INTDER2005

User's Manual

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This manual documents the INTDER2005 program, which was developed by Wesley D. Allen and co-workers. While much care has been exercised in preparing the program package and this manual, no representation is made that the manual and/or the program are without error or suitable for every application to which the user may attempt to apply them. Any expressed or implied warranties of merchantability or fitness of the software described herein are disclaimed. No part of the software may be reproduced or transmitted in any form or by any means, or stored in a data base or retrieval system, for any purpose without the consent of Wesley D. Allen. Users are responsible for testing the program package on their own system and comparing results with those supplied with the software. INTDER2005 is written in standard FORTRAN.

<div align="center">Required citations for INTDER2005</div>

General:

[1] INTDER2005 is a general program developed by Wesley D. Allen and co-workers which performs various vibrational analyses and higher-order nonlinear transformations among force field representations.

For force field transformations or Cartesian projection scheme:

[2] W. D. Allen and A. G. Császár, "On the Ab Initio Determination of Higher-Order Force Constants at Nonstationary Reference Geometries," J. Chem. Phys. **98**, 2983 (1993).

[3] W. D. Allen, A. G. Császár, V. Szalay, and I. M. Mills, "General Derivative Relations for Anharmonic Force Fields," Mol. Phys. **89**, 1213 (1996).

For Scaled Quantum Mechanical (SQM) force field analyses:

[4] W. D. Allen, A. G. Császár, and D. A. Horner, "The Puckering Inversion Barrier and Vibrational Spectrum of Cyclopentene. A Scaled Quantum Mechanical Force Field Algorithm," J. Am. Chem. Soc. **114**, 6834 (1992).

Table of Contents

Introduction

INTDER2005 is a connected set of programs for performing general curvilinear transformations and associated tasks often encountered in the calculation of anharmonic molecular force fields. The capabilities of INTDER2005 include:

(1) Force field transformations between Cartesian and general internal coordinate spaces up to fourth order, including nonstationary reference structures. Both forward and reverse transformations are possible; hence, by using intermediate Cartesian coordinates, force fields can be transferred among alternate representations in the internal space.

(2) Harmonic frequency and infrared intensity analyses, both in Cartesian and internal coordinate spaces.

(3) Scaled quantum mechanical (SQM) force field analyses, including efficient nonlinear optimization of scale factors.

(4) Transformation of dipole-moment derivatives between Cartesian and internal coordinates.

(5) Generation of displaced Cartesian geometries along general internal coordinates for use in finite-difference computations of molecular force fields

(6) Direct Cartesian projection of any external (translation/rotation) variable dependence out of Cartesian anharmonic force fields.

The original program INTDER was developed to run within the *ab initio* molecular orbital package PSI (PSITECH Inc., Watkinsville, Georgia). Accordingly, it used several conventions for the naming and handling of files adopted. Such conventions are essentially retained in INTDER2005, although new output and scratch files have been added. Appendix B contains a description of all files used by INTDER2005.

Input description

A.   One card
       (IOPT(K), K= 1, 16)   FORMAT 16I5

IOPT(1)   NA = number of atoms

IOPT(2)   NS = number of simple internal coordinates

IOPT(3)   NSYM = number of symmetry internal coordinates

IOPT(4)   NDER = highest order of derivative to be transformed. If NDER = 0, only the
                 geometrical parameters and the **B** matrix are evaluated. NDER ≤ 4 is allowed for
                 all coordinates except RCOM, even if NEQ = 1. For RCOM only
                 NDER + NEQ ≤ 3 is functional.

IOPT(5)   NEQ = 0 if the molecule is at a stationary point and/or no first derivatives are to
                 be transformed. Set NEQ = 1 otherwise.

IOPT(6)   NPRT ≥ 0, a print option. Additional material is provided which describes the
                 control of printing with NPRT.

IOPT(7)   NINV = 0. Transform Cartesian derivatives to internal coordinate derivatives.

                 NINV = ±1. Transform internal coordinate derivatives to Cartesian derivatives.

                 NINV = ±2. The same as NINV = 1 except that the internal coordinates
                 derivatives are input from the INTDER input file (see below).

                 NINV = ±3. Project Cartesian force constants onto the internal space of the
                 molecular system. Direct projection is currently not available for linear
                 molecules. However, such analyses can be performed indirectly by neglecting
                 Cartesian gradients (NEQ = 0), transforming the force field into any valid,
                 complete set of internal coordinates (NINV = 0), and finally back-transforming
                 the results once again to the Cartesian space (NINV = 1).

                 If NINV ≥ 0, then the mass of each atom is set to one. If NINV < 0, then masses
                 are read in from the INTDER input file (*vide infra*).

