01
    1    0   0   3    1   0   2  2372.032      15.077    2356.955  0.123E-04  0.980E+04  0.256E-03  0.503E-01
    1    1   0   5    1   1   1  2386.008      19.331    2366.677  0.178E-04  0.774E+04  0.202E-03  0.246E-01
    1    1   1   3    1   0   1  2392.531      13.691    2378.840  0.218E-04  0.215E+05  0.560E-03  0.306E-01
    1    1   0   6    0   0   1  2387.751       0.000    2387.751  0.141E-04  0.100E+06  0.262E-02  0.201E-01
    1    0   0   4    1   0   2  2620.429      15.077    2605.352  0.456E-04  0.403E+05  0.105E-02  0.253E+00
    1    1   0   7    1   1   1  2633.926      19.331    2614.595  0.735E-04  0.354E+05  0.923E-03  0.137E+00
    1    0   0   5    1   0   1  2630.981      13.691    2617.290  0.361E-04  0.392E+05  0.102E-02  0.203E+00
    1    1   1   4    1   0   1  2639.482      13.691    2625.791  0.820E-04  0.892E+05  0.233E-02  0.155E+00
    1    1   0  10    1   1   1  2645.796      19.331    2626.465  0.544E-04  0.263E+05  0.686E-03  0.103E+00
    1    1   1   5    1   0   2  2650.021      15.077    2634.944  0.659E-04  0.590E+05  0.154E-02  0.126E+00
    1    1   0   8    0   0   1  2635.280       0.000    2635.280  0.607E-04  0.475E+06  0.124E-01  0.116E+00
    1    1   0   9    0   0   1  2644.542       0.000    2644.542  0.407E-04  0.319E+06  0.834E-02  0.786E-01

     SPECTRUM COMPLETED SUCCESSFULLY
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