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TRIATOM, SELECT AND ROTLEV – FOR THE CALCULATION OF THE RO-VIBRATIONAL LEVELS OF TRIATOMIC MOLECULES

Jonathan TENNYSON

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

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PROGRAM SUMMARY

Title of program: TRIATOM

Catalogue number: AALO

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 tested: NAS7000 at Daresbury Laboratory

Programming language used: FORTRAN 77

High speed storage required: case dependent

Overlay structure: optional

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

No. of lines in program and test deck: 8062 of which 2685 form TRIATOM

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 the solutions. The method is variational allowing basis set parameters to be optimised. Input can either be direct or from SELECT [2]. TRIATOM gives the data necessary to drive ROTLEV [3].

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 533 basis functions (requiring 350000 words storage) takes 8 s on the CRAY-1.

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, this article, second program (SELECT).
[3] J. Tennyson, this article, third program (ROTLEV).

PROGRAM SUMMARY

Title of program: SELECT

Catalogue number: AALP

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 tested: NAS7000 at Daresbury Laboratory

Programming language used: FORTRAN 77

High speed storage required: case dependent

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

No. of lines in program: 1915

Keywords: basis set selection, first-order perturbation theory

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

Method of solution
A basis function is selected either according its quantum numbers and/or the value of its diagonal elements.

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

Typical running time
Case dependent but much less than 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 can be read directly into TRIATOM.

Reference
[1] J. Tennyson, this article, first program (TRIATOM).

PROGRAM SUMMARY

Title of program: ROTLEV

Catalogue number: AALQ

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 tested: NAS7000 at Daresbury Laboratory

Programming language used: FORTRAN 77

High speed storage required: case dependent

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

No. of lines in program: 3424

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

Nature of physical problem
ROTLEV performs the second step in a two-step variational calculation for the bound ro-vibrational levels of a triatomic system, especially those with large total angular momentum, using the generalised body-fixed coordinates developed by Sutcliffe and Tennyson [1].

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

Restrictions on the complexity of the problem
The size of matrix that can practically be diagonalised. ROTLEV allocates arrays dynamically at execution time and in the present version the total space available is a single parameter which can be preset as required.

Typical running time
Case dependent. A problem with 902 basis functions takes 20 s on the CRAY-1 [2].

Unusual features of the program
Most of the data input is read in directly from TRIATOM [3].

References
[1] B.T. Sutcliffe and J. Tennyson, Mol. Phys. 58 (1986) 1053.
[2] J. Tennyson and B.T. Sutcliffe, Mol. Phys. 58 (1986) 1067.
[3] J. Tennyson, this article, first program (TRIATOM).

LONG WRITE-UP

1. Introduction

The calculation of the bound ro-vibrational levels of small, especially triatomic, molecules has been an area of much recent research activity. Much of this work has focused on the use of variational techniques which allow one to obtain the eigen energies and wavefunctions of a given potential to high accuracy. Typical of this approach is Whitehead and Handy's [1] use of Watson's [2] form of the Eckart Hamiltonian [3]. However, the realisation that this Hamiltonian is unsatisfactory for systems with large amplitude vibrational modes, which includes most highly excited vibrational states, has led to the development of techniques which do not rely on the concept of a special (equilibrium) geometry for defining the internal coordinates of the system. An example of this approach for triatomics is the one used by Carter and Handy who express their Hamiltonian in terms of two bond lengths and the angle between them [4–6].

An alternative representation that has proved popular is the use of scattering coordinates. In these, a triatomic is representated as a diatomic bond length, the distance of the third atom to the diatomic centre of mass and the angle between these two coordinates. This coordinate system was the basis of the secular equation method developed by Tennyson and Sutcliffe [7–9], and implemented in programs ATOMDIAT [10] and ATOMDIAT2 [11]. The method has recently been reviewed [12].

Since programs ATOMDIAT and ATOMDIAT2 were published there has been a several significant developments in the calculation of ro-vibrational levels using this methodology. The most fundamental of these is the derivation of a parameterised Hamiltonian by Sutcliffe and Tennyson [13] which allows suitable coordinates to be selected from a continuum of coordinate sets. These coordinates, given in fig. 1, consist of all those in which a triatomic molecule is represented by a diatomic bondlength, r_1, the distance of the third atom to any fixed point on this bond, r_2, and the angle between $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. Clearly, both scattering coordinates and bond length–bond angle coordinates are special cases of this generalised coordinate system.

