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# ATOMDIAT2 AND GENPOT: ADAPTATIONS OF ATOMDIAT FOR THE RO-VIBRATIONAL LEVELS OF ANY FLOPPY TRIATOMIC USING A GENERAL POTENTIAL FUNCTION

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## ADAPTION SUMMARY

*Title of adaptation:* ATOMDIAT2

*Adaptation number:* ACEN 0001

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

*Reference to original program:* CPC Library File ACEN [1]

*Author of original program:* J. Tennyson [1]

*Computer*: NAS 7000; *Installation*: Daresbury Laboratory

*Other machines on which the adaption has been tested:* CRAY-1

*No. of bits in a byte:* 8

*No. of lines required to effect adaptation:* 190

*Additional keywords:* spherical oscillator functions

*Nature of physical problem*
ATOMDIAT2 solves the ro-vibrational problem for an atom (1)–diatom system (2–3) for which the linear 213 structure is significant.

*Method of solution*
Spherical oscillator-like functions are used for the $R$-coordinate basis [2]. An option allowing the problem to be embedded along $\boldsymbol{r}$ is also included.

*References*

[1] J. Tennyson, Comput. Phys. Commun. 29 (1983) 307.
[2] J. Tennyson and B.T. Sutcliffe, J. Mol. Spectr. 101 (1983) 71.

## ADAPTION SUMMARY

*Title of adaptation*: GENPOT – addendum to ATOMDIAT(2)

*Adaptation number*: ACEN 0002

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

*Reference to original program*: CPC Library files ACEN [1] and ACEN 0001 [2]

*Author of original program*: J. Tennyson [1,2]

*Computer*: NAS 7000; *Installation*: Daresbury Laboratory

*Other machines on which the adaption has been tested*: CRAY-1 and IBM4341/2

*No. of bits in a byte*: 8

*No. of lines required to effect adaptation*: 215

*Additional keywords*: Gauss–Legendre quadrature, isotopic substitution

*Nature of physical problem*
GENPOT generalises ATOMDIAT [1] or ATOMDIAT2 [2] so that the ro-vibrational states may be obtained for any triatomic potential function, not just one fitted in Legendre polynomials. It can also be used to perform shifts of a potential fitted as a Legendre expansion caused by isotopic substitution [3].

*Method of solution*
GENPOT uses Gauss–Legendre quadrature to obtain a Legendre expansion for each $R$ and $r$ [4].

*References*

[1] J. Tennyson, Comput Phys. Commun. 29 (1983) 307.
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## LONG WRITE-UP

### 1. Introduction

Recently, I published a program, ATOMDIAT [1], which performed variational ro-vibrational calculations on "floppy" triatomics using the method of Tennyson and Sutcliffe [2,3]. Two constraints on this program prevent it from providing a completely general method for obtaining the ro-vibrational levels of any triatomic.

Firstly, the Morse oscillator-like functions used by ATOMDIAT for the basis of the atom (1)–diatom (2–3) stretching coordinate $R$ are only valid if the vibrational wavefunctions have effectively vanished at $R = 0$. This problem was first noted by Ter Haar [4] and is associated with the use of the incorrect integration range for the Morse problem. For most triatomics this condition does not present a problem; however, for systems which have significant amplitude for the 2–1–3 linear structure the Morse-like functions are no longer appropriate. Examples of such systems are $X_3$, $X_3^+$ ($X$ = rare gas), $CH_2^+$, $CO_2$ and highly excited $H_2O$. Recently, Tennyson and Sutcliffe [5] have shown how the use of spherical oscillator-like functions [6] can overcome this problem and ATOMDIAT2 is an adaptation of ATOMDIAT which uses these basis functions.

Secondly, a requirement of ATOMDIAT is a subroutine ⟨47⟩ POT containing the (analytic) potential energy surface in the form of a Legendre expansion

$$V(R, r, \theta) = \sum_{\lambda=0}^{\lambda_{\max}} V_\lambda(R, r) P_\lambda(\cos\theta). \tag{1}$$

This requirement limits the utility of ATOMDIAT as many surfaces do not give obvious analytic expressions for the $V_\lambda(R, r)$ of such an expansion. GENPOT provides the subroutines which generalise ATOMDIAT or ATOMDIAT2 allowing the triatomic potential energy surface to be presented in any convenient (analytic) form, such as pair potentials or a Sorbie–Murrell potential [7].

