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ATOMDIAT – A PROGRAM FOR CALCULATING VARIATIONALLY EXACT RO-VIBRATIONAL LEVELS OF "FLOPPY" TRIATOMICS

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PROGRAM SUMMARY

Title of program: ATOMDIAT

Catalogue numbers: ACEN

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

Computer: IBM 4341/2: *Installation:* Universitair Rekencentrum Nijmegen

Operating systems: MVS release 3.7

Programming language used: FORTRAN IV

High speed storage required: case dependent

No. of bits in a byte: 8

Overlay structure: yes

Peripherals used: card reader, line printer, up to 4 optional disk files

No. of cards in program and test desk: 3706

Card punching code: EBCDIC

Keywords: ro-vibrational, body-fixed, associated Laguerre polynomials, associated Legendre polynomials, Gauss–Laguerre quadrature, orthogonalised Lanczos, LC-RAMP, variational, close-coupled equations

Nature of physical problem
ATOMDIAT calculates the bound ro-vibrational levels of a triatomic system using body-fixed coordinates. The embedded coordinates are appropriate to atom–diatom systems and the diatom bondlength may be frozen [1].

Method of solution
A basis set is constructed as the product of Morse oscillator functions (associated Laguerre polynomials) for the radial coordinate(s) and associated Legendre polynomials for the bending coordinate, with rotation matrices representing the rotations. The method is variational and the parameters used in constructing the radial basis set(s) can be optimized [1,2]. A secular matrix is constructed by use of Gauss–Laguerre integration for the radial coordinate(s) and analytic integration for the angular coordinates. This matrix is diagonalised to give the solutions. A choice of Givens–Householder and orthogonalised Lanczos procedures are supplied with the program [2].

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

Typical running time
Running times are case dependent but dominated by the time required for diagonalising the secular matrix. A problem with 350 basis functions (which can be held in 512 K) takes 7 min on the IBM 4341/2.

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

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LONG WRITE-UP

1. Introduction

The calculation of the bound ro-vibrational levels of molecules with one or more large amplitude internal modes has been a centre of much recent research [1–9]. In particular, the variational treatment of the problem by setting up and diagonalising a secular matrix in the style of Le Roy and Van Kranendonk [1] has been a particular area of interest. The acronym LC-RAMP (linear combination of radial and angular momentum function products) has been coined [9] to distinguish the basis functions used in these methods.

Recently, Tennyson and Sutcliffe [7,8] have developed a general LC-RAMP method for atom–diatom systems. this method is characterised by its use of a body-fixed coordinate and polynomial basis sets for the radial coordinate(s). Use of the polynomial basis allows the full three-dimensions to be tackled, making the method appropriate not only for atom–diatom collision complexes such as Van der Waals molecules, but also any triatomic system which performs large amplitude motions. Unlike methods based on the BOARS approximation [3,6], the method is exact within the usual limitations of the Born–Oppenheimer approximation and the variational principle, for both bent and linear molecules. For rotationally excited states, the body-fixing of the coordinate system causes the coupling between basis functions differing in k (the component of the total angular momentum on the body-fixed z axis) to be small and neglect of these Coriolis interactions has been found to be an useful approximation [4,7,9,10] as it leads to a considerable simplification of the computational problem involved.

ATOMDIAT is a general program which uses the method of Tennyson and Sutcliffe to solve the ro-vibrational problem for triatomic systems. It can perform calculations on full triatomic systems, atom-rigid diatom complexes and simple diatomics (this is useful for optimizing basis sets); options allow the Coriolis interactions to be included or neglected as desired. For given quantum numbers, the program automatically generates both angular and radial basis sets, the appropriate quadrature scheme for the radial integration and hence the secular matrix. A choice of diagonalisers [11,12] is provided depending on whether the secular matrix can or cannot be retained in high speed storage.

ATOMDIAT has been applied to molecules as diverse as KCN [7], H_2Ne [7], HF [8] and HFHe [8]. A generalisation of the program has been used for rigid-diatom rigid-diatom calculations on the $(N_2)_2$ Van der Waals dimer [9]. A similar program in space-fixed coordinates was used for calculations on the spin–orbit coupling and weak field Zeeman interactions in O_2 Ar [13], ATOMDIAT generates vibrational wavefunctions suitable for the calculation of transition intensities [13,14] and vibrationally averaged properties. The wavefunctions have also been used as input to plot routines which given physical insight into the nature of the large amplitude vibrations [9,15].