Another development has been the use of a two-step variational procedure for the calculation of rotational excited states [14]. This has greatly extended the range of rotational states that can be practicably considered. Progress has also been made in the use of basis set selection to give more compact basis sets for the representation of vibrationally excited states [12,15]. Finally, improvements have been made in the algorithms used for construction of the secular matrices in ATOMDIAT and ATOMDIAT2, a step which could become rate limiting if the codes were used with a fast, vectorised diagonaliser [12].

In this work a suite of programs are presented which allow ro-vibrational calculations to be performed on any user supplied triatomic potential using the generalised (r_1, r_2, θ) coordinates. The core of this suite is program TRIATOM which can be used on its own for ro-vibrational calculations; it replaces both ATOMDIAT and ATOMDIAT2, also including GENPOT [11] as an option. TRIATOM can be used for either fully-coupled ro-vibrational calculations, calculations which neglect off-diagonal Coriolis interactions or to loop over such calculations thus providing the data necessary to drive ROTLEV.

ROTLEV performs the second variational step in a two-step variational procedure [14]. Program SELECT allows the basis set used by TRIATOM

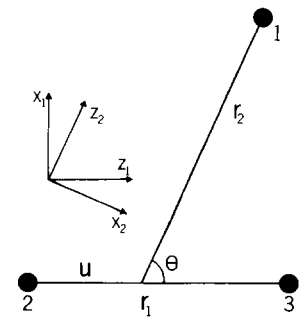

Fig. 1. Body-fixed coordinate system: axes (x_i, z_i) refer to embedding i. $0 \le u \le r_1$.

to be preselected. Criteria used are based on the total number of quanta of excitation or the value of the diagonal matrix element for a particular product function. A mixture of criteria can also be employed. SELECT can be used to generate all the input required by program TRIATOM, which is designed flexibly to allow users to implement alternative basis set selection procedures if desired.

2. Method

Using the generalised coordinates of fig. 1, a body-fixed Hamiltonian can be written

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

where V represents the potential. Suitable symmetrised angular basis functions for the Hamiltonian are

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

where $D^J_{\mathrm{M}k}$ is a rotation matrix element as defined by Brink and Satchler [16] and Θ_{jk} an associated Legendre polynomial [17]. The total parity under inversion is given by $(-1)^{J+p}$, for $p = 0$ or 1. J is the total angular momentum and k is its projection on the body-fixed z axis. j is the angular momentum of the diatomic represented by atoms 2 and 3. The Euler angles (α, β, γ) are those required to place the z axis along $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ in the positive x–z plane – embedding 1. Similar functions may be written down for embedding 2 which places z parallel to $\boldsymbol{r}_2$ and $\boldsymbol{r}_1$ in the positive x–z plane.

Following the close-coupling approach of Arthurs and Dalgarno [18] yields an effective radial Hamiltonian [13]:

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

$$\hat{K}_{\mathrm{V}}^{(2)} = -\frac{\hbar^2}{\mu_{12}} d_{jk}\delta_{j'j+1}\delta_{k'k}\left(\frac{\partial}{\partial r_1} - \frac{(j+1)}{r_1}\right) \times \left(\frac{\partial}{\partial r_2} - \frac{(j+1)}{r_2}\right) - \frac{\hbar^2}{\mu_{12}} d_{j-1,k}\delta_{j'j-1}\delta_{k'k} \times \left(\frac{\partial}{\partial r_1} + \frac{j}{r_1}\right)\left(\frac{\partial}{\partial r_2} + \frac{j}{r_2}\right), \tag{4}$$

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

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

In the above, the auxiliary quantities are defined as follows *

$$C^{\pm}_{jk} = \left[J(J+1) - k(k\pm1)\right]^{1/2}, \tag{7}$$

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

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

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

which are special cases of Clebsch–Gordon coefficients. The reduced masses are defined in terms of the atomic masses (m_i) and g, the parameter which determines the internal coordinates

$$\mu_1^{-1} = m_2^{-1} + m_3^{-1}, \tag{11}$$

* Note that eq. (8) is given incorrectly in ref. [13].

$$\mu_{12}^{-1} = g\left(m_2^{-1} + m_3^{-1}\right) - m_3^{-1}, \tag{12}$$

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

$$g = (r_2 - u)/r_2, \tag{14}$$

where u is the distance from particle 2 to the intersection of $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, see fig. 1. For scattering coordinates

$$g = m_2/(m_2 + m_3) \tag{15}$$

which means that r_1 cuts r_2 at the diatomic centre of mass. In these coordinates $\mu_{12} = K_{\mathrm{V}}^{(2)} = K_{\mathrm{VR}}^{(2)} = 0$ and the Hamiltonian reduces to the one used in program ATOMDIAT. If $g = 0$ or 1, one obtains the bond length–bond angle Hamiltonian used by Carter and Handy. Other values of g between 0 and 1 yield different coordinate systems which can be used as appropriate. For example $g = \frac{1}{2}$ has been recommended for Van der Waals complexes whose symmetry has been reduced by isotopic substitution [13].

