

INITIAL PARAMETERS (1)

- NATOM: Number of atoms
- $\begin{cases} \text{NSTAT}>0: & \text{Number of specific VSCF states} \\ \text{NSTAT}<0: & \text{Number of VSCF states in increasing energy} \end{cases}$
- CONV: VSCF convergence
- $\begin{cases} \text{ICOUPL}>0: & \text{Potential coupling (grids in R*8)} \\ \text{ICOUPL}<0: & \text{Potential coupling (grids in R*4)} \end{cases}$
- $\begin{cases} \text{ICOUVPC}>0: & \text{Coriolis coupling (grids in R*8)} \\ \text{ICOUVPC}<0: & \text{Coriolis coupling (grids in R*4)} \end{cases}$

- $\left\{ \begin{array}{ll} ISCFCl > 0: & \text{Number vibrational VCI states required} \\ ISCFCl = 0: & \text{VSCF calculation only} \\ ISCFCl < 0: & \text{Terminate after preliminary investigation} \end{array} \right.$

- $\left\{ \begin{array}{ll} IWICH > 0: & \text{User-supplied potential (cartesian interface)} \\ IWICH = 0: & \text{Normal coordinate force field} \\ IWICH < 0: & \text{Fitted (interpolated) potential} \end{array} \right.$

- $\left\{ \begin{array}{ll} IDISC \neq 0: & \text{Potential and Coriolis grids already exist} \\ IDISC = 0: & \text{Write potential and Coriolis grids} \end{array} \right.$

- $\left\{ \begin{array}{ll} NROTR > 0: & NMODE = 3N - 6 + NROTR \\ NROTR = 0: & NMODE = 3N - 6 \\ NROTR < 0: & NMODE = 3N - 5 \text{ (linear molecules)} \end{array} \right.$

- $\left\{ \begin{array}{ll} J_{MAX} > 0: & \text{Full rotational analysis} \\ J_{MAX} = 0: & \text{Vibration only} \\ J_{MAX} < 0: & \text{Adiabatic rotation (redundant)} \end{array} \right.$

- $\left\{ \begin{array}{ll} M_{CHECK} > 0: & \text{Move to P.A. System (I_y representation)} \\ M_{CHECK} = 0: & \text{Use input reference} \\ M_{CHECK} < 0: & \text{Search for minimum} \end{array} \right.$

- $\left\{ \begin{array}{ll} INORM > 0: & \text{Calculate N. Coords. at minimum} \\ INORM = 0: & \text{Input N. Coords.} \\ INORM < 0: & \text{Calculate N. Coords. at Saddle point} \end{array} \right.$

INITIAL PARAMETERS (2)

- $\{$ $|ICI| > 0$: Number of specific VSCF states in VCI
- $\{$ $|ICI| < 0$: $|ICI|$ quanta in VCI matrix — depends on NMAX
- $\{$ $NMAX > 0$: Maximum sum-over-quanta in VCI basis
- $\{$ $NMAX = 0$: Unrestricted sum-over-quanta (beware!)
- $NMAX < 0$: Maximum mode-coupling in VCI basis
- CUT : Cut-off energy for reported band origins
- EVALT ϕ Reference zero-point energy

- $NVALR$: Number final rovibrational states ($J_{MAX} > 0$)
- $\begin{cases} KSTEP > 0: \text{ Increment between successive } K \text{ from } 0 \text{ to } 2J+1 \\ KSTEP = 0: \text{ } K=0 \text{ fns. used for all } K\text{-blocks} \end{cases}$
- $\begin{cases} IPRINT > 0: \text{ Print largest coefficient in } VCI; \text{ print all RPH output} \\ IPRINT = 0: \text{ Print limited output only} \\ IPRINT < 0: \text{ Print } |IPRINT| \text{ coefficients in } VCI \end{cases}$
- $\begin{cases} MATSIZ \neq 0: \text{ Print current } VCI \text{ matrix size - terminate} \\ MATSIZ = 0: \text{ Print nothing and continue} \end{cases}$