2. Method

Fig. 1. illustrates the body-fixed coordinate system used by Tennyson and Sutcliffe [7,8]. R, which connects the diatom centre-of-mass to the atom, lies along the body-fixed z axis and the whole molecule in the x–z plane. This embedding defines three Euler angles α, β and γ. A symmetrized wavefunction appropriate to this system can be written

$$\Psi_{J,p} = \sum_{k=p}^{J} \sum_{m,n,l} \psi_{m,n}(r, R)\big[\theta_{l,k}(\theta) D^{J}_{M,k}{}^{*}(\alpha, \beta, \gamma)$$

$$+(-1)^{p} \theta_{l,-k}(\theta) D^{J}_{M,-k}{}^{*}(\alpha, \beta, \gamma)\big](1+\delta_{k,0})^{-1/2} 2^{-1/2}, \qquad (1)$$

where $D_{m,k}^{J}$ is a rotation matrix element as defined by Brink and Satchler [16] and $\theta_{l,k}$ and associated Legendre polynomial [17]. p equals 0 or 1 for $(-1)^{J+p}$ parity under inversion. J is the total angular momentum and k is its projection on the body-fixed z axis. l is the angular momentum of the diatomic.

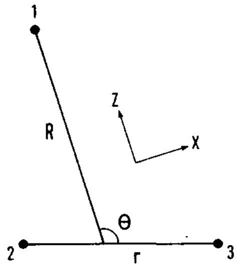

Fig. 1. Body-fixed coordinate system of ATOMDIAT.

Following the close-coupling approach of Arthurs and Dalgarno [18], integration over the angular basis functions yields an effective radial Hamiltonian [7,8]:

$$\begin{aligned}\hat{H} = {} & \delta_{kk'}\delta_{ll'}\left[\frac{-\hbar^2}{2\mu_2 R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{\hbar^2}{2\mu_1 r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r^2}\right) + \frac{\hbar^2}{2}l(l+1)\left(\frac{1}{\mu_2 R^2}+\frac{1}{\mu_1 r^2}\right) + \frac{J(J+1)}{2\mu_2 R^2}\right] \\ & + \delta_{kk'}\langle\theta_{1'k}|V|\theta_{lk}\rangle \\ & - \frac{\hbar^2}{2\mu_2 R^2}\delta_{ll'}\left[\delta_{kk'}2k^2 + \delta_{k',k+1}C_{Jk}^{+}C_{lk}^{+}(1+\delta_{k0})^{1/2} + \delta_{k',k-1}C_{Jk}^{-}C_{lk}^{-}(1+\delta_{k0})^{1/2}\right],\end{aligned} \tag{2}$$

where $\mu_1^{-1} = m_2^{-1} + m_3^{-1}$, $\mu_2^{-1} = m_1^{-1} + (m_2+m_3)^{-1}$ with m_i as the mass of atom i and

$$C_{Jk}^{\pm} = [J(J+1) - k(k \pm 1)]^{1/2}. \tag{3}$$

If the potential is given in form of a Legendre expansion,

$$V(R, r, \theta) = \sum_{\lambda} V_\lambda(R, r) P_\lambda(\cos\theta), \tag{4}$$

the angular integral becomes analytic

$$\langle\theta_{l'k}|V|\theta_{lk}\rangle = \sum_{\lambda} g_\lambda(l', l, k) V_\lambda(R, r), \tag{5a}$$

$$g_\lambda(l', l, k) = (-1)^k[(2l'+1)]^{1/2}\begin{pmatrix} l' & \lambda & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & \lambda & l \\ -k & 0 & k \end{pmatrix}, \tag{5b}$$

where the $3-j$ symbols in the Gaunt coefficient are standard [16]. If the diatom is homonuclear only terms with even λ appear in (4) and the problem block factorises according to whether l is odd or even.

Tennyson and Sutcliffe expanded solutions of the two-dimensional coupled differential equations given by $\hat{H}$ acting on $\psi_{m,n}(R, r)$ in Morse oscillator like functions,

$$\psi_{n_1,n_2}(r, R) = r^{-1}H_{n_1}(r)R^{-1}H_{n_2}(R), \tag{7}$$

$$H_{n_i} = \beta_i^{1/2} N_{n_i\alpha_i} \mathrm{e}^{-y_i/2} y_i^{(\alpha_i+1)/2} L_{n_i}^{\alpha_i}(y_i), \quad i = 1,2, \tag{8}$$

where $N_{n\alpha}L_n^\alpha$ is a normalised associated Laguerre polynomial [19] and