IOPT(8)   NDUM = number of dummy atoms. Dummy atoms are to be used only for the
                 specification of linear bending angles (LIN1).

IOPT(9)   Numerical testing of derivatives of internal coordinates with respect to the Cartesian coordinates (debugging tool) [Abs(NTEST) ≤ 2], or check of conditions required for Cartesian projection [NTEST = ± 3, ± 4], or search for near singularities in **B** matrix.

NTEST = 1 : Numerically test the analytic B_{ij}^p and C_{qr}^p matrices.

NTEST = -1 : Form the B_{ij}^p and C_{qr}^p matrices numerically and use them in the transformation of derivatives.

NTEST = 2 : Numerically test the analytic B_{ijk}^p and C_{qrs}^p matrices.

NTEST = -2 : Form the B_{ijk}^p and C_{qrs}^p matrices numerically and use them in the transformation of derivatives.

NTEST = ± 3 : Check orthogonality conditions among derivatives of internal and external variables according to the value of NDER. [NSTOP = 1 and NINV = ISIGN(NTEST,1) are assigned automatically.]

NTEST = 4   Test Cartesian force field for invariance with respect to external variables (translations/rotations).

NTEST = 5   Analyze the generalized overlap matrix ($\mathbf{BuB^T}$) to gauge the linear dependence of the internal coordinates used to construct the first-order **B** matrix.

IOPT(l0)   NGEOM = 0 Read the Cartesian geometry from FILEll.

NGEOM = 1 Read the Cartesian geometry from the INTDER input file.

IOPT(ll)   NFREQ = 1 Perform a frequency analysis in internal coordinates (GFMAT).

NFREQ = 2 Perform a frequency analysis in Cartesian coordinates (NORMCO).

NFREQ = 3   Perform a frequency analysis in both Cartesian and internal coordinates.

NFREQ = 4   The same as NFREQ = 1 except that the force constants are input from the INTDER input file (*vide infra*).

NFREQ = 5   Perform a scaled quantum mechanical force constant (SQMFC) calculation. A separate input section for an SQMFC calculation is required. See the accompanying information below.

NFREQ = 6   Perform a projected frequency analysis in internal coordinates for a point along an intrinsic reaction path. (Internal gradients are read from FILE12).

NFREQ = 7   Perform a projected frequency analysis in Cartesian coordinates for a point along an intrinsic reaction path. (Cartesian gradients are read from FILE11).

NFREQ = 8   Perform a projected frequency analysis in both internal and Cartesian coordinates along an intrinsic reaction path.

NFREQ = 9   Perform a projected frequency analysis in internal coordinates for a point along a distinguished reaction path generated by constrained optimizations.

NFREQ = 10 + r Perform a frequency analysis in a reduced-dimension internal coordinate space wherein coordinate r is a constrained reaction variable. The **G** matrix elements for the reduced space (G_{ij}^o) are modified from their usual values (G_{ij}) according to $G_{ij}^o = G_{ij} - G_{ri}G_{rj}G_{rr}^{-1}$.

NFREQ < 0   Skip the transformation of derivatives; perform frequency analysis alone.

IOPT(12)   IRINT ≠ 0 if IR intensities are to be computed in the double-harmonic approximation (NFREQ ≠ 0).

If IRINT = 1 internal coordinate dipole moment derivatives for GFMAT are read in from FILE18. Otherwise these dipole moment derivatives are read in from the INTDER input file (see below). Cartesian coordinate dipole moment derivatives are always read in by NORMCO from FILE17.

IOPT(13)   NVEC indicates the dimension of the property whose derivatives are being transformed.

NVEC = 0 for a scalar quantity, *e.g.*, the potential energy.

NVEC = 1 for a vector quantity, *e.g.*, the dipole moment (Sets NEQ = 1).

NVEC ≠ 0 necessitates that masses are read in later so that the Eckart conditions can be imposed.

Furthermore, FILE17 or FILE18 must contain the total charge and dipole moment (in debye) on the first line in order to transform dipole moment derivatives. FORMAT (5X, I5, 3F20.10).

IOPT(14)   NSTOP = 1 to stop after forming the B_{ij}^p, C_{qr}^p, B_{ijk}^p, and C_{qrs}^p matrices (as governed by NDER + NEQ). No auxiliary files are required (unless NGEOM = 0).

NSTOP = 2 to stop after forming the $B_{i_1 i_2 \ldots i_n}^\eta$ matrices for Cartesian projection.

NSTOP = 3 to stop after forming the Cartesian projection matrices.

IOPT(15)   NDISP $\neq 0$ Generate Cartesian geometries for internal coordinate displacements.

NDISP < 0 Read in the masses for the atoms (below) and invoke the Eckart conditions for the displacements.

NDISP > 0 Assume all masses are equal in the calculation.