The form of the kinetic energy operators given above in (5) and (6) is appropriate for embedding 1. Embedding 2 is obtained simply by making the exchanges $r_1 \leftrightarrow r_2$ and $\mu_1 \leftrightarrow \mu_2$.

So far only the kinetic energy operators have been considered. It is of course possible to write the potential solely in terms of the internal coordinates (r_1, r_2, θ). In these coordinates one can make the Legendre expansion

$$V(r_1, r_2, \theta) = \sum_{\lambda} V_{\lambda}(r_1, r_2) P_{\lambda}(\cos\theta). \tag{16}$$

For the angular basis functions, matrix elements over such a potential expansion can be computed analytically

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

where the integral is over all the angular coordinates and the $3-j$ symbols in the Gaunt coefficient are conventional [16]. In the atom–diatom scattering coordinates the potential is often given as a Legendre expansion, but this is unlikely to be generally the case. However Gauss–Legendre integration can be used to express a general potential function in the form of eq. (16) [9,11].

Integration over angular coordinates yields a set of two-dimensional coupled differential equations, solutions of which can be expanded in terms of one dimensional basis functions

$$\Psi_{m,n}(r_1, r_2) = r_1^{-1} H_m(r_1) r_2^{-1} H_n(r_2). \tag{18}$$

These radial basis functions can be expressed in terms of known analytic functions. The best suited of these to such problems are the Morse oscillator-like functions [7,10]

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

where

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

and 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 coordinate, respectively. In practice (r_e, ω_e, D_e) are usually treated as variational parameters and optimised accordingly. $N_{n,\alpha} L_n^{\alpha}$ is a normalised Laguerre polynomial [22]. With these functions the matrix elements of the differential terms in the kinetic energy operators (3)–(6) can be calculated analytically [7,13]

$$\begin{aligned}\left\langle n' \left| \frac{\partial^2}{\partial r^2} \right| n \right\rangle &= \frac{\beta^{1/2}}{4} \big(\delta_{n'n} [2n(\alpha+n+1) + \alpha + 1]^{1/2} \\ &- \delta_{n'n-2} [(\alpha+n)(\alpha+n-1)n(n-1)]^{1/2} \\ &- \delta_{n'n+2} [(\alpha+n+2)(\alpha+n+1) \\ &\times (n+2)(n+1)]^{1/2} \big),\end{aligned} \tag{21}$$

$$\left\langle n' \left| \frac{\partial}{\partial r} \right| n \right\rangle = \frac{\beta}{2} \big(\delta_{n'n+1} [(n-1)(\alpha+n-1)]^{1/2} - \delta_{n'n-1} [(n-2)(\alpha+n-2)]^{1/2} \big). \tag{22}$$

There is no simple closed form for the matrix elements of r^{-1}, r^{-2} or $V_\lambda(r_1, r_2)$, but these integrals are evaluated using Gauss–Laguerre integration [20] using the normalised basis functions to ensure numerical stability [10].

However, because Morse functions do not obey the correct boundary conditions at $r = 0$, these functions are not satisfactory for the special case that the wavefunction has amplitude at $r = 0$. This is unlikely to occur for the r_1 coordinate because of the strongly repulsive nature of diatomic potentials at small separations, but is possible for the r_2 coordinate when scattering coordinates are used [9,11]. Spherical oscillator functions do not suffer from this problem and are offered in TRIATOM as an alternative for this special case. These functions are defined by

$$\begin{aligned} |n\rangle &= H_n(r) \\ &= r2^{1/2}\beta^{3/4}N_{n,\alpha}\exp(-y/2)\,y^{\alpha/2}L_n^{\alpha+1/2}(y), \\ y &= \beta r^2, \end{aligned} \tag{23}$$