$$y_1 = A_1 \exp(-\beta_1(r - r_e)), \tag{9a}$$

$$y_2 = A_2 \exp(-\beta_2(R - R_e)). \tag{9b}$$

The constants (A_1, β_1, r_e) and (A_2, β_2, R_e) are those associated with the solutions of the Morse potential for diatomic molecules [20]. If D_i is the dissociation energy and ω_i the fundamental frequency of diatomic i, then

$$A_i = 4D_i/\omega_i, \quad \beta_i = \omega_i(\mu_i/4D_i)^{1/2}. \tag{10}$$

Choosing α_i as the nearest integer to A_i gives an orthonormal basis complete for all n. As the method is variational, the constants (r_e, D_1, ω_1) and (R_e, D_2, ω_2) can be optimized to give the best basis set for a particular problem. Experience [7–9] has shown the choice of R_e (and r_e) to be critical and optimal values to generally be larger than the equilibrium separation.

With these radial functions, the matrix elements

$$\langle n_i'|\hat{K}_i|n_i\rangle = \frac{\hbar^2\beta_i^2}{8\mu_i}\left[\delta_{n_i',n_i}(2n_i(\alpha_i + n_i + 1) + \alpha_i + 1) - \delta_{n_i,n_i+2}((\alpha_i + n_i)(\alpha_i + n_i + 1)n_i(n_i - 1))^{1/2}\right],$$

$$n_i \geqslant n_i', \; i = 1,2 \tag{11}$$

are analytic where $\hat{K}_i$ is the appropriate second derivative operator from (2) [7]. Other radial matrix elements, those over r^{-2}, R^{-2} and $V_\lambda(r, R)$, are obtained by Gaussian quadrature. For this a modification of the program given by Stroud and Secrest [21] has been used, this allows problems with $\alpha > 20$ to be tackled and involves rewriting the quadrature formula for normalised Laguerre polynomials. For M_i point Gauss–Laguerre integration the formula for the weight of the pth point becomes

$$W_p = M_i!\left[\left(\mathrm{d}L_{M_i}^{\alpha}(x_p)/\mathrm{d}x\right)L_{M_{i-1}}^{\alpha}(x_p)\right]^{-1}. \tag{12}$$

With α in the quadrature scheme equal to α_i in the basis set, the numerical integration performs well if $M_i \geqslant n_i^{\max} + 3$ [7].

Diagonalising the secular matrix forms the computational bottleneck of the problem. It dominates the time taken and if a procedure is used which requires the whole matrix to be retained in fast store, it also gives a limit to the size of problem that can be tackled. In core diagonalisation is the simplest for small problems and comparison of several out of core diagonalisation methods [8] showed the orthogonalised Lanczos procedure [22] to be particularly well suited to LC-RAMP secular matrices. A choice of diagonalisers has thus been included in ATOMDIAT, although it is anticipated that the user might wish to use other diagonalising packages particularly if vectorisation is desired.

3. Program organisation

ATOMDIAT is divided into five segments which form the basis of the overlayed structure, see fig. 2. The subroutines have been numbered sequentially as they appear in the listing and these numbers are used in the following subsection where each section of the overlay is discussed.

ATOMDIAT uses the convention that variable names beginning with the letters A–H and O–Y are for double precision reals, I–N are for integers and variables whose names begin with Z are logical. Where possible constants have been placed in data statements to ease conversion to machines with different word lengths.

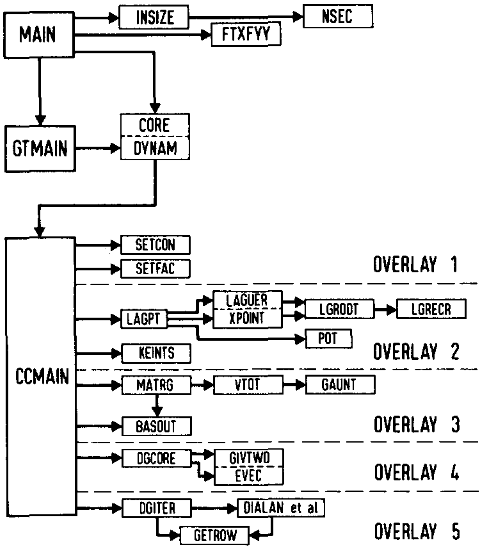

Fig. 2. Program structure. Service routines SYMOUT, TIMER, OUTROW and DATETI, which are in the main segment, have not be depicted.

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.