NDISP $= \pm 1$ Iteratively converge on the new Cartesian geometry using first-order information, *i.e.*, simply invert the **B** matrix.

NDISP $= \pm 2$ Iteratively converge on the new Cartesian geometry using first- *and* second-order information, *i.e.*, use analytic B_{ij}^{p} matrices to accelerate the process.

IOPT(16)   NMODE $\neq 1$ Assign normal modes according to the diagonal elements of the total energy distribution (TED).[3]

NMODE $= 1$ Assign normal modes according to a simplified potential energy distribution (PED) method.[3]

B.   NS cards

TYPE(J), (IA(J,K), K=1, 5), NUMTST

FORMAT A5, 5I5, A5

Read in the types of internal coordinates and the integers defining the atoms involved. If fewer than five integers are required, omit the remaining IA(J,K) elements. If NTEST ≠ 0 is set from above, all coordinates are tested by default. Specify NUMTST = 'ST' to "suppress testing" of individual coordinates.

Appendix A gives the precise, mathematical definitions (including sign conventions) of the types of internal coordinates available.
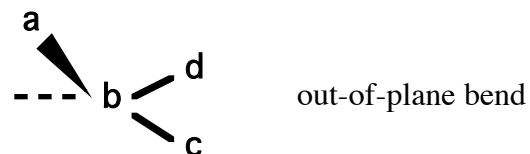
STRE **a b**
a-**b** bond length

BEND **a b c**
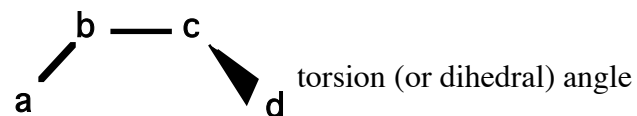**a**-**b**-**c** bond angle

LINl **a b c d**
a-**b**-**c** linear angle bend

> A fixed direction vector perpendicular to the bending plane is to be specified as the coordinates of dummy atom **d**.

OUT **a b c d**

out-of-plane bend

TORS **a b c d**

torsion (or dihedral) angle

SPF   **a b c**

> Simons-Parr-Finlan coordinate for **a**-**b** bond length. If **c** ≠ 0 an additional card is read immediately afterward in F20.l0 format defining the reference bond length in Å. If **c** = 0 the current value of the **a**-**b** length is taken as the reference.

LINX   **a b c d**

The *x* component of the   **c** → **d** unit vector in the local coordinate system in which the **b** →**c** vector defines the +*z* axis and the **a** atom lies in the *xz* plane in the +*x* direction.

LINY   **a b c d**

The *y* component of the   **c** → **d** unit vector in the local coordinate system in which the **b** →**c** vector defines the +*z* axis and the **a** atom lies in the *xz* plane in the +*x* direction.

RCOM   **a b c d**

The distance between the center of mass of fragment A (range of atoms: [**a,b**]) and that of fragment B (range of atoms: [**c,d**]). Specification necessitates input of masses below.

C.   Several cards defining the NSYM symmetry coordinates. If NSYM = 0, this section is skipped.

L, (IR(K), XR(K), K=1, 4)
FORMAT I5, 4(I4, Fl4.l0)

L = symmetry coordinate number

IR = simple internal coordinate number involved

XR = coefficient of IR in L definition. Use several cards for the same L if necessary.
All coefficients are automatically normalized in the program.

Use L = 0 to exit this section.

D.   If NGEOM = 1 the Cartesian geometry is input in bohr.

DO: I = 1, NA
READ: (XA(I,J), J= 1, 3)
FORMAT 3F20.l0

(If NGEOM = 0 the geometry is read from the bottom of FILEll, after skipping back over the gradients.)

E.   If NDUM > 0 dummy atom vectors are input in bohr (even if the geometry of the other atoms is read from FILE11).

DO: I = NA + 1, NA + NDUM
READ: (XA(I,J),J=1,3)
FORMAT 3F20.10

F.   If NFREQ ≠ 0 or ± 5, or NVEC ≠ 0, or NDISP < 0, or NINV < 0, or RCOM is present, then read in the atomic masses (in a.m.u.).

READ: (XMASS(I), I=1,NA)
FORMAT 6Fl2.6

For H-Ar one may alternatively specify a character label (anywhere in the 12- space sections allotted in the 6A12 format)) which will signal INTDER to extract the atomic mass from a list programmed internally. Valid character labels:

H	H1	H2	H3	D	T
HE	HE3	HE4	LI	LI6	LI7
BE	BE9	B	B10	B11	C
C12	C13	N	N14	N15	O
O16	O17	O18	F	F19	NE
NE20	NE21	NE22	NA	NA23	MG
MG24	MG25	MG26	AL	AL27	SI
SI28	SI29	SI30	P	P31	S
S32	S33	S34	S36	CL	CL35
CL37	AR	AR36	AR38	AR40	

(A check of the output to confirm that the desired mass was identified is warranted.)