• {
 IREACT > 0: MM-RPH with half-integral torsion for odd K
 IREACT = 0: MM-SR run
 IREACT < 0: MM-RPH with integral torsion for odd K

• {
 MOLPRO > 0: Fit ab initio potentials by polynomials
 MOLPRO = 0: Use standard potentials
 MOLPRO < 0: Interpolate ab initio potentials

• {
 MOLINC ≠ 0: Special features (see later)
 MOLINC = 0: Normal setting

PRELIMINARY INVESTIGATIONS (ISCFCI < 0)

- { MCHECK > 0 : Move to P.A. in Ir representation ($A = Z$, $B = X$, $C = Y$)
- { MCHECK < 0 : Search for minimum close to input reference;
Fit 1-dim. potentials to $V(\alpha_{\text{HEG}})$;
Move to $\underline{\Phi} = 0$
- IReact $\neq 0$: Use IPRINT > 0 to print all RPH output
- { INORM > 0 : Obtain N. Coords. for minimum
INORM < 0 : Obtain N. Coords. for Saddle point $(-\omega_i)$
- { MOLPRO > 0 : Fit 'ab initio' potentials
MOLPRO < 0 : Interpolate 'ab initio' potentials

SPECIFIC FEATURES

1. MAXBAS/MAXSUM/NMAX

VCI basis established in terms of 1-mode coupling of basis functions ($n = 0, \dots, |NMAX|$)

Expressed in terms of excitation quanta for each mode as MAXBAS ($NMODE, |NMAX|$) and

sum-over-quanta for coupled modes as

MAXSUM ($|NMAX|$), where $NMODE = 3 \times NATOM - 6$.

node 1

0

1

2

.

1

$n_i \leftarrow \text{MAXBAS}(1, 1)$

0

0

$$\sum_{i=1}^{N\text{NODE}} m_i$$

$\leq \text{MAXSUM}(1)$

1

0

$\text{MAXBAS}(N\text{NODE}, 1) \rightarrow n'_{N\text{NODE}}$

1

2

.

2

$n'_1 \quad n'_2 \leftarrow \text{MAXBAS}(N, 2)$

0

1

2

.

$$\sum_{i=1}^{N\text{NODE}} \sum_{j < i} r_i + r_j$$

$\leq \text{MAXSUM}(2)$

$\text{MAXBAS}(N, 2) \rightarrow n'_{N\text{NODE}-1}, n'_{N\text{NODE}}$

3

$\text{MAXBAS}(N, 3)$

$\text{MAXSUM}(3)$

4

$\text{MAXBAS}(N, 4)$

$\text{MAXSUM}(4)$

SPECIFIC FEATURES

2. GAUSS/HEG

Parameters NBF, MBF denote number of primitives / Gauss quadrature points, respectively.

MBF \gg NBF will ensure exact integration, even though Gauss Rules ($2MBF - 1$) not obeyed.

NVF (from MAXBAS if VCI), MVF denote number of contracted functions / HEG integration points.