⟨1⟩ MAIN	Reads in namelist data, checks file allocations and calls initializing routines including CORE and GTMAIN.
⟨5⟩ CORE	Calculates storage requirements and sets up array pointers. Entry DYNAM calls CCMAIN if sufficient array space is available.
⟨6⟩ CCMAIN	Driver routine which calls the overlayed branches. Calls ERRSET an IBM supplied routine which suppresses underflow errors.
⟨8⟩ SYMOUT	Prints a symmetric matrix stored in lower triangular form.
⟨10⟩ TIMER	Calls CPUSED and prints CPU time used.
⟨24⟩ OUTROW	Fast unformatted write.
⟨44⟩ 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 storage available.
⟨45⟩ DATETI	Fortran dummy of assembler routine DATETIME. In assembler entry CPUSED should return the CPU time used and RTIME the time remaining (both as integers in hundredths of a second). It is not possible to initiate a dump in the Lanczos routines without a genuine RTIME.

3.2. Overlay 1: data input and initialization

There are 3 forms of data input. Namelist data which changes present defaults is read in ⟨1⟩ MAIN. Integer data which characterizes the size of the problem is read in ⟨3⟩ INSIZE, prior to array allocation. Real data is read in ⟨7⟩ SETCON. The other subroutines in this segment are concerned with initialization.

⟨3⟩ INSIZE	reads in integer parameters controlling problem size (stored in COMMON/SIZE/) and sets flow parameters.
⟨4⟩ NSEC	determines size of secular problem to be solved.
⟨7⟩ SETCON	reads in real constants of the problem and sets radial basis set parameters, reduced masses (and rotational constants).
⟨20⟩ SETFAC	uses Pascal's triangle to initialize array of binomial coefficients (BINOM).
⟨21⟩ NORMS	sets up array of pseudo-normalisation constants.
⟨46⟩ FTXFYY	Fortran dummy of an assembler routine which checks that the necessary disk files are pre-allocated. This dummy assumes that all the files are allocated and thus *i/o* errors can occur; in particular if there is insufficient storage for in core diagonalisation, the program will attempt to run using Lanczos and this may lead to failure in ⟨12⟩ MATRG if no diskfile is allocated for the secular matrix.

3.3. Overlay 2: radial basis functions and integration

This segment sets up matrices V0, V1, RM21, RM22, HBL1 and HBL2 which contain all the matrix elements of the radial basis functions needed in setting up the Hamiltonian. Note that performing the radial integration before the angular integration is the reverse of the order in which the formalism is generally presented, eq. (2) and refs. [1,5,7–10,15,18].

⟨11⟩ KEINTS	forms the analytic matrix elements of eq. (11), stored in HBL1 and HBL2.
⟨13⟩ LAGPT	sets up the radial basis set(s) at the numerical integration points and forms matrix elements over r^{-2} (RM21), R^{-2} (RM22), $V_0(R, r)$ (V0) and $V_\lambda(R, r)$ (V1). Checks the sum of integration points and weights against analytic formulae.
⟨14⟩LAGUER	adaptation of the Gauss–Laguerre integration points and weights routine of Stroud and Secret [21] for large α. Note that the initial guess formulae are arbitrary and may fail e.g. if $\alpha > 1000$. The ith call to entry XPOINT returns the ith point and weight; i must be in ascending order.
⟨15⟩ LGROOT	Improves the guess to the integration point [21].
⟨16⟩ LGRECR	Uses recurrence relations to generate associated Laguerre polynomials [21].
⟨47⟩ POT	returns the potential at the requested point. This routine must be supplied for each problem, see section 4.1.

3.4. Overlay 3: angular integration and the Hamiltonian matrix

This segment sets up the Hamiltonian matrix HAMIL and writes it to disk if required. Angular matrix elements are formed as needed.

⟨9⟩ BASOUT	prints out the basis set labels as in eq. (1).
⟨12⟩ MATRG	performs the angular integration and forms the Hamiltonian matrix in lower triangular form. Note that use of the IBM H extended complier with OPT(2) can cause spurious errors for this routine.
⟨17⟩ VTOT	performs the angular integration over the potential.
⟨18⟩ GAUNT	a double precision function which calculates Gaunt coefficients, eq. (5b).

3.5. Overlay 4: in core diagonalisation

This segment handles the diagonalisation when the secular matrix can be retained in fast storage.

⟨22⟩ DGCORE	routine which controls in calls to the Givens–Householder diagonaliser and prints the results.
⟨26⟩ GIVTWO	Givens–Householder diagonalising routine due to Prosser [11]. Entry EVEC(I) returns the Ith eigenvector.

3.6. Overlay 5: iterative diagonalisation

This segment controls the iterative diagonalisation of the secular matrix for which 3 diskfiles are necessary, see section 4.2. The method used is orthogonalised Lanczos [8,22] and routines are adapted from a Paige style Lanczos program [12].