The Legendre expansion of eq. (1) is based on the diatomic centre of mass. If results are required for different isotopes of a molecule, then it is often necessary to re-expand (1) in a new series. An approximate transformation for this based on a truncated Taylor series was proposed by Kreek and LeRoy [8] and employed in several calculations on diatomic-rare gas Van der Waals molecules [8–11]. GENPOT performs this transformation exactly, limited only by the number of terms taken in the Legendre expansion. This means that the adapted ATOMDIAT can conveniently be used for calculations on several isotopic species with the same potential. Indeed, GENPOT itself provides a suitable subroutine suite for the transformation of Liu et al. [12].

The adaptions thus provide a suite of programs (ATOMDIAT and ATOMDIAT2) which can be used to find the bound ro-vibrational levels of any triatomic system. It is anticipated, however, that the programs will find widest application for systems, such as Van der Waals complexes, which have one or more large amplitude vibrational mode – so called floppy molecules. ATOMDIAT2 has been successfully applied to $CH_2^+$ [5] and gave better results than those obtained using more conventional (Eckart) methods [13,14].

The choice between ATOMDIAT and ATOMDIAT2 depends on the physics of the problem: ATOMDIAT being for molecules for which a 2–1–3 linear structure is not energetically accessible. An indication of whether ATOMDIAT is suitable for a problem is given by the stability of the numerical integrals. In particular, if the integrals over $R^{-2}$ are not stable to increasing the number of Gauss–Laguerre integration points, then use of ATOMDIAT2 is recommended. Conversely, if large values for $\alpha_2$ and $\beta_2$ (see below) are required by ATOMDIAT2 then ATOMDIAT might well prove more efficient.

Finally, ATOMDIAT contains an option which allows the off-diagonal Coriolis terms to be neglected, a simplifying approximation which has often been found useful [2,11,15,16]. These Coriolis interactions depend on the form of the coordinate embedding. ATOMDIAT2 contains an option which allows the user to choose between embedding the axis along $\boldsymbol{R}$ (as in ATOMDIAT) or $\boldsymbol{r}$ (in the fashion of Istomin et al. [17]). The latter embedding is more appropriate for the near linear systems that ATOMDIAT2 is designed for and was found to give errors an order of magnitude smaller when the off-diagonal Coriolis interactions in $CH_2^+$ were neglected [5]. The results of a full calculation are, of course, independent of the embedding used.

## 2. Method

ATOMDIAT2 follows the method of ATOMDIAT [1] with the exception of the functions used for the $R$ (atom–diatom stretch) coordinate basis functions. These are now based on spherical oscillator functions and are defined as

$$H_{n_2} = 2^{1/2}\beta^{3/4}N_{n_2\alpha_2}\,\mathrm{e}^{-y_2/2}y^{\alpha_2/2}L_{n_2}^{\alpha_2+1/2}(y_2), \qquad (2)$$

$$y_2 = \beta_2 R^2, \qquad (3)$$

$$\beta_2 = (\mu_2\omega_2)^{1/2}, \qquad (4)$$

where $N_{n\alpha}L_n^{\alpha+1/2}$ is a normalised Laguerre polynomial [18] and $\omega_2$ is the frequency of the $R$ stretching fundamental. In practice, the parameters $\alpha_2$ and $\omega_2$ are optimised variationally to give the best basis for each problem.

It should be noted that all functions with $\alpha_2 = 0$ have amplitude at $R = 0$, whilst all functions with $\alpha_2 > 0$ are zero at $R = 0$. Symmetry considerations can thus determine an optimum value of $\alpha_2$ and this value will not necessarily be appropriate for all quantum numbers of a particular problem [5].

Kinetic energy integrals over these functions are performed analytically [5,6]

$$\begin{aligned}\langle n_2'|\hat{K}_2|n_2\rangle = \frac{\beta_2\hbar^2}{2\mu_2}&\delta_{n_2'n_2-1}\left(n_2\left(n_2+\alpha_2+\tfrac{1}{2}\right)\right)^{1/2}\\ &+\delta_{n_2'n_2}\left(2n_2+\alpha_2+\tfrac{3}{2}\right)\\ &+\langle n_2'|\left(2\mu_2R^2\right)^{-1}|n_2\rangle,\\ &n_2 \geqslant n_2', \end{aligned} \qquad (5)$$

$$\begin{aligned}&\langle n_2'|\left(2\mu_2R^2\right)^{-1}|n_2\rangle\\ &\quad=\frac{\beta_2\hbar^2}{2\mu_2}\left[\frac{n_2!}{n_2'!}\,\frac{\Gamma(n_2'+\alpha_2+3/2)}{\Gamma(n_2+\alpha_2+3/2)}\right]^{1/2}\\ &\qquad+\sum_{\sigma=0}^{n_2'}\frac{\Gamma(\sigma+\alpha_2+1/2)}{\Gamma(n_2'+\alpha_2+3/2)}\,\frac{n_2'!}{\sigma!}, \quad n_2 \geqslant n_2', \end{aligned} \qquad (6)$$

and those over the potential are performed using Gauss–Laguerre integrations [2,19] based on $L_{M_2}^{\alpha_2+1/2}$. $M_2$ is input and the points and weights are generated automatically.

