INTDER2000

User's Manual

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This manual documents the INTDER2000 program, which was

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IntroductQon

INTDER2000 is a program for performing ected set of
in the calculatQon of anharUonic Uolecular

and general internal coordinas paces up to
structures.   Both forward and reverse
mediate Cartesian coordinates, force fQelds
the internal space.

es, both in Cartesian and internal

nalyses, including effQcient noVlinear

s between Cartesian and internal coordinates.

long general internal coordinates for use in
Qelds

atQon/rotatQon) variable dependence out of

run within the *ab initQo* Uolecular orbital

(PSITECH Inc., Watkinsville, Georgia   ). Accordingly, it used several conventQons
for the naming and handling of fQles adopted. Such conventQons are essentQally retained in
INTDER2000, althWugh new output and scratch fQles have been added. Appendix B contains a
descriptQon of all fQles used by INTDER2000.

Input description

A. One card
    (IOPT(K), K= l, l*) t t t FORMAT t16I5

IOPT(l)   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. tIf NDER = 0, only the geometrical parameters and the **B** matrix are evaluated. tNDER ≤ 4 is allowed for all coordinates except RCOM, even if NEQ = 1.   For RCOM only NDER + NEQ ≤ 3

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

IOPT(*)   NPRT   0, a print option.   AddQtional material isprovided which describes the control of printing with+ T.

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

              NINV = ±l. Transform internal coordQnate derivatives to Cartesian derivatives.

              NINV = ±2. tThe same as NINV = l except that the internal coordinates derivatives arf snput froU the INTDER input file (see below).

              NINV = ±3.   Project Cartesian force constants onto t
              molecular system. Direct projection is currently not available for linear molecules. However, such analyses c
              gradQents (NEQ =0), transforming t   valid, c   set of
              internal coordQnates(NINV = 0), and finally back-transforming the results once again to the Cartesian space (NINV = 1).

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

IOPT(8)   NDUM = number of dummy atoms. D   atoms are to be used only for the specifQcation of linear beVdQng angles (LINl).

IOPT(9)   NumerQcal testing of derivatives of internal coordinates with respect to the Cartesian coordinates (debugging tool) [*Abs*(NTEST) ≤ 2], or checS of condQtions required for

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

NTEST $= 2$: Num74cally test the aValytic B_{Qjk}^p and C matrices.

NTEST $= -2$: Form the B_{Qjk}^p and C matrices numerically and use them in tPe transformation of derivatives.

NTEST $= \pm$

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

IOPT(l2)   IRINT   0 if IR intensities are to be computed in the dWuble-harmonic approximation (NFREQ 0).

If IRINT = l internal coordinate dipole moment derivatives for GFMAT are read in from FILEl8. Otherwise these dipole moment derivati0 7s are read infrom tPe INTDER input file (see belWw). Cartesian coordinate dipole moment derivati0es are always read in by NORMCO from FILEl7.

IOPT(l3)   NVEC indicates the dimension Wf the property whose derivatives are being transformed.

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

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

NVEC   0 necessitatese 258t masses are read in later so thate 2e EcSart conditions can be imposed.

Furthermore, FILEl7 or FILEl8 must containe 2e total charge and dipole moment (in debye) Wn the first line ineorder to transform dipole momenderivatives. FORMAT (5X, I5, 3F20.l0).

IOPT(l4)   NSTOP = l to stop after forminge 2e B_{iR}^{p}, C_{qr}^{p}, B_{ijk}^{p}, and C_{qrs}^{p}

B.   NS cards

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

FORMAT A5, 5I5, A5

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

Appendix A gives the precise, mathematical definitiWns (includiVg sign conventiWns) of the types of interVal coordinates available.

STRE **a b**
a-b bond Tength

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

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

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

OUT   **a b c d**
 a

▇

LINX   **a b c d**

The *x* component of the **c** → **d** unit vector in the lWcal F5ordinatesystem in which the **b** → **c**
vector defines the +*z* axis and the **a** atom lies in the *xz* plane in the +   *from the*
gradients.)

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

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

F.   If NFREQ 0 or *1 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 iV the 12- space
sectQons allotted in the 6A12 format)) which wQll signal INTDER to extract the atomic mass
from a Tist programmed internally. Valid character Tabels:

H	H1	H2	H3	D	T
HE	HE3	HE4	LI	LI6	LI7
BE	BE9	B	B10	B11	C
C12	C13	N	N14	N15	O
O16O17O18F		F19	NE		
NE20	NE21	NE22NA	NA23 MG		
				AL27	SI
SI28	SI29	SI30	P	P31	S

(A check of the output to confirU that the desired mass was ihentified 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

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

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

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

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

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

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

J. If NRAN is to be read in the internal (symmetry) coordinate GFMAT Turn and
ipole moment derivatQves 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 tPe INTDER input file, begin a new section witP tPe Tabel # SQMFC ##.