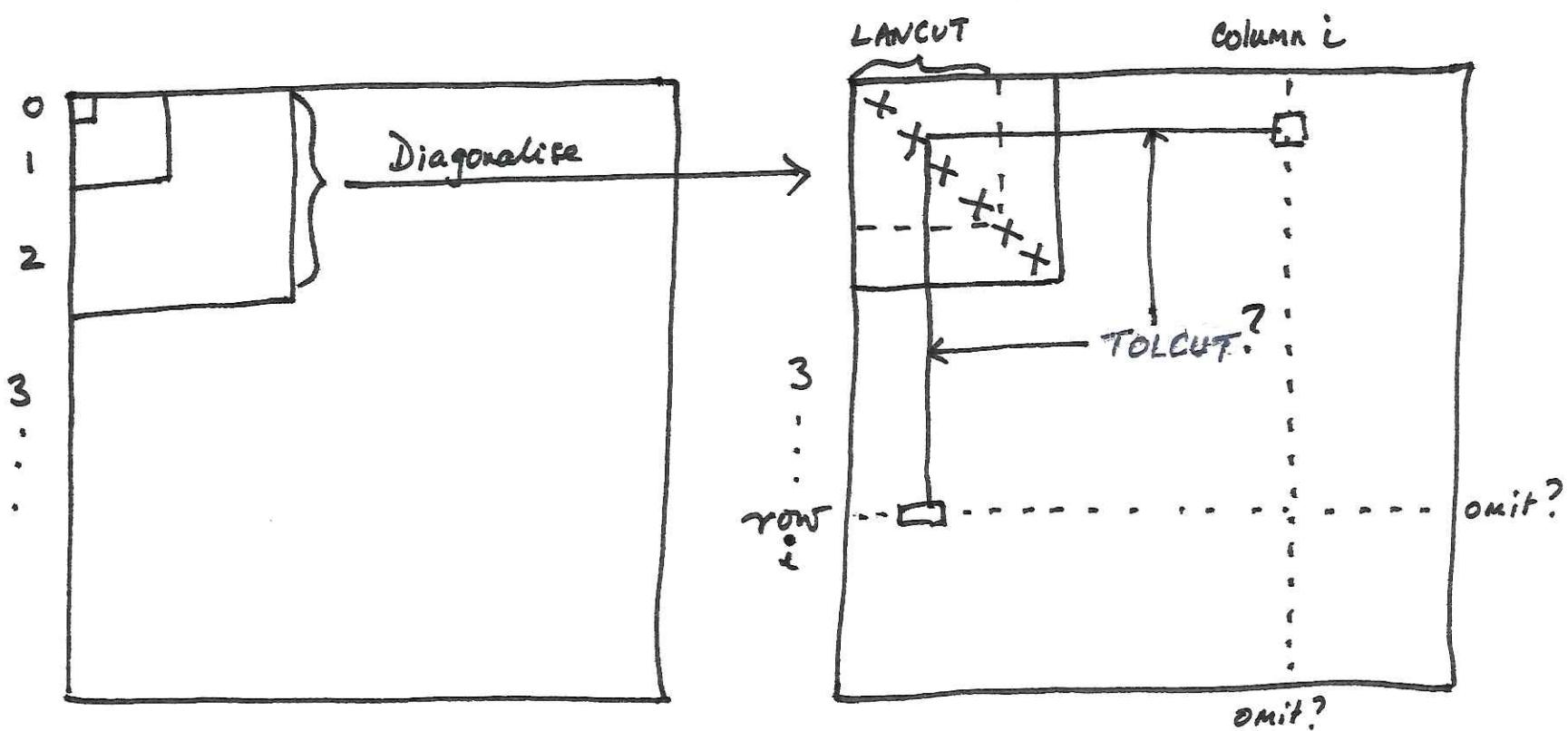
If MVF $>$ NBF (maximum no. contracted fns. / HEG points) revert to Gauss integration.

SPECIFIC FEATURES

3. LANCZOS / PERTURBATION THEORY

- NCYCLE: Number Lanczos cycles (NCYCLE=0: GIVENS)
- TOLLAN: Tolerance for convergence of e-values
- LANMAX: Order of half-matrix used to build complete H-matrix - formed in stages and written to disc
- LGIV: Indicator for diagonaliser of internal matrix (GIVENS/QL)
- LAN20: (obsolete) Write to single disc for temporary file (20) if < LAN20, or multiple discs (> LAN20)

- LANCUT: Number of 2-node e-functions (> 0) or 3-node functions (< 0) to retain
- TOLCUT: Tolerance of 2nd-order terms with remaining elements
- LANCYC: Number final e-values/e-vectors required (cf ESCFCI)
- TOLHAT: $H_{rs} = 0$ if $H_{rs} < \text{TOLHAT}$