⟨23⟩ DGITER	provides a starting vector, calls the orthogonalised Lanczos routines and prints the answers.
⟨25⟩ GETROW	Fast unformatted read.
⟨27⟩ DIALAN–⟨43⟩ SETT	Suite to perform orthogonalised Lanczos diagonalisation.

4. Program use

ATOMDIAT requires not only card input, but a subroutine giving the potential.

4.1. The potential

The potential must be specified as a Legendre expansion, eq. (4). It should be provided for each system studied as

SUBROUTINE POT (V0, V1, R1, R2)

yielding for R1 = r and R2 = R, V0 = $V_0(R, r)$ and V1 = $V_\lambda(R, r)$. If IDIA = 2, only even V_λ are required.

If NCOORD = 1, R1 and V1 are dummies. If NCOORD = 2, R1 is the rigid diatom bondlength, r_e. If NCOORD > 1, the dimension of V1 is LPOT. Note that this version of ATOMDIAT works in atomic units, so V0 and V1 must be in Hartrees for R1 and R2 in Bohr. To change the units it is necessary to alter subroutines ⟨7⟩ SETCON, ⟨22⟩ DGCORE, ⟨23⟩ DGITER and ⟨47⟩ POT only.

4.2. Card input

The program requires 9 lines of card input for all runs although if NCOORD $\neq$ 3, some of the data is not used; Table 1 gives the structure of the data input. Defaults given in parentheses are assigned to all namelist input in ⟨2⟩ BLOCK DATA.

Card 1 NAMELIST/PRT/

ZHAMIL [F] = T	requests printing of the Hamiltonian matrix.
ZRAD [F] = T	request printing of the radial matrix elements.

Card 2 Namelist/UNT/

IHAM [2]	stream to which the Hamiltonian is written if ZLANC = T.
ISCR1 [1]	Lanczos scratchfile used if ZLANC = T.
ISCR2 [3]	Lanczos scratchfile used if ZLANC = T, these scratchfiles must be retained if the Lanczos process is to be restarted.

Table 1
Format of data input

```
C                                                                      ACEN0060
C                  MAIN PROGRAM                                  #001 ACEN0061
C                                                                      ACEN0066
      COMMON /OUTP/ ZHAMIL,ZRAD                                        ACEN0069
      NAMELIST / PRT/ZHAMIL,ZRAD                                       ACEN0070
      COMMON /UNITS/ IHAM,IVEC,ISCR1,ISCR2,ZVEC,ZLANC                  ACEN0071
      NAMELIST / UNT/ IHAM,IVEC,ISCR1,ISCR2,ZVEC,ZLANC                 ACEN0072
      COMMON /LANC/ EPSV,MAXCYC,LPRINT,IER,NSTRT,INCR                  ACEN0073
      NAMELIST / LNC/EPSV,MAXCYC,LPRINT,IER,NSTRT,INCR                 ACEN0074
C     READ IN NAMELIST INPUT DATA (DEFAULTS IN BLOCK DATA)             ACEN0081
      READ(5,PRT)                                                      ACEN0082
      READ(5,UNT)                                                      ACEN0083
      READ(5,LNC)                                                      ACEN0084
C                                                                      ACEN0209
C     SUBROUTINE INSIZE                                            #003ACEN0210
C                                                                      ACEN0211
      READ(5,5) NCOORD                                                 ACEN0248
    5 FORMAT(10I5)                                                     ACEN0249
      READ(5,5) NPNT2,NMAX2,JROT,NEVAL,LMAX,LPOT,IDIA,KMIN,NPNT1,NMAX1 ACEN0254
      READ(5,500)   TITLE                                              ACEN0295
  500 FORMAT(18A4)                                                     ACEN0296
C                                                                      ACEN0645
C     SUBROUTINE SETCON                                            #007ACEN0646
C                                                                      ACEN0647
      READ(5,5)     XMASS                                              ACEN0661
    5 FORMAT(3F20.0)                                                   ACEN0662
      READ(5,5)     RE1,DISS1,WE1                                      ACEN0666
      READ(5,5)     RE2,DISS2,WE2                                      ACEN0673
```

IVEC [4]	stream to which the eigenvector and eigenvalues are written if ZVEC = T.
ZVEC [F]	= T request writing to stream IVEC.
ZLANC [F]	false for in core diagonalisation, true for Lanczos diagonalisation.

Card 3 NAMELIST/LNC/

Ignored if ZLANC = F, except that IER must not be < 0.