A.   One card

NSF, NISO, NOPT, NH, NWT

FORMAT 5I5

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

NISO = number of isotopomers involved in tPe analysis.

NOPT = 0   Perform tPe SQMFC analysis usiVg fixed scale factors.
      = 1   Optimize tPe scale factors in tPe SQMFC analysis.

NH   = 0   ATlow tPe program to make initQal guesses for tPe dQagonal elements of tPe scale factor HessQan.

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

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

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

      = –2 Obtain tPe scale factor HessQan within tPe linearized least s

NWT   = 0   Set tPe weQghts accordiVg to $q_i^A = {}_i^A$

NH = −1 is not as cost-effective as either... One can overrQde the choice of a relatQve weight by input of particuTar *w*

For isotopomer N, the funda£ntals are to be numbered from lowest wavenumber to highest wave *accounting for missing ass* . In essence, after the eigenvalues of the GF matrix have b the optimization, the integers K indi to the experi£ntal funda£ental freque

If 0, then HF(K,N) this value is used to overri the corresponding funda£ental by the NWT optio

FORMAT I5,2F10.7

D. If NH = 1, input the diagonal ele£nts of the ins use sca

READ: (HF(I,I), I=1,NSF)

Print Control

T

±3 case:

with respect

LPRT(l,NPRT) = 0   Default standard output. tW the Cartesian coordinates are printed.

≥

≥

≥ 3   Derivatives of the external coordinates of the molecule

B.   The second digit of NPRT

Control of printing tW the output file for use with the NTEST Wption.
LPRT(2,NPRT) = 0   Default, nW printing of B

1   Analytic B

p
Cq q ... $- B$ ... perhaps
... an@lytic q –   governed by

NTEST.

NPRT=iORTDER An conetgehefduhnction LPRT(K,NPRT) is

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** Uatrix and its eigenvalues are printed in
                        subroutine GFMAT.
                = 2   The dipole moment derivatives with respect tW
                        norUal coordinates are printed in subroutiVes GFMAT
                        and NORMCO.
                = 3   EigenvectWrs for the zero frequeVcies are printed in
                        subroutiVTwORMCO.

D.   The fourth digit of NPRT

Control of printing to the check file.
LPRT(4,NPRT)   = 0   Default, standard output.   and YOUT are
                ≥ 1   Messages from subroutiVes XIN, XOUT, YIN,
                ≥ 2   Force constants are printed in NHV or U2 format by the   n   u
        BMAT program.
    ≥ 4   Input for use with the old GFMAT program is printed.

Appendix A: Mathematical definitions of internal coordinates

abb a

ab ab ab

$$r = \mathbf{0} < r \qquad\qquad\qquad < \infty$$

BEND $_{abc} = \left(\mathbf{e}_{bc} \cdot {}_{ba}\right) \quad \mathbf{e} \qquad 0 < {}_{abc} < \pi$

LINl $= \quad \cdot (\quad \times \quad)$

is assumed tW be a fixed direction vector perpendicular tW the bending
is invarQant to translations but Vot all rotations.

$$\!\sin\ [\mathbf{e}\mathbf{e}\mathbf{e} \qquad /\sin \quad] \qquad -\pi < \gamma_{abcd} < \pi$$

OUT

A positive displacement atoms
whW sees the terminal atoms a, c, and counterclockwise
$\phi 2$ $_{abcd}$ $_{3}c$, $_2$

$$\tau_{abcd} = \mathbf{e}_{bacb}\ \mathbf{e}\ _{bcd}\ \mathbf{e} \qquad \phi$$

$_{abcdba}\ (\mathbf{e}_{babd}\ \times\ \mathbf{e}_{cb})\ \sin\ TORS \times \mathbf{e}\ /$

There are nW discontinuitQes in thb vectors Wr hQgher derivatives of τ_{abcd} at the
endpoints of its defined raVge.S

$$=-r \quad r \quad r = -r \quad r$$

is a (fixed) refereVce bond length. r is typically the equilQbrium value of .

$$_{abcd}^{x} \quad \left(\ _{bcd}\ \right)\left(\qquad \right)$$

$\mathbf{R}$ $\mathbf{r}$ $\left| \qquad \right|$ $\mathbf{R}$ $\mathcal{U}$ $\mathbf{r}$ m

$_{i}$ $\in \mathbf{ab}\ \mathbf{ab}$ $i\,[\,]i$ $\in[\ ,\ ]$ $\in$,

$_{ii}$

Appendix B: Files used by INTDER

INTDER1   Standard input file.

INTDERO   Standard output file.

FILE07   Cartesian coordinates of displaced structures.

FILE11 Contains Cartesian gradients
and total energy (hartree). (The energy is used

ordinate values (Å or rad) and the internal
ond derivatives in hartree/bohr

. NC = 3*NA.
((F2(I,J), J=1,NC), I=1,NC) in 3F20.10 format.