In ATOMDIAT, the $z$ axis is embedded along $\boldsymbol{R}$ [1–3]. When the off-diagonal Coriolis terms are neglected, $k$, the projection of the total angular momentum $J$ along the $\boldsymbol{R}$ axis, is a good quantum number. If the $z$ axis is embedded along $\boldsymbol{r}$ [5,17], $\Omega$, the projection of $J$ along $\boldsymbol{r}$, is a good quantum number in this approximation. Which approximation is appropriate will depend on the system in question and in particular on the relative magnitude of the $(2\mu_1 r^2)^{-1}$ and $(2\mu_2 R^2)^{-1}$ terms. ATOMDIAT2 contains an option which allows either embedding to be employed when the off-diagonal Coriolis interactions are neglected. For a full calculation the choice of embedding is immaterial and ATOMDIAT2 uses the same embedding as ATOMDIAT.

GENPOT allows the surface to be fitted to a Legendre expansion for each $R$ and $r$ at execution time, rather than requiring a pre-fitted surface in the form of eq. (1). This is done using $\Lambda$ point Gauss–Legendre integration [19]. When the request for a potential in the form of eq. (1) is issued by CALL POT(V0, V1, R1, R2), the amended POT performs a $\Lambda$ point ($\Lambda > \lambda_{\max}$) integration with $(r, R)$ fixed. This gives the best Legendre expansion for each set of radial separations, and providing $\lambda_{\max}$ is chosen large enough, entails no loss of accuracy over using the exact potential.

If a transformed Legendre expansion is required to cope with isotopic substitution, the potential given by the original expansion can simply be given in POTV and the correctly transformed potential is automatically generated. Care need only be taken with the definition of R2.

## 3. Organisation

### 3.1. ATOMDIAT2

Although several of the ATOMDIAT subroutines are adapted in ATOMDIAT2, none change their basic function. One new subroutine, belonging to overlay 2, is required by

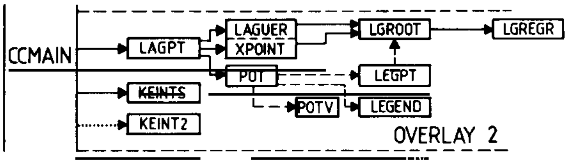

Fig. 1. Adapted program structure. The dotted call is made by ATOMDIAT2 and the dashed calls by the addendum GENPOT.

ATOMDIAT2.

⟨11A⟩ KEINT2 forms the analytic matrix element of eqs. (5) and (6). Stored in HBL2 and RM22.

### 3.2. GENPOT

The extra routines are all contained in a revised overlay 2 (see fig. 1) and are numbered sequentially from ⟨47⟩ POT, which replaces ⟨47⟩ POT as the final subroutine in ATOMDIAT or ATOMDIAT2.

⟨47⟩ POT Calls ⟨50⟩ POTV at R1, R2, X(I), where X(I) ($= \cos\theta$) is a Gauss–Legendre integration point.

⟨48⟩ LEGPT Sets up (and checks) Gauss–Legendre integration points and weights, an adaptation of subroutine JACOBI of Stroud and Secrest [19].

⟨49⟩ LEGEND Sets up weighted normalised Legendre polynomials.

⟨50⟩ POTV User supplied potential subroutine, see section 4.3.

## 4. Program use

The adapted programs require input in the same form as ATOMDIAT. However, some of the input parameters have a slightly altered meaning.

### 4.1. Card input for ATOMDIAT2

Card 2 NAMELIST/UNT/
There is an additional parameter
ZEMBED [T]= T gives $z$ embedded along $\boldsymbol{R}$,
= F gives $z$ embedded along $\boldsymbol{r}$ (ignored unless JROT < 0).

Card 9 RE2, ALF2, WE2
RE2 is ignored, ALF2 = $\alpha_2$, WE2 = $\omega_2$, see eqs. (2)–(4).

### 4.2. Card input for GENPOT

Card 5 NPNT2, NMAX2, JROT, NEVAL, LMAX, LPOT, IDIA, KMIN, NPNT1 NMAX1
LPOT has a slightly altered meaning. It is now the length of the Legendre expansion requested and hence determines the integration scheme:

$$\Lambda = \mathrm{LPOT} + 1 + \mathrm{MOD(LPOT,2)}.$$

All other input parameters have an unchanged meaning.