EPSV [1×10^4]	convergence criteria for Lanczos vectors.
MAXCYC [100]	maximum number of Lanczos iterations.
LPRINT [0]	≠ 0 requests extra printing.
IER [0]	negative for the restart option.
NSTRT [10∗NEVAL]	initial number of iterations, if IER < 0, NSTRT *must be* set to the number of iterations already completed.
INCR [2∗NEVAL]	number of iterations performed at each subsequent increment.

Card 4 NCOORD

NCOORD is the number of vibrational coordinates of the problem: 1 for a simple diatomic, 2 for an atom rigid diatom system and 3 for a full triatomic. Other values results in termination.

Card 5 NPNT2, NMAX2, JROT, NEVAL, LMAX, LPOT, IDIA, KMIN, NPNT1, NMAX1

NPNT2	order of Gaussian quadrature in the R coordinate (must be greater than NMAX2).
NMAX2	order of the largest radial basis function $H_n(R)$, giving an R bases of NMAX2 + 1 functions.

JROT	|JROT| is the total rotational quantum number of the system. If JROT > 0 the off diagonal Coriolis terms are included, see eq. (2). 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	the number of eigenvalues and vectors required.

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

LMAX	order of the highest associated Legendre polynominal in the basis.
LPOT	highest value of λ in the Legendre expansion, eq. (4).
IDIA	1 for a heteronuclear diatomic and 2 for a homonuclear diatomic. For homonuclears, the parity of l is taken from the parity of LMAX.
KMIN	For JROT < 0, KMIN = k. For JROT > 0, KMIN = $1 - p$, see eq. (1).

If NCOORD = 2, the rest of the card is ignored.

NPNT1	order of Gaussian quadrature in the r coordinate (must be greater than NMAX1).
NMAX1	order of the largest radial basis function $H_m(r)$ giving a diatomic basis of NMAX1 + 1 functions.

Card 6 TITLE
A 72 character title.

Card 7 (XMASS(I), I = 1, 3)
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, thus treating the diatom as atoms 1 and 2, not 2 and 3.

CARD 8 RE1, DISS1, WE1
If NCOORD = 1, this card is read but ignored.
If NCOORD = 2, RE1 is the fixed diatomic bondlengths, DISS1 and WE1 ignored.
If NCOORD = 3, RE1 = r_e, DISSI = D_1 and WE1 = ω_1, see eqs. (8)–(10).

Card 9 RE2, DISS2, WE2
RE2 = R_e, DISS2 = D_2 and WE2 = ω_2, see eqs. (8)–(10).

4.3. Test cases

Three test cases have been included corresponding to runs with NCOORD = 1,2 and 3. The test subroutine POT contains a full surface for the HeHF Van der Waals molecule [4]. POT has been written for all 3 values of NCOORD, although it is anticipated that this will not usually be the case. Some pages from these runs which have the print parameters set for maximal printing are reproduced.

Acknowledgements

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[22] B.N. Parlett, The Symmetric Eigenvalue Problem (Prentice-Hall, Englewood Cliffs, NJ, 1980) chap. 13.