G.   If NDISP ≠ 0 read in specifications for the internal coordinate displacements.
READ: LABEL, MDISP
FORMAT A4,I4
LABEL = 'DISP', and MDISP is the number of sets of internal coordinate displacements.

DO: M = 1, MDISP
        READ: IC,XDISP
        FORMAT I5, F20.10
        IC = the number of the internal coordinate to be displaced.
        XDISP = the size of the displacement in Å or rad.
        Repeat IC and XDISP entries for each internal coordinate which is to be displaced in each set. End the specification of each set of displacements with IC = 0.
END DO

H. If NINV = 2, read in the *unique, nonzero* internal coordinate derivatives. Use units consistent with the energy in mdyne · Å. [If NFREQ < 0, this section is skipped, and the force constants must be input elsewhere.]

If NEQ ≠ 0, read M, Fl(M)   FORMAT(I5,l5X,F20.l0)
End string with M = 0.

If NDER ≥ 2 then
READ M, N, F2(M,N)   FORMAT(2I5,l0X,F20.l0)
M ≥ N is required. End string with M = 0.

If NDER ≥ 3 then
READ M, N, P, F3(M,N,P)   FORMAT(3I5,5X,F20.l0)
M ≥N ≥ P is required. End string with M = 0.

If NDER ≥ 4 then
READ M, N, P, Q, F4(M,N,P,Q)   FORMAT(4I5,F20.l0)
M ≥ N ≥ P ≥ Q is required. End string with M = 0.

I. If NFREQ = ± 4, read in the quadratic force constants in GFMAT from the INTDER input file. Use units consistent with the energy in mdyne · Å.

((F2(M,N), N=M,NSX), M=l,NSX)
FORMAT 7Fl0.6

J. If IRINT ≠ 0 or l and GFMAT is to be run, read in the internal (symmetry) coordinate dipole moment derivatives in D/Å or D/rad.

DO: I = l, NSX
READ: (U(I,J), J=l,3)
FORMAT 3F20.l0

Input for SQM force field analyses

In the INTDER input file, begin a new section with the label # SQMFC ##.

A.   One card

NSF, NISO, NOPT, NH, NWT

FORMAT 5I5

NSF = number of distinct scale factors for the SQMFC analysis.

NISO = number of isotopomers involved in the analysis.

NOPT = 0   Perform the SQMFC analysis using fixed scale factors.
       = 1   Optimize the scale factors in the SQMFC analysis.

NH   = 0   Allow the program to make initial guesses for the diagonal elements of the scale factor Hessian.

       = 1   Input the diagonal elements of the inverse of the scale factor Hessian.

       = 2   Compute the scale factor Hessian analytically at each step.

       = –1 Compute the scale factor Hessian numerically at each step by a finite-difference procedure.

       = –2 Obtain the scale factor Hessian within the linearized least squares approximation.

NWT = 0   Set the weights according to $w_i^A = \left(v_i^A\right)^{-1}$.

       = 1   Set all weights equal to 1.

       = 2   Set the weights according to $w_i^A = \left(v_i^A\right)^{-2}$.

Notes on NH

NH =   2   is a full second-order algorithm which employs the Newton-Raphson method.   This   choice   provides   the   most   rapid   *and*   cost-effective convergence.

NH =   –2   employs the Newton-Raphson method but with the analytic Hessian appropriate for a linear least-squares problem. Convergence is significantly degraded relative to NH = 2 in the later iterations.

Statistics are provided by the program only for NH = 2 and NH = –2, the former option providing rigorously correct results and the latter option providing conventional results from linear least-squares theory.

NH =   –1   is not as cost-effective as either NH = 2 or NH = –2, even though convergence is obtained in the same number of steps as for NH = 2. The primary utility of this option is in testing the analytic Hessians computed with NH = 2. Note that the Hessian at each iteration is printed in the CHECK file.

NH =   1   Provides rapid iterations, but several cycles may be necessary for convergence. This option allows one to damp the initial steps by appropriate choice of the diagonal elements of the inverse Hessian. Both NH = 0 and NH = 1 utilize a Davidon-Fletcher-Powell scheme with cubic interpolation.

Notes on NWT

The various NWT options refer to relative weights. Pulay et al. recommend NWT = 0. One can override the choice of a relative weight by input of particular w_i^A values below. Subsequently, weights are normalized for the problem before scale factor optimization is begun.