where

$$\beta = (\mu\omega_e)^{1/2}, \tag{24}$$

μ, ω_e and $N_{n,\alpha}L_n^\alpha$ are as defined for the Morse-like functions. Again α and ω_e can be treated as variational parameters. For scattering coordinates, all the kinetic energy matrix elements over the spherical oscillator functions can be computed analytically [9,11]

$$\begin{aligned} \left\langle n'\left|\frac{\partial^2}{\partial r^2}\right|n\right\rangle &= \beta\left(\delta_{n'n}\left(2n+\alpha+\tfrac{3}{2}\right)\right. \\ &\quad \left. -\delta_{n'n-1}\left[n\left(\alpha+n+\tfrac{1}{2}\right)\right]^{1/2}\right) \\ &\quad +\langle n'|r^{-2}|n\rangle \quad n \geq n', \end{aligned} \tag{25}$$

$$\begin{aligned} \langle n'|r^{-2}|n\rangle &= \beta\left(\frac{n!}{n'!}\frac{\Gamma(n'+\alpha+3/2)}{\Gamma(n+\alpha+3/2)}\right)^{1/2} \\ &\quad +\sum_{\sigma=0}^{n'}\left(\frac{n'!}{\sigma!}\frac{\Gamma(\sigma+\alpha+1/2)}{\Gamma(n'+\alpha+3/2)}\right) \\ n &\geq n'. \end{aligned} \tag{26}$$

Radial integrals over the potential are again evaluated using Gauss–Laguerre quadrature.

Having computed the matrix elements, TRIATOM constructs a secular matrix which is then diagonalised to give the solutions of the problem. SELECT can optionally use the diagonal elements of the secular matrix to select the LBASS lowest basis functions. First-order perturbation theory suggests that these functions should be the most important. Alternatively, the quantum numbers of the basis functions can be inspected according to the formula

$$N^{\max} \geq \frac{j}{d_j} + \frac{m}{d_m} + \frac{n}{d_n}, \tag{27}$$

where j, m, n are the quantum numbers associated with the basis functions in the in θ, r_1 and r_2 coordinates, respectively, which are weighted by d_j, d_m and d_n to allow more functions to be selected for low energy modes.

ROTLEV solves the second step in a two-step variational procedure [14]. The first variational step is performed by TRIATOM using the Hamiltonian

$$\begin{aligned} \hat{H}_{J,k} &= \hat{K}_V^{(1)} + \hat{K}_V^{(2)} + \delta_{k,k'}\hat{K}_{VR}^{(1)} \\ &\quad + V(r_1, r_2, \theta) \end{aligned} \tag{28}$$

for which both J and k (the projection of J on the body-fixed axis) are good quantum numbers. Solutions of this Coriolis decoupled problem are obtained for all the appropriate values of k. ROTLEV then solves the full Hamiltonian of eq. (1) using these solutions as the basis functions. Matrix elements for this step are given by

$$\begin{aligned} &\langle i, k|H|i', k'\rangle \\ &= \delta_{i,i'}\delta_{k,k'}\epsilon_i^{J,k} + \delta_{k\pm1,k'}(1+\delta_{k0}+\delta_{k'0})^{1/2} \\ &\quad \times C_{J,k}^{\pm}\sum_{jmn}\sum_{j'm'n'}c_{j,m,n}^{J,k,i}c_{j',m',n'}^{J,k',i'} \\ &\quad \times\left(\delta_{j,j'}\delta_{n,n'}C_{j,k}^{\pm}\left\langle m'\left|\frac{1}{2\mu_1 r_1^2}\right|m\right\rangle\right. \\ &\quad \left. +\delta_{j+1,j'}\frac{a_{j,\pm k}}{2\mu_{12}}\left\langle m'\left|\frac{1}{r_1}\right|m\right\rangle\right. \end{aligned}$$

$$\times\left[(j+1)\left\langle n'\left|\frac{1}{r_2}\right|n\right\rangle+\left\langle n'\left|\frac{\mathrm{d}}{\mathrm{d}r_2}\right|n\right\rangle\right]$$

$$+\delta_{j-1,j'}\frac{b_{j,\pm k}}{2\mu_{12}}\left\langle m'\left|\frac{1}{r_1}\right|m\right\rangle$$

$$\times\left[j\left\langle n'\left|\frac{1}{r_2}\right|n\right\rangle-\left\langle n'\left|\frac{\mathrm{d}}{\mathrm{d}r_2}\right|n\right\rangle\right]\Bigg), \qquad (29)$$

where the ith solution of $H_{J,k}$ has eigen energy $\epsilon_i^{J,k}$ and eigenvector $c^{J,k,i}$, and the radial matrix elements are the same as those used in solving the fully coupled problem. In constructing the secular matrix $|k|$ runs from p to J and i runs from 1 to N for each k. If N is chosen as the number of functions of the first variational step then the two-step procedure yields results identical to directly solving the fully-coupled problem, see ref. [14] for a numerical example.