TEST RUN OUTPUT

Test run 1

```
      ATOM - RIGID DIATOM VIBRATIONAL ANALYSIS WITH:

        14    POINT NUMERICAL INTEGRATION FOR
         4    TH ORDER BIG R RADIAL BASIS FUNCTIONS
         3    TH ORDER ANGULAR BASIS FUNCTIONS
         6    TERMS IN THE POTENTIAL EXPANSION
         5    LOWEST EIGENVECTORS REQUIRED FOR
        20    DIMENSION SECULAR PROBLEM

      TITLE:  HF-HE J=0 COMPUTER PHYS. COMMS. TEST DATA

      PRINTING OF HAMILTONIAN MATRIX REQUESTED
      PRINTING OF RADIAL MATRIX ELEMENTS REQUESTED

       DIATOMIC ASSUMED HETRONUCLEAR

       J =  0 ROTATIONAL STATE

      DIAGONALISATION IN CORE REQUESTED

      RUN REQUIRES      5 K OF CORE

NUCLEAR MASSES IN AMU:      4.000000      1.000000    19.000000

DIATOMIC FIXED BONDLENGTH =  1.7328 BOHR & REDUCED MASS =    0.1731703D+04 A.U.

MORSE FUNCTION PARAMETERS FOR COMPLEX BASIS
R EQUILIBRIUM =   8.2500 BOHR, DISSOCIATION ENERGY   0.1500000D-03 HARTREE &  VIBRATIONAL FREQUENCY =  0.1000000D-03 HARTREE

CONSTANT USED TO CONSTRUCT MORSE OSCILLATORS:
REDUCED MASS =    0.6076149D+04 A.U., BETA =  0.4500 (1/BOHR), A =    0.6000000D+01 AND U =    6
INTEGRATION POINTS            WEIGHTS            CORRESPONDING R

  1.426930588957395       0.939864724462D-18      11.44133
  2.685459112478244       0.147083352177D-16      10.03629
  4.236644850795886       0.586602931882D-16       9.02323
  6.107205807471306       0.967659530511D-16       8.21065
  8.319796407411851       0.794451519568D-16       7.52367
 10.901069628474501       0.353071845654D-16       6.92323
 13.885040861619858       0.879022530678D-17       6.38562
 17.316714310023691       0.122824833058D-17       5.89486
 21.257605287109541       0.938429645960D-19       5.43925
 25.795355406558919       0.370109311248D-20       5.00934
 31.062365213201161       0.679937845737D-22       4.59648
 37.277140938438478       0.485066748931D-24       4.19123
 44.857146463472507       0.940967948884D-27       3.77993
 54.871525123986647       0.200741729271D-30       3.33216

COMPUTED SUM OF POINTS      0.28000000000000D+03 & WEIGHTS      0.29594286887848 5D+15
EXACT    SUM OF POINTS      0.28000000000000D+03 & WEIGHTS      0.29594286887847 6D+15

    LOWEST  5 EIGENVALUES IN HARTREES

    -0.286376945638D-04       0.296329301539D-04       0.117292877738D-03       0.157354710992D-03       0.219076117994D-03

    LOWEST  5 EIGENVALUES IN WAVENUMBERS

    -0.628524724561D+01       0.650368717838D+01       0.257428102394D+02       0.345353660297D+02       0.480816486241D+02


EIGENVECTORS OF BOUND STATES

    0.8386159    -0.4072953      0.3400726    -0.1073291      0.0485883      0.0144780    -0.0067989    -0.0076440      0.0132558    -0.0151958
    0.0093905    -0.0137171      0.0135153    -0.0090872      0.0040523      0.0010182    -0.0004729    -0.0014325      0.0030263    -0.0035780
```

Test run 2

```
     DIATOMIC VIBRATIONAL ANALYSIS WITH:
       14    POINT NUMERICAL INTEGRATION FOR
        4    TH ORDER BIG R RADIAL BASIS FUNCTIONS
        0    TH ORDER ANGULAR BASIS FUNCTIONS
        0    TERMS IN THE POTENTIAL EXPANSION
        5    LOWEST EIGENVECTORS REQUIRED FOR
        5    DIMENSION SECULAR PROBLEM
     TITLE:  H-F J=0 COMPUTER PHYS. COMMS. TEST DATA

     PRINTING OF HAMILTONIAN MATRIX REQUESTED
     PRINTING OF RADIAL MATRIX ELEMENTS REQUESTED

      J =  0 ROTATIONAL STATE
     DIAGONALISATION IN CORE REQUESTED
     RUN REQUIRES      3 K OF CORE

NUCLEAR MASSES IN AMU:    19.000000     1.000000     0.0

MORSE FUNCTION PARAMETERS FOR COMPLEX BASIS
R EQUILIBRIUM =  1.7788 BOHR, DISSOCIATION ENERGY  0.18215000D+00 HARTREE &  VIBRATIONAL FREQUENCY =  0.15022000D-01 HARTREE
CONSTANT USED TO CONSTRUCT MORSE OSCILATORS:
REDUCED MASS =   0.1731703D+04 A.U., BETA =  1.0357 (1/BOHR), A =    0.4850220D+02 AND U =   49

   LOWEST  5 EIGENVALUES IN HARTREES
   -0.215661536684D+00      -0.197574158906D+00      -0.180264109317D+00      -0.158866285171D+00      -0.997246966343D-01

   LOWEST  5 EIGENVALUES IN WAVENUMBERS
   -0.473322346750D+05      -0.433625142380D+05      -0.395633976135D+05      -0.348671182041D+05      -0.218870402973D+05


EIGENVECTORS OF BOUND STATES
   0.9977596    0.0223580   -0.0625761   -0.0070774    0.0031712

  -0.0059251    0.9661362    0.2536901   -0.0382925   -0.0268467

   0.0588926   -0.1900912    0.8174158    0.5275649    0.1179143

   0.0300630   -0.1641569    0.4665160   -0.6587979   -0.5661245

   0.0082806   -0.0547614    0.2142892   -0.5349245    0.8153947
```