FILE16   Contains internal (symmetry) coordinate
2.
((F2(M,N), N=1,NSX), M=1,NSX) in 3F20.10 format.

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

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

FILE18   ContaiVs internal (symmetry) coordinate dQpole moment derivatives
D/rad. ((U(M,N), M=1,NSX), J=1,3) in 3F20.10 for12()]TJ -and2FIL

rad, mdyne/Å
2, or mdyne ·   3.(((F3(M,N,P), P=1,N),N=1,M), M=1,NSX)
derivatives in hartree/bohr execution the projected Cartesian /bird

. (((F3(I,J,K), K=1,J), J=1,I), I=1,NC) i   3F20.10
FILE24 format.   ContaiVs 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
                rad, mdyne/Å rad^2, mdyne/rad^3, or mdyne $\cdot$ 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 executQon the projected Cartesianfourth
                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 optQon:

FILE31   Contains the first derivatQves ofthe external translation and rotatQon variables with
                respect to the Cartesian coordinates. ((DK1(I,J), J=1,NC), I=1,6) Qn3F20.10
                format in Å-type units.

FILE32   Contains the second der1 TDtQves of the external rotation variables with respect to the
                Cartesian coordinates.   (((DK2(I,J,K), K=1,J), J=1,NC), I=1,3) Qn3F20.10
                format in Å-type units.

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

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

FILE36   Contains the third-order pBojectQon matc (.)]TJ 6 -1 TD 0.005 Tc 0.054 Tw ((((P(I,J,K), K=1,NC

$_{ijk}^{p}$ 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* QnterVal coordQnate. This file Qs used the formation of FILE93 when *symmetry* interVal coordQnates are used.

FILE95

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

FILE96

> An unformatted scratch file on which numerical B_{ij}^p

[3] ketene transitQon state for fragmentatQon to CH$_2$ + CO
[W. D. Allen and H. F. Schaefer III, J. Chem. PPys. **89**, 329 (1988)]
DZP CISD quadratQc force field; NDER = 2; NINV = 2; NFREQ = 3.

DZ1B CCSD(T) // EXPT quartQc force field for F

2

[3]

2

2

MULTI = 6, NDER = 1, NDUM = 2

(HF)9

t10

QZ(2*dp*2) CCS
QZ(2*dp*2) CCSD quad
NDER = 2; NEQ = 1;

t11

QZ(2*dp*2) CCSD(T) const
QZ(2*dp*2) CCSD quadratic force
HarUonic vibrational analysis wit
NFREQ = 11

t12

Cartesian projection of C

2 4

H_4 DZ(d) RHF quartic force field
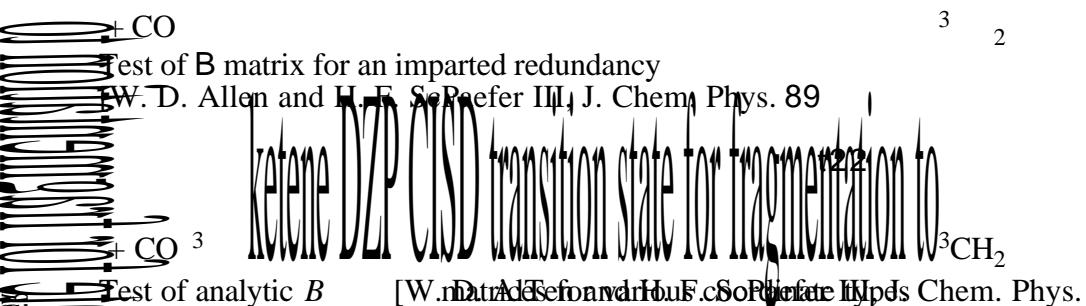NDER = 4; NEQ = 1; NINV = 2

C t15

2 4

$_2$ TZ2Pf RHF normal Uode and intensity analysis
[C. D. Sherrill and H. F. ScPaefer III, J. Phys. Chem. **99**, 1949 (1995).]
NFREQ = –3; IRINT = 1

SiCH7

$_2$ TZ2Pf RHF dipoTe derivative transformation
[C. D. Sherrill and H. F. ScPaefer III, J. Phys. Chem. **99**, 1949 (1995).]
NDER = 1; NVEC = 1

t21

^{3} $_2$ + CO
Test of **B** matrix for an imparted redundancy
[W. D. Allen and H. F. ScPaefer III, J. Chem. Phy

ketene DZP CISD transition state for fragmentation to $^3CH_2$ + CO

[W. D. Allen and H. F. ScPaefer III, J. Chem. Phys. analytic *B*

$^3A''$ ketene TZ(2d1f,2p) CCSD; Intrinsic reaction path for fragmentation to $^3CH_2$