The two-step procedure has the advantage that not all the solutions of the first variational step are required to obtain good convergence in the second step and that the resulting secular matrix has a tridiagonal blocked structure. Further details on both these points can be found in refs. [12,14].

3. Program structure

All the programs follow the convention that names beginning with letters A–H and O–Y are for REAL*8 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 FORTRAN 77 generic function names have been used to ease conversion between machines with different word lengths.

TRIATOM can be divided into four segments which form the basis of a possible overlay structure – see fig. 2. 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).

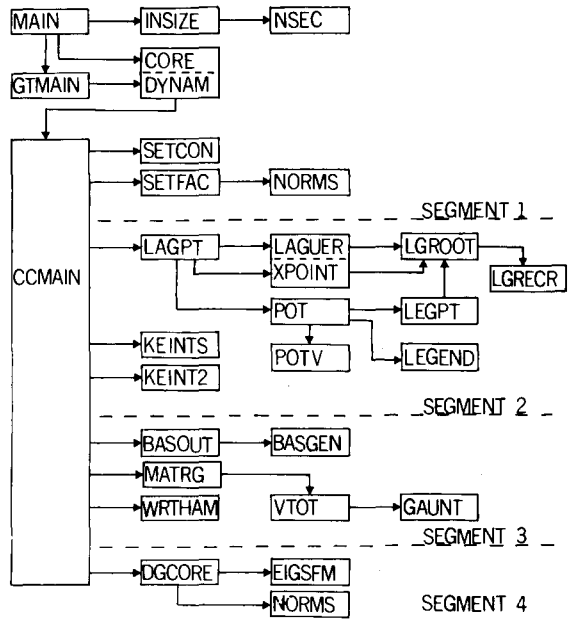

Fig. 2. Structure of program ATOMDIAT. Service routines OUTROW, TIMER, SECOND and SYMOUT have been omitted.

⟨1⟩ MAIN reads in namelist data (stored in COMMON/OUTP/) and calls the initialising routines ⟨3⟩ INSIZE, ⟨5⟩ CORE and ⟨31⟩ 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.

⟨25⟩ OUTROW fast unformatted write.

⟨30⟩ TIMER calls ⟨32⟩ SECOND and prints CPU time used.

⟨31⟩ GTMAIN Fortran version of an assembler routine which requests space for the dynamic allocation of storage. The array ARRAY(NAVAIL) should be dimensioned to the limit of the storate available.

⟨32⟩ SECOND Fortran dummy. Should return the CPU time used in seconds.

3.2. Overlay 1: data input and intialisation

There are several forms of data input in TRIATOM. 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. Finally, if a basis is selected by SELECT, it is read in ⟨9⟩ BASOUT.

⟨3⟩ INSIZE reads the integer parameters of the problem which are then stored in COMMON/SIZE/.

⟨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/).

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

⟨22⟩ 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.

⟨12⟩ KEINTS forms the analytic matrix elements of eq. (21) (HBL1, HBL2) and (22) (HBL3, HBL4) for the Morse-like functions.

⟨13⟩ KEINT2 forms the analytic matrix elements of eq. (25) (HBL2) and (26) (R2M2) for the spherical oscillator functions.

⟨15⟩ 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).

⟨16⟩ LAGUER adaption of the Gauss–Laguerre integration points and weights routine of Stroud and Secrest [20] for large α. Note that the initial guess formulae are arbitrary and may need to be adjusted. The ith call to entry XPOINT returns the ith point and weight.

⟨17⟩ LGROOT improves the guess to the integration point [20].

⟨18⟩ LGRECR uses recurrence relations to generate orthogonal polynomials [20].

⟨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; this option is equivalent to calling program GENPOT [11].

⟨27⟩ LEGPT sets up Gauss–Legendre integration points and weights, an adaptation of subroutine JACOBI [20].

⟨28⟩ LEGEND sets up weighted normalised Legendre polynomials.

⟨33⟩ 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.

⟨11⟩ WRTHAM prints the Hamiltonian matrix if requested.