### 4.3. GENPOT: the potential

With the GENPOT addendum the potential function can now be specified in any form. It should be provided for each system studied as

SUBROUTINE POTV(V, R1, R2, X)

yielding V, the potential in hartree, at the point R1 = $r$, R2 = $R$ (both in bohr) and $X = \cos\theta$ ($\theta$ is the angle between $r$ and $R$). If NCOORD = 1, R1 and X are dummies and no Gauss–Legendre integration is performed. If NCOORD = 2, R1 is set to the rigid diatom bondlength, $r_e$.

Note that COMMON/MASS/XMASS(3) has been added to ⟨7⟩ SETCON. This stores the mass of atom I in XMASS(I) (numbering as in ref. [1]). As the calling program defines R2 according to the centre of mass of the current isotopes, the array XMASS can be accessed in POTV to give a routine which is general for all isotopes.

## 5. Test output

Some test results of ATOMDIAT2/GENPOT using the $CH_2^+$ potential of Carter and Handy [14] are printed below. In order to keep the test problem small, these results use a truncated basis set and are thus far from the converged results of ref. [5].

## References

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## TEST RUN OUTPUT

```
 INTEGRATION POINTS          WEIGHTS.          CORRESPONDING R

  0.147399184616311      0.114136764489D-14      0.10358
  0.590901811243187      0.294631840271D-14      0.20739
  1.334487511614576      0.318117482748D-14      0.31166
  2.385011552004653      0.200459576450D-14      0.41665
  3.752567873874767      0.812054437487D-15      0.52263
  5.451062939568396      0.218775201292D-15      0.62990
  7.499085532907371      0.394842091059D-16      0.73881
  9.921219136072429      0.473236189494D-17      0.84979
 12.750055460117065      0.368556402828D-18      0.96335
 16.029386360375124      0.179985370322D-19      1.08016
 19.819512877102021      0.522559600232D-21      1.20109
 24.206680643468303      0.833308727828D-23      1.32738
 29.321456103352332      0.646096973584D-25      1.46090
 35.379550787175560      0.198952300171D-27      1.60474
 42.793255970754640      0.165615695869D-30      1.76489
 52.618366255753244      0.141730912091D-34      1.95703

 COMPUTED SUM OF POINTS     0.264000000000000D+03 & WEIGHTS      0.103488899352582D-13
 EXACT    SUM OF POINTS     0.264000000000000D+03 & WEIGHTS      0.103488899352659D-13


  22 POINT GAUSS-LEGENDRE INTEGRATION

 INTEGRATION POINTS          WEIGHTS

  0.994294585482399      0.146279952982D-01
  0.970060497835429      0.337749015844D-01
  0.926956772187174      0.522933351525D-01
  0.865812577720300      0.697964684245D-01
  0.787816805979208      0.859416062171D-01
  0.694487263186683      0.100414144443D+00
  0.587640403506912      0.112932296081D+00
  0.469355837986757      0.123252376811D+00
  0.341935820892084      0.131173504787D+00
  0.207860426688221      0.136541498346D+00
  0.069739273319722      0.139251872856D+00
 -0.994294585482399      0.146279952982D-01
 -0.970060497835429      0.337749015844D-01
 -0.926956772187174      0.522933351525D-01
 -0.865812577720300      0.697964684245D-01
 -0.787816805979208      0.859416062171D-01
 -0.694487263186683      0.100414144443D+00
 -0.587640403506912      0.112932296081D+00
 -0.469355837986757      0.123252376811D+00
 -0.341935820892084      0.131173504787D+00
 -0.207860426688221      0.136541498346D+00
 -0.069739273319722      0.139251872856D+00

 COMPUTED SUM OF WEIGHTS     0.199999999999858D+01
 EXACT    SUM OF WEIGHTS     0.200000000000000D+01


1
 MOMENT OF INERTIA MATRIX CALCULATED NUMERICALLY


         1            2            3            4            5
 1   0.0000356
 2  -0.0000039    0.0000367
 3   0.0000001   -0.0000056    0.0000378
 4  -0.0000000    0.0000002   -0.0000069    0.0000389
 5  -0.0000000   -0.0000000    0.0000003   -0.0000082    0.0000401


LOWEST  6 EIGENVALUES IN HARTREES

-0.320421311983D+00     -0.316983993875D+00     -0.312379190922D+00     -0.306786930342D+00     -0.305528916848D+00

-0.303322963605D+00
```