B.   NSF cards

       DO: I = 1, NSF
       READ: FA(I), NSC(I,0)   FORMAT F10.5, I5
       READ: (NSC(I,J), J=1,NSC(I,0))   FORMAT 16I5

       FA(I) = initial value for the ith scale factor. If NOPT = 0 this value is fixed and is used to perform the SQMFC analysis. If NOPT = 1 this value is an initial guess for the SQMFC optimization.

       NSC(I,0) = the number of internal coordinates to which the ith scale factor applies.

       NSC(I,J) contains integers designating to which coordinates the ith scale factor applies.

C. DO: N=1,NISO

   (1) Input the masses for each atom in the isotopomers.

        READ: (XMASS(I,N), I=1,NA)

FORMAT 6F12.6

For H - Ar one may alternatively specify a character label as described previously.

(2) If NOPT = 1, input the experimental data to which the scale factors are to be fit.

READ: NFUND = the total number of experimental fundamentals for each isotopomer involved in the SSQMFC optimization.

FORMAT I5

DO: K = 1, NFUND
READ: K, V(K,N), WT(K,N)

For isotopomer N, the fundamentals are to be numbered from lowest wavenumber to highest wavenumber, disregarding symmetry species but *accounting for missing assignments*. K corresponds to the number of the fundamental in this ordering and V(K,N) is its value in cm^{-1}. In essence, after the eigenvalues of the GF matrix have been determined and ordered in a given step of the optimization, the integers K indicate the correspondence of these eigenvalues to the experimental fundamental frequencies involved in the SQMFC procedure.

If WT(K,N) ≠ 0, then this value is used to override the relative weight chosen for the corresponding fundamental by the NWT option.

FORMAT I5,2F10.7

D. If NH = 1, input the diagonal elements of the inverse scale factor Hessian.

READ: (HF(I,I), I=1,NSF)
FORMAT 5E10.3

Print Control

Printing in INTDER is controlled by NPRT = IOPT(6). An integer function LPRT(K,NPRT) is used to find the K-th digit (from the right) of NPRT (K $\geq$ 4 and 9999 $\geq$ NPRT $\geq$ 0).

A. The first digit of NPRT

  Control of printing to the output file.

  General case:

  LPRT(1,NPRT) = 0 Default standard output.
       ≥ 1 Cubic and quartic force constants are printed.
       ≥ 2 The symmetrized **B** matrix is printed.
       ≥ 3 The **A** matrix (= **B** inverse) is printed.
       ≥ 4 The symmetrized $\mathbf{BB}^{\mathrm{T}}$ matrix is printed.
       ≥ 5 Linear transformation contributions to the force
         constants are printed.
  NINV = ±3 case:

  LPRT(1,NPRT) = 0 Default standard output.
       ≥ 1 Projected force constants are printed.
       ≥ 2 Projection matrices are printed.
       ≥ 3 Derivatives of the external coordinates of the molecule with
         respect to the Cartesian coordinates are printed.

B. The second digit of NPRT

  Control of printing to the output file for use with the NTEST option.
  LPRT(2,NPRT) = 0 Default, no printing of $B^p_{i_1 i_2 \ldots i_n}$ matrices.
       ≥ 1 Analytic $B^p_{i_1 i_2 \ldots i_n}$ and $C^p_{q_1 q_2 \ldots q_n}$ matrices are printed as governed by
         NTEST.
       ≥ 2 Error matrices ($B^p_{i_1 i_2 \ldots i_n}$ analytic $-$ $B^p_{i_1 i_2 \ldots i_n}$ numerical and perhaps
         $C^p_{q_1 q_2 \ldots q_n}$ analytic $-$ $C^p_{q_1 q_2 \ldots q_n}$ numerical) are printed as governed by
         NTEST.

C.   The third digit of NPRT

Control of printing to the output file for use with the NFREQ option.
LPRT(3,NPRT)   = 0   Default, standard output.
                             = 1   The **G** matrix and its eigenvalues are printed in
                                   subroutine GFMAT.
                             = 2 The dipole moment derivatives with respect to
                                   normal coordinates are printed in subroutines GFMAT
                                   and NORMCO.
                           = 3 Eigenvectors for the zero frequencies are printed in
                                   subroutine NORMCO.

D.   The fourth digit of NPRT

Control of printing to the check file.
LPRT(4,NPRT)   = 0   Default, standard output.
                             ≥ 1 Messages from subroutines XIN, XOUT, YIN, and YOUT are
                                   suppressed.
                           = 2   Force constants are printed in NINV = 2 format.
                           ≥ 3 Quadratic force constants are printed in the format used by the
                                 BMAT program.
                           ≥ 4 Input for use with the old GFMAT program is printed.

Appendix A: Mathematical definitions of internal coordinates

$\mathbf{r}_{ab} = \mathbf{r}_b - \mathbf{r}_a$ = vector directed from atom a to atom b.