⟨14⟩ MATRG performs the angular integration and forms the lower triangle of the Hamiltonian matrix. This version uses an improved algorithm [12] and is written to allow for a bug in some optimising compilers [10].

⟨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.
⟨34⟩ EIGSFM this is a mock-up of an EISPACK routine of the same name [21] which calls routines ⟨35⟩–⟨45⟩ 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. 2, 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. Only those routines that are substantially different in purpose or structure from TRIATOM are considered explicitly below.

⟨1⟩ MAIN reads in data controlling basis set selection (stored in COMMON /SELEC/).
⟨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 ROTLEV

Fig. 3 gives the structure of program ROTLEV. Routines which have the same name as routines in TRIATOM serve the same purpose and will not be considered below.

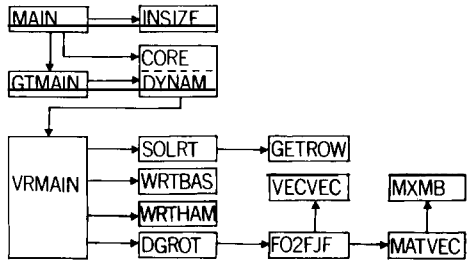

Fig. 3. Structure of program ROTLEV.

⟨5⟩ VRMAIN driver routine which would be the main program if there was no dynamic overlay.
⟨6⟩ WRTBAS prints the basis set labels.
⟨7⟩ SOLRT reads matrix elements, eigenvalues and eigenvectors from TRIATOM. Constructs the diagonal (array DIAG) and non-zero off-diagonal (OFFDG) matrices, see eq. (29).
⟨9⟩ DGROT sets up the diagonalisation including shifting the diagonal elements so the highest is zero, which ensures that ⟨17⟩ F02FJF returns the lowest eigenvalues.
⟨10⟩ GETROW fast unformatted read.
⟨12⟩ VECVEC dot product for ⟨17⟩ F02FJF.
⟨13⟩ MATVEC performs the vector matrix multiplication required by ⟨17⟩ F02FJF taking advantage of the structure of the Hamiltonian.
⟨14⟩ MXMB fast vector matrix multiplier.
⟨17⟩ F02FJF–⟨45⟩ G05CAF are a NAG Library [22] subroutine suite for diagonalising sparse matrices, based on the algorithm of Nikolai [23]. The implementation given here is appropriate for IBM machines and it is recommended that users replace this call with the local NAG implementation where possible. In particular, ⟨45⟩ G05CAF is an assembler pseudo-random number generator; the FORTRAN version provided is only equivalent for the first 79 calls.

4. Program use

TRIATOM requires both card input (which can generated by SELECT) and a subroutine giving the potential.

4.1. The potential

For both TRIATOM and SELECT there are two ways of supplying the potential. If the potential is specified as a Legendre expansion, eq. (16), 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 required. If NCOORD = 1, R1 and V1 are dummies. If NCOORD = 2, R1 contains the rigid diatom bond length, r_e. If NCOORD > 1, VL has dimension LPOT.

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

SUBROUTINE POTV(V,R1,R2,XCOS)

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

COMMON /MASS/ XMASS(3), G is included in ⟨7⟩ SETCON 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.

4.2. Card input for TRIATOM

TRIATOM requires 8 lines of card input for *all* runs, extra cards are required if the basis set is selected. 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.

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

ZROT[F] = T TRIATOM to perform the 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 $\boldsymbol{r}_2$; = F z axis embedded along $\boldsymbol{r}_1$.

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 ROTLEV to be written to stream IVEC.

IVEC[4] stream for ROTLEV data.

Card 2: NCOORD (I5)

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

Card 3: NPNT2,NMAX2,JROT,NEVAL,LMAX, LPOT,IDIA,KMIN,NPNT1,NMAX1,ISYM, NBASS(12I5)

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. If JROT > 0 the off-diagonal Coriolis terms are included. If JROT < 0, they are neglected and k (KMIN) is treated as a good quantum number. If JROT = 0 or NCOORD = 1 there are no Coriolis terms.

NEVAL[10] the number of eigenvalues and eigenvectors required.

If NCOORD = 1 the rest of the card 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 + 1] highest value of λ in the

Legendre expansion, eq. (16). If ZLPOT = F, LPOT + 1 + MOD (LPOT,2) point Gauss–Legendre integration is used for the θ coordinate.