METHANOL

<u>Full matrix</u>	<u>2-dim matrix</u>	<u>LANCUT</u>	<u>TOLCUT</u>	<u>Final matrix</u>
35,615*	2830	500	10^{-5}	32,510
			10^{-4}	28,179
		200		18,710
			10^{-3}	13,967
			10^{-2}	10,136
192,195*	2642	200	10^{-2}	23,838
232,903	2830			25,715
304,724	3215			26,054

SPECIFIC FEATURES

4. SYMMETRY

- NVSYM: Number IRs in point group; NWSYM: Number mode IRs
- NSYM(NWSYM): Number of nodes with symmetry NWSYM
- ISYM(NSYM(NWSYM)): Specific nodes with symmetry NWSYM
- MVSYM: Number blocks required; MWSYM: Specific blocks required
- MXDJP: IRs of M_x, M_y, M_z (P.A. system)
- MX: Symmetry axes (x, y, z) equivalent to P.A. (X, Y, Z)
- MXROT: IRs of R_x, R_y, R_z
- ISYMT: IR of $\sin(n\pi/2)$ if RPH
- MODINT(NMODE): Totally symmetric (1) or otherwise (2) for NMODE nodes

SPECIFIC FEATURES

5. TWO-GROUP BASIS / CONTRACTION SCHEME

- $|NCONT| = 1$: Single basis
- $|NCONT| = 2$: Two-group basis or contraction scheme
- $|ICONT(|NCONT|)|$: Number nodes in group $|NCONT|$
- $ICONT > 0$: Contraction scheme ($NVAL_1, NVAL_2$)
- $ICONT < 0$: Two group basis (ISCFCI)
- $JCONT(|NCONT|)$: Specific nodes in group $|NCONT|$
- $NCOUPL(|NCONT|), NCOUPLC(|NCONT|)$: Potential and Coriolis coupling for group $|NCONT|$ (contraction scheme)
- $MAXSUM(|NMAX|, |NCONT|)$: Sum-over-quanta group $|NCONT|$

- $|NCONT| = 1$: VCI basis established via MAXBAS etc.
for all $3N - 6$ nodes
- $|NCONT| = 2$: Two individual bases established via MAXBAS
for $|ICONT(NCONT)|$ nodes of group $|NCONT|$
- $ICONT(NCONT) < 0$: Final basis formed from product of two
individual bases, and using maximum of
 $MAXSUM(|NMAX|, |NCONT|)$
- $ISCFCI$: Number of final functions required

- $I_{CONT}(INCON1) > 0$: Two VCI calculations performed for each basis in turn, storing NVAL1, NVAL2 fractions $\bar{\Psi}^{(1)}$ and $\bar{\Psi}^{(2)}$
- $N_{CONT} > 0$: Final stage involves two-dimensional basis $\bar{\Psi}^{(1)}, \bar{\Psi}^{(2)}$ of size $NVAL1 \cdot NVAL2$
- $N_{CONT} < 0$: Terminates after initial two-group VCI calculations of NVAL1, NVAL2 fractions $\bar{\Psi}^{(1)}, \bar{\Psi}^{(2)}$

SPECIFIC FEATURES

6. FITS/INTERPOLATIONS/INTRINSICS

- $I \text{WHICH} \geq 0, \text{MOLPRO} > 0$: Fit intrinsic potentials
 $\text{MOLPRO} < 0$: Interpolate full potentials
- $| \text{MOLPRO} | = 1$: Produce 1-dim grid from GAUSS pts. (We)
 - +2: Fit $V^{(1)}(\varphi_k)$
 - 2: Save $V(\varphi_k)$ and $\frac{\partial V}{\partial \varphi_k}$
 - 3: Produce 2-dim grid from HEG pts.
 - +4: Fit $V^{(2)}(\varphi_k, \varphi_\ell) = V - \sum_K V^{(1)}(\varphi_K)$
 - 4: Save $V(\varphi_k, \varphi_\ell)$ and $\frac{\partial V}{\partial \varphi_k}, \frac{\partial V}{\partial \varphi_\ell}$