$\mathbf{e}_{ab} = \dfrac{\mathbf{r}_{ab}}{|\mathbf{r}_{ab}|}$ = unit vector directed from atom a to atom b.

STRE $\qquad r_{ab} = |\mathbf{r}_{ab}|$ $\qquad\qquad\qquad\qquad 0 < r_{ab} < \infty$

BEND $\qquad \phi_{abc} = cos^{-1}(\mathbf{e}_{bc} \cdot \mathbf{e}_{ba})$ $\qquad\qquad 0 < \phi_{abc} < \pi$

LINl $\qquad \theta_{abc}^{d} = sin^{-1}[\mathbf{e}_d \cdot (\mathbf{e}_{bc} \times \mathbf{e}_{ba})]$

$\mathbf{e}_d$ is assumed to be a fixed direction vector perpendicular to the bending plane. Thus, for LIN1, θ is invariant to translations but not all rotations.

OUT $\qquad \gamma_{abcd} = sin^{-1}[\mathbf{e}_{ba} \cdot (\mathbf{e}_{bc} \times \mathbf{e}_{bd}) / sin\phi_{cbd}]$ $\qquad\qquad -\pi < \gamma_{abcd} < \pi$

A positive displacement occurs when the terminal atoms move towards the viewer who sees the terminal atoms $a, c,$ and d in counterclockwise order.

TORS

$sin\tau_{abcd} = \mathbf{e}_{ba} \cdot (\mathbf{e}_{cb} \times \mathbf{e}_{cd}) / [sin\phi_{abc} sin\phi_{bcd}]$ $\qquad -\pi/2 < \tau_{abcd} < 3\pi/2$

$cos\tau_{abcd} = (\mathbf{e}_{ba} \times \mathbf{e}_{bc}) \cdot (\mathbf{e}_{cb} \times \mathbf{e}_{cd}) / [sin\phi_{abc} sin\phi_{bcd}]$

There are no discontinuities in the $\mathbf{b}$ vectors or higher derivatives of τ_{abcd} at the endpoints of its defined range.

SPF $\qquad \rho_{ab} = (r_{ab} - r_{ab}^{\circ}) / r_{ab} = 1 - r_{ab}^{\circ} / r_{ab}$

r_{ab}° is a (fixed) reference bond length. r_{ab}° is typically the equilibrium value of r_{ab}.

LINX $\qquad \alpha_{abcd}^{x} = (cos\, \tau_{abcd})(sin\phi_{bcd})$

LINY $\qquad \alpha_{abcd}^{y} = (sin\tau_{abcd})(sin\phi_{bcd})$

RCOM $\qquad$ $R_{AB} = \left| \mathbf{R}_A - \mathbf{R}_B \right|$ where $\mathbf{R}_A = \left. \sum_{i \in [\mathbf{a},\mathbf{b}]} m_i \, \mathbf{r}_i \middle/ \sum_{i \in [\mathbf{a},\mathbf{b}]} m_i \right.$ and $\mathbf{R}_B = \left. \sum_{i \in [\mathbf{c},\mathbf{d}]} m_i \, \mathbf{r}_i \middle/ \sum_{i \in [\mathbf{c},\mathbf{d}]} m_i \right.$

Appendix B: Files used by INTDER

INTDER1   Standard input file.

INTDERO   Standard output file.

FILE07   Cartesian coordinates of displaced structures.

FILE11   Contains Cartesian geometry (bohr, 3F20.10 format), Cartesian gradients (hartree/bohr, 3F20.10 format), and total energy (hartree). (The energy is used only as a label.)

FILE12   Contains internal (symmetry) coordinate values (Å or rad) and the internal coordinate gradients (mdyne).

FILE15   Contains Cartesian second derivatives in hartree/bohr^2. NC = 3*NA. ((F2(I,J), J=1,NC), I=1,NC) in 3F20.10 format.

FILE16   Contains internal (symmetry) coordinate second derivatives in mdyne/Å, mdyne/rad, or mdyne · Å/rad^2. ((F2(M,N), N=1,NSX), M=1,NSX) in 3F20.10 format.

               If NINV = ±3, this file will contain after execution the projected Cartesian second derivatives in hartree/bohr^2. NC = 3*NA. ((F2(I,J), J=1,NC),I=1,NC) in 3F20.10 format.

FILE17   Contains Cartesian dipole moment derivatives in D/Å . NC = 3*NA. ((U(I,J), I=1,NC),J=1,3) in 3F20.10 format.

FILE18   Contains internal (symmetry) coordinate dipole moment derivatives in D/Å or D/rad. ((U(M,N), M=1,NSX), J=1,3) in 3F20.10 format.