IDIA = −1 for generalised 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 (e.g. where the symmetry has been broken by isotopic substitution).

KMIN[0] = k for JROT < 0, = $(1-p)$, see eq. (2), 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 bond length–bond angle coordinates ($g = 0$ or 1): = 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 [13].

NBASS[0] number of basis function in the secular problem: = 0 determined internally, > 0 basis preselected and to be read in (see card 9).

Card 4: TITLE (9A8)

A 72 character title.

Card 5: (XMASS(I),I = 1,3) (3F20.0)

XMASS(I) contains the mass of atom I (numbering as in fig. 1) in atomic mass units. If NCOORD = 1, XMASS(3) is set to zero, the diatom comprising atoms 1 and 2.

Card 6: G (F20.0)

Parameter g determines the coordinate system, see eq. (14), needed if IDIA = −1 and ISYM = 0. Otherwise this card is ignored and:

if IDIA > 0 G = $m_2/(m_2+m_3)$,
if IDIA = −2 G = $\frac{1}{2}$,
if ISYM ≠ 0 G = 1.

Card 7: RE1,DISS1,WE1 (3F20.0)

If NCOORD = 1, this card is read but ignored.

If NCOORD = 2, RE1 is the fixed diatomic bondlength, DISS1 and WE1 ignored.

If NCOORD = 3, RE1 = r_e, DISS1 = D_e and WE1 = ω_e are Morse parameters for the r_1 coordinate, see eqs. (19) and (20).

Card 8: RE2,DISS2,WE2 (3F20.0)

If |ISYM| = 2, this card 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, see eqs. (19) and (20).

If ZMORSE = F, RE2 is ignored; DISS2 = α and WE2 = ω_e are spherical oscillator parameters, see eqs. (23) and (24).

Card 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. Data input for SELECT

If the basis is to be selected using the diagonal elements of the secular matrix, then a potential subroutine (either POT or POTV) must be supplied, see section 4.1.

Card 1: LBASS,NQMAX,NQJ,NQM,NQN, IFLAG,IOUT (7I5)

LBASS[0] select the LBASS lowest basis functions ordered by their diagonal elements.

NQMAX[0] = $N^{\max}$, see eq. (27).

NQJ[1] = d_j, see eq. (27).

NQM[1] = d_m, see eq. (27).

NQN[1] = d_n, see eq. (27).

IFLAG[0] ≠ 0: select basis for different (J, k) or symmetery than the full calculation.

IOUT[7] output stream for TRIATOM data file.

Cards 2–9

These are the same as cards 1–8 of the TRIATOM input, with the exceptions:

If IFLAG ≠ 0, then TRIATOM card 3 is repeated: first, to characterise the basis for the selection run and second to characterise the TRIATOM run.

If NQMAX > 0, then NMAX1 and NMAX2 default to NQM * NQMAX and NQN * NQMAX, respectively.

4.4. Data input for ROTLEV

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

Card 1: NAMELIST/PRT/

TOLER[0.0d0] tolerance for convergence of the eigenvalues, zero gives machine accuracy [22].

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

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

IVEC[4] stream for data from TRIATOM.

Card 2: NVIB,NEVAL,KMIN

NVIB number of vibrational levels (N) from TRIATOM for each k to be used in the second variational step.

NEVAL[10] the number of eigenvalues required.

KMIN[0] = $(1 - p)$, see eq. (2).

Card 3: TITLE (9A8)

A 72 character title.

4.5. Test output

A test run of SELECT, TRIATOM and ROTLEV for the D_2H^+ molecule has been prepared. The potential used is the BVDH potential of Martire and Burton [24].

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TEST RUN OUTPUT

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

SELECTION CRITERIA:
LOWEST  100 BASIS FUNCTIONS CHOSEN
FUNCTIONS WITH UP TO   5 QUANTA CHOSEN USING
3 ANGULAR FUNCTIONS PER QUANTA
1 R1 FUNCTIONS PER QUANTA
1 R2 FUNCTIONS PER QUANTA

PRESELECTION PERFORMED FOR J = 0 CASE

FULL TRIATOMIC VIBRATIONAL PROBLEM WITH

  11   POINT NUMERICAL INTEGRATION FOR
   5   TH ORDER R1 RADIAL BASIS FUNCTIONS
  11   POINT NUMERICAL INTEGRATION FOR
   5   TH ORDER R2 RADIAL BASIS FUNCTIONS
  14   TH ORDER ANGULAR BASIS FUNCTIONS
  28   TERMS IN THE POTENTIAL EXPANSION
 288   CANDIDATE BASIS FUNCTIONS