Test run 3

```
     FULL ATOM-DIATOM VIBRATIONAL PROBLEM WITH:

       14    POINT NUMERICAL INTEGRATION FOR,
        5    TH ORDER DIATOMIC RADIAL BASIS FUNCTIONS
       14    POINT NUMERICAL INTEGRATION FOR
        4    TH ORDER BIG R RADIAL BASIS FUNCTIONS
        3    TH ORDER ANGULAR BASIS FUNCTIONS
        6    TERMS IN THE POTENTIAL EXPANSION
        5    LOWEST EIGENVECTORS REQUIRED FOR
      120    DIMENSION SECULAR PROBLEM

     TITLE:  HF-HE J=0 COMPUTER PHYS. COMMS. TEST DATA

     PRINTING OF HAMILTONIAN MATRIX REQUESTED
     PRINTING OF RADIAL MATRIX ELEMENTS REQUESTED

      DIATOMIC ASSUMED HETRONUCLEAR

      J =  0 ROTATIONAL STATE

     DIAGONALISATION IN CORE REQUESTED

     RUN REQUIRES    79 K OF CORE

NUCLEAR MASSES IN AMU:    4.000000    1.000000   19.000000

MORSE FUNCTION PARAMETERS FOR DIATOM BASIS
R EQUILIBRIUM =  1.7738 BOHR, DISSOCIATION ENERGY  0.18215000D+00 HARTREE &  VIBRATIONAL FREQUENCY =  0.15022000D-01 HARTREE

CONSTANT USED TO CONSTRUCT MORSE OSCILATORS:
REDUCED MASS =   0.17317030D+04 A.U., BETA =  1.0357 (1/BOHR), A =   0.48502200D+02 AND J =   49

MORSE FUNCTION PARAMETERS FOR COMPLEX BASIS
R EQUILIBRIUM =  3.2500 BOHR, DISSOCIATION ENERGY  0.15000000D-03 HARTREE &  VIBRATIONAL FREQUENCY =  0.10000000D-03 HARTREE

CONSTANT USED TO CONSTRUCT MORSE OSCILATORS:
REDUCED MASS =   0.60761490D+04 A.U., BETA =  0.4500 (1/BOHR), A =   0.60000000D+01 AND U =   6

   LOWEST  5 EIGENVALUES IN HARTREES

   -0.290013213256D-04       0.294724877323D-04       0.116895531152D-03       0.153650769625D-03       0.215214437681D-03


   LOWEST  5 EIGENVALUES IN WAVENUMBERS

   -0.636516394050D+01       0.646846315339D+01       0.256556137206D+02       0.337224448907D+02       0.472341077394D+02



EIGENVECTORS OF BOUND STATES

   0.3379931   -0.4059763    0.3370805   -0.1052743    0.0473390    0.0133722   -0.0091954    0.0075706   -0.0022830    0.0009374
  -0.0525593    0.0254652   -0.0211623    0.0066342   -0.0030000   -0.0030659    0.0028965   -0.0024045    0.0007492   -0.0003289
   0.0029440   -0.0014245    0.0011941   -0.0003721    0.0001706    0.0006522   -0.0003209    0.0002667   -0.0000836    0.0000377
   0.0145124   -0.0050113   -0.0109141    0.0161300   -0.0170291    0.0003633   -0.0000501   -0.0003939    0.0006004   -0.0006110
  -0.0009012    0.0003201    0.0006487   -0.0009571    0.0010136   -0.0001049    0.0000329    0.0000875   -0.0001291    0.0001343
   0.0000504   -0.0000193   -0.0000317    0.0000476   -0.0000518    0.0000116   -0.0000045   -0.0000076    0.0000116   -0.0000127
   0.0099260   -0.0141001    0.0133065   -0.0094473    0.0032357    0.0003132   -0.0004355    0.0003833   -0.0001918    0.0000022
  -0.0006075    0.0008692   -0.0008342    0.0005503   -0.0002376   -0.0000730    0.0001120   -0.0001064    0.0000657   -0.0000194
   0.0000323   -0.0000467    0.0000468   -0.0000352    0.0000216    0.0000031   -0.0000122    0.0000131   -0.0000108    0.0000071
   0.0010297   -0.0002913   -0.0018683    0.0035095   -0.0038592    0.0000355    0.0000123   -0.0001257    0.0002070   -0.0002024
  -0.0000627    0.0000245    0.0000962   -0.0001903    0.0002174   -0.0000032    0.0000014    0.0000177   -0.0000322    0.0000343
   0.0000034   -0.0000020   -0.0000035    0.0000037   -0.0000106    0.0000009   -0.0000005   -0.0000011    0.0000025   -0.0000032
```