FILE20   Contains Cartesian third derivatives in hartree/bohr^3. (((F3(I,J,K), K=1,J), J=1,I), I=1,NC) in 3F20.10 format.

FILE21   Contains internal (symmetry) coordinate third derivatives in mdyne/Å^2, mdyne/Å rad, mdyne/rad^2, or mdyne · Å/rad^3.(((F3(M,N,P), P=1,N),N=1,M), M=1,NSX) in 3F20.10 format.

               If NINV = ±3, this file will contain after execution the projected Cartesian third derivatives in hartree/bohr^3. (((F3(I,J,K), K=1,J), J=1,I), I=1,NC) in 3F20.10 format.

FILE24   Contains Cartesian fourth derivatives in hartree/bohr^4.
((((F4(I,J,K,L), L=1,K), K=1,J), J=1,I), I=NC) in 3F20.10 format.

FILE25   Contains internal (symmetry) coordinate fourth derivatives in mdyne/Å^3, mdyne/Å^2 rad, mdyne/Å rad^2, mdyne/rad^3, or mdyne · Å/rad^4.
((((F4(M,N,P,Q), Q=1,P), P=1,N), N=1,M), M=1,NSX) in 3F20.10 format.

If NINV = ±3, this file will contain after execution the projected Cartesian fourth derivatives in hartree/bohr^4.
((((F4(I,J,K,L), L=1,K), K=1,J), J=1,I), I=NC) in 3F20.10 format.

Special files saved with NTSOP ≠ 0 option:

FILE31   Contains the first derivatives of the external translation and rotation variables with respect to the Cartesian coordinates. ((DK1(I,J), J=1,NC), I=1,6) in 3F20.10 format in Å-type units.

FILE32   Contains the second derivatives of the external rotation variables with respect to the Cartesian coordinates. (((DK2(I,J,K), K=1,J), J=1,NC), I=1,3) in 3F20.10 format in Å-type units.

FILE33   Contains the third derivatives of the external rotation variables with respect to the Cartesian coordinates. (((((DK3(I,J,K,L), L=1,K), K=1,J), J=1,NC), I=1,3) in 3F20.10 format in Å-type units.

FILE35   Contains the second-order projection matrix.
((P(I,J), J=1,NC), I=1,NC) in 3F20.10 format in Å-type units.

FILE36   Contains the third-order projection matrix.
(((P(I,J,K), K=1,NC), J=1,NC), I=1,NC) in 3F20.10 format in Å-type units.

FILE37   Contains the fourth-order projection matrix.
((((P(I,J,K,L), L=1,NC), K=1,NC), J=1,NC), I=NC) in 3F20.10 format in Å-type units.

Scratch files used by INTDER

FILE91
An unformatted scratch file on which the B_{ij}^p and C_{qr}^p matrices are written for each internal coordinate.

FILE92

An unformatted scratch file on which the B_{ij}^p and C_{qr}^p matrices are written for each *simple* internal coordinate. This file is used in the formation of FILE91 when *symmetry* internal coordinates are used.

FILE93

An unformatted scratch file on which the B_{ijk}^p and C_{qrs}^p matrices are written for each internal coordinate.

FILE94

An unformatteed scratch file on which the B_{ijk}^p and C_{qrs}^p matrices are written for each *simple* internal coordinate. This file is used in the formation of FILE93 when *symmetry* internal coordinates are used.

FILE95

A formatted scratch file used to store half-transformed derivatives used in the linear transformation step.

FILE96

An unformatted scratch file on which numerical B_{ij}^p and C_{qr}^p matrices are written for each *simple* internal coordinate for which testing is specified. Blocks of zeros are written for untested coordinates so that the structure of FILE96 is the same as that of FILE92 (or FILE91).

FILE97

An unformatted scratch file on which numerical B_{ijk}^p and C_{qrs}^p matrices are written for each *simple* internal coordinate for which testing is specified. Blocks of zeros are written for untested coordinates so that the structure of FILE97 is the same as that of FILE94 (or FILE93).

FILE98

An unformatted scratch file on which numerical B_{ijkl}^p and C_{qrst}^p matrices are written for each *simple* internal coordinate.

FILE80

An unformatted scratch file on which the B_{ijkl}^p and C_{qrst}^p matrices are written for each internal coordinate.

FILE81

An unformatted scratch file on which the B_{ijkl}^p and C_{qrst}^p matrices are written for each *simple* internal coordinate. This file is used in the formation of FILE80 when *symmetry* internal coordinates are used.

FILE85, FILE86, FILE87, FILE88   Reserved for future development of Cartesian projection scheme for linear molecules.