LOWEST  100 FUNCTIONS SELECTED FROM   -0.2662624634E+00 HARTREE TO   -0.1672416929E+00 HARTREE

   13 FUNCTIONS SELECTED WITH LESS THAN  5 QUANTA

NBASS =  113 FUNCTIONS CHOSEN WITH THE REVISED PARAMETERS


        FULL TRIATOMIC VIBRATIONAL PROBLEM WITH

          11   POINT NUMERICAL INTEGRATION FOR
           5   TH ORDER R1 RADIAL BASIS FUNCTIONS
          11   POINT NUMERICAL INTEGRATION FOR
           5   TH ORDER R2 RADIAL BASIS FUNCTIONS
          14   TH ORDER ANGULAR BASIS FUNCTIONS
          28   TERMS IN THE POTENTIAL EXPANSION
          40   LOWEST EIGENVECTORS REQUIRED FOR
         113   DIMENSION SECULAR PROBLEM

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

   LOWEST  40 EIGENVALUES IN WAVENUMBERS

-0.714068722794E+05   -0.694353775883E+05   -0.686699830589E+05   -0.675546976196E+05   -0.673727788630E+05

-0.667371987610E+05   -0.660027939589E+05   -0.656524442688E+05   -0.653812343100E+05   -0.649274511947E+05

-0.648063468882E+05   -0.640898430523E+05   -0.637901928308E+05   -0.635199144447E+05   -0.633582357493E+05

-0.632857100691E+05   -0.629422580436E+05   -0.626786554230E+05   -0.624231139330E+05   -0.619670654139E+05

-0.618224216590E+05   -0.614088206123E+05   -0.612594598808E+05   -0.611221346112E+05   -0.607263121757E+05

-0.605715288293E+05   -0.600599870895E+05   -0.598708704578E+05   -0.594997668185E+05   -0.592892560815E+05

-0.592407515111E+05   -0.590072038907E+05   -0.589297440620E+05   -0.586953483929E+05   -0.585282529019E+05

-0.582417480770E+05   -0.578329290682E+05   -0.576358738867E+05   -0.572559026414E+05   -0.567924926990E+05
```

```
      ***  VIBRATIONAL PART OF ROT-VIB CALCULATION  ***
                   J =  1  K =  1
      ***  OPTION TO NEGLECT CORIOLIS INTERACTIONS  ***
  LOWEST  40 EIGENVALUES IN WAVENUMBERS

-0.693434778845E+05   -0.673520908937E+05   -0.667367529737E+05   -0.655680535567E+05   -0.653695235544E+05

-0.647581207137E+05   -0.641584650351E+05   -0.636506785096E+05   -0.633898691954E+05   -0.631210496908E+05

-0.627350705008E+05   -0.620451074873E+05   -0.619321100478E+05   -0.615131872731E+05   -0.614401083279E+05

-0.611137891970E+05   -0.609561219989E+05   -0.605059997466E+05   -0.602762609382E+05   -0.596969618421E+05

-0.594707724476E+05   -0.591486300333E+05   -0.585680502052E+05   -0.582846334058E+05   -0.579434392730E+05

-0.577146293484E+05   -0.570798691057E+05   -0.569522030011E+05   -0.567372233855E+05   -0.562657059258E+05

-0.557006622625E+05   -0.549539344639E+05   -0.547516093382E+05   -0.543753631137E+05   -0.540765764232E+05

-0.530367647568E+05   -0.524147046677E+05   -0.520570286981E+05   -0.516503198823E+05   -0.511880330027E+05


      ROTATIONAL PART OF ROT-VIB CALCULATION  WITH:
        40   LOWEST VIBRATIONAL EIGENVECTORS SUPPLIED FROM
       113   DIMENSION VIBRATION SECULAR PROBLEM
        40   LOWEST VIBRATIONAL EIGENVECTORS ACTUALLY USED
         6   LOWEST ROTATIONAL EIGENVECTORS REQUIRED FOR
        80   DIMENSION ROTATION SECULAR PROBLEM

      TITLE:  D2H+ : E PARITY

  LOWEST   6 EIGENVALUES IN WAVENUMBERS

-0.714277079814E+05   -0.694627380851E+05   -0.693607860944E+05   -0.686893214285E+05   -0.675780556790E+05

-0.674101182911E+05
```