- $IWHICH < 0$, $MOLPRO > 0$: Build fitted intrinsics $V^{(n)}(\underline{\varphi})$
 $MOLPRO < 0$: Build total interpolated $V(\underline{\varphi})$
- $XTANPM$: Asymptotic value of γ/ϱ_{\max} .
 $MOLPRO > 0$: use $y = \tanh(\gamma \varphi)$ for fits
 $MOLPRO < 0$: use $y = \varphi$ to interpolate
- $MOLINC = 1, 2$: Use for $IWHICH > 0$, $MOLPRO \neq 0$ to
 include all (1) or alternate (2) grid points
- $MOLINC > 0$: Use for $IWHICH > 0$, $MOLPRO = 0$ to
 generate intrinsic potentials from GETPOI.
 See Contraction Scheme.

SPECIFIC FEATURES

7. REACTION PATH (RPH)

- |IREACT|: Special (torsional) mode, requiring primitive basis (NBF) in Fourier series and equally spaced integration points (MBF).
- IREACT > 0: Odd ka uses half-integral $\sin \frac{m\ell}{2}, \cos \frac{m\ell}{2}$
< 0: All ka use integral $\cos m\ell, \sin m\ell$
- ISYMT: I.R. of $\sin \frac{m\ell}{2}$ in chosen point group

PROPERTIES

- $IDUMP = 0$: Dump data if $KDUMP(MSYM) \neq 0$
 - 1: Generate dipole matrix elements for $J=0$ (GETDIP)
 - 2: Expectation values of Q
 - 3: Expectation values of Q^2
 - 4: Wavefunction plots
 - 5: Expectation values of P (GETPRP)
 - 6: Frank - Condon factors (2 electronic states)
 - 7: P, Q, R branches of vibrational spectrum

8: Raman spectrum (untested)

9: Partition functions

- $KDUMP > 0$: Dump data for $KDUMP (J=0)$ functions
or $(2J+1)KDUMP (J>0)$ functions for each
symmetry block $MVSYM$

USER-WRITTEN MODULES

- REACT: Obtain minimum-energy Reaction Path for torsion (cf HOOH) from $\tau=0$ to $\tau=2\pi$ in intervals of $1/2$ degree
- ROTATE: Used whenever near-degeneracies might be present in normal modes. Used to 'clean' vectors
- RTGEOM: Used after transformation of axis system to P.A.
Used to 'clean' high-symmetry geometry
- USERIN: Read in parameters needed for V, μ , P etc
ONCE ONLY
- GETPOT: Calculate V for any X
- GETDIP: Calculate μ for any X
- GETPRP: Calculate P for any X

OTHER FEATURES

• EFFECTIVE POTENTIALS

$M_{EFF}(NMODE, 1) = N$: if mode $NMODE$ optimized to N
 $= 0$: if no optimisation required

$M_{EFF}(NMODE, 2) = N$: if mode $NMODE$ optimized to
both N and M

• SCALING POTENTIALS

$X_{MODQ}(NMODE) = X$: (default value 1.0).

Define $Q(NMODE) = X \cdot Q(NMODE)$

• POTENTIAL CHECK

$MAXCHK(I_{COUPL}) = N$: Mode N to be investigated
whenever it appears in
 I_{COUPL} - coupling schemes

NOCYCLE = 0 GIVES

TO DAVIDSON NO CYCLES

TOLLAN = DAVIDSON CONVERGENCE

LAMAX = ORDER OF Y₂ MATRIX MAXIMUM
20,000 FINAL - WRITE TO
DISC, BLOCKSIZE

LGIV = 1 GIVENS FOR DAVIDSON
= 0 QR DIAG

LANZY IGNORE NOW

LANCUT (AKA ICUT)

TOLCUT (AKA TOL)

LANCYC = ISCF (~~if less~~ leave it alone)

TOLMAT = SPARSITY OF FINAL MATRIX
drop matrix element?

LANINC = 10 IN Pert. analysis
need B'

10 blocks for memory
management, to
disk