INTDER Test Cases

t1

$^3A''$ ketene transition state for fragmentation to $^3CH_2$ + CO
[W. D. Allen and H. F. Schaefer III, J. Chem. Phys. **89**, 329 (1988)]
DZP CISD quadratic force field; NDER = 2; NINV = 2; NFREQ = 3.

t3

DZP CCSD(T) // EXPT quartic force field for F_2O
[W. D. Allen and A. G. Császár, J. Chem. Phys. **98**, 2983 (1993)]
NINV = 2; NDER = 4; NEQ = 1.

t4

$^3A''$ cyclopentyne DZ(d) RHF SQM analysis with fixed scale factors from cyclopentene.
NFREQ = –5; NISO = 1; NOPT = 0. Preliminary NINV = 2 and NFREQ = 0 run required.

t5

$(HF)_2$ DZP CCSD(T) structure
NDISP = 1; MDISP = 4
[W. D. Allen, A. L. L. East, and A. G. Császár, "*Ab Initio* Anharmonic Vibrational Analyses of Non-Rigid Molecules," in *Structures and Conformations of Non-Rigid Molecules*, edited by J. Laane, M. Dakkouri, B. van der Veken, and H. Oberhammer (Kluwer Academic Publishers, Dordrecht, Netherlands, 1993) pp. 343-373.]

t6

SQM (ω/ω) optimization of DZP CCSD//EXPT quadratic force field for HNCO
[A. L. L. East, C. S. Johnson, and W. D. Allen, J. Chem. Phys. **98**, 1299-1328 (1993).]
NFREQ = –5; NISO = 2; NOPT = 1; NH = 2. Preliminary NINV = 2 and NFREQ = 0 run required.

t7

DZP RHF//EXPT quartic force filed for HNCO
[A. L. L. East, C. S. Johnson, and W. D. Allen, J. Chem. Phys. **98**, 1299-1328 (1993).]
NDER = 4; NINV = 2; NEQ = 0

t8

Finite-difference computation of DZP RHF quadratic force field for BeH_2
MULTI = 6, NDER = 1, NDUM = 2

t9

$(HF)_2$ DZP CCSD(T) structure

NDISP = –2; MDISP = 2
[W. D. Allen, A. L. L. East, and A. G. Császár, "*Ab Initio* Anharmonic Vibrational Analyses of Non-Rigid Molecules," in *Structures and Conformations of Non-Rigid Molecules*, edited by J. Laane, M. Dakkouri, B. van der Veken, and H. Oberhammer (Kluwer Academic Publishers, Dordrecht, Netherlands, 1993) pp. 343-373.]

t10

QZ($2d1f,2p1d$) CCSD(T) constrained optimum structure for R(C-C) = 2.2 Å
QZ($2d,2p$) CCSD quadratic force field
NDER = 2; NEQ = 1; NINV = 2

t11

QZ($2d1f,2p1d$) CCSD(T) constrained optimum structure for R(C-C) = 2.2 Å
QZ($2d,2p$) CCSD quadratic force field
Harmonic vibrational analysis with constrained center-of-mass reaction coordinate
NFREQ = 11

t12

Cartesian projection of C_2H_4 DZ(d) RHF quartic force field with spurious gradients appended

t13

C_2H_4 DZ(d) RHF quartic force field
NDER = 4; NEQ = 1; NINV = 2

t15

C_2H_4 DZ(d) RHF quartic force field
NDER = 4; NEQ = 1; NINV = 0

t16

$SiCH_2$ TZ2Pf RHF normal mode and intensity analysis
[C. D. Sherrill and H. F. Schaefer III, J. Phys. Chem. **99**, 1949 (1995).]
NFREQ = –3; IRINT = 1

t17

$SiCH_2$ TZ2Pf RHF dipole derivative transformation
[C. D. Sherrill and H. F. Schaefer III, J. Phys. Chem. **99**, 1949 (1995).]
NDER = 1; NVEC = 1

t21

$^3A''$ ketene DZP CISD transition state for fragmentation to $^3CH_2$ + CO
Test of **B** matrix for an imparted redundancy
[W. D. Allen and H. F. Schaefer III, J. Chem. Phys. **89**, 329 (1988)]

NTEST = 5

t22

$^3A''$ ketene DZP CISD transition state for fragmentation to $^3CH_2$ + CO
Test of analytic B_{ij}^p matrices for various coordinate types
[W. D. Allen and H. F. Schaefer III, J. Chem. Phys. **89**, 329 (1988)]
NDER = 4; NTEST = 1; NSTOP = 1

t23

$^3A''$ ketene TZ(2d1f,2p) CCSD; Intrinsic reaction path for fragmentation to $^3CH_2$ + CO
Test of projected vibrational analyses as $s = 1$ au outside the transition state.
[R. A. King, W. D. Allen, B. Ma, and H. F. Schaefer III, Faraday Discuss. **110**, 23 (1998)]
NFREQ = 8