INITIAL PARAMETERS (1)

- NATOM: Number of atoms

- NSTAT>0:   Number of specific VSCF states
  NSTAT<0:   Number of VSCF states in increasing energy

- CONV: VSCF convergence

- ICOUPL>0:   Potential coupling (grids in R*8)
  ICOUPL<0:   Potential coupling (grids in R*4)

- ICOUPC>0:   Coriolis coupling (grids in R*8)
  ICOUPC<0:   Coriolis coupling (grids in R*4)

- $\begin{cases} \text{ISCFCI} > 0: & \text{Number vibrational VCI states required} \\ \text{ISCFCI} = 0: & \text{VSCF calculation only} \\ \text{ISCFCI} < 0: & \text{Terminate after preliminary investigation} \end{cases}$

- $\begin{cases} \text{IWHICH} > 0: & \text{User-supplied potential (cartesian interface)} \\ \text{IWHICH} = 0: & \text{Normal coordinate force field} \\ \text{IWHICH} < 0: & \text{Fitted (interpolated) potential} \end{cases}$

- $\begin{cases} \text{IDISC} \neq 0: & \text{Potential and Corials grids already exist} \\ \text{IDISC} = 0: & \text{Write potential and Corials grids} \end{cases}$

- $\begin{cases} \text{NROTTR} > 0: & \text{NMODE} = 3N-6 + \text{NROTTR} \\ \text{NROTTR} = 0: & \text{NMODE} = 3N-6 \\ \text{NROTTR} < 0: & \text{NMODE} = 3N-5 \text{ (linear molecules)} \end{cases}$

- $\begin{cases} \text{JMAX} > 0: & \text{Full rotational analysis} \\ \text{JMAX} = 0: & \text{Vibration only} \\ \text{JMAX} < 0: & \text{Adiabatic rotation (redundant)} \end{cases}$

- $\begin{cases} \text{MCHECK} > 0: & \text{Move to P.A. System } (I_\gamma \text{ representation}) \\ \text{MCHECK} = 0: & \text{Use input reference} \\ \text{MCHECK} < 0: & \text{Search for minimum} \end{cases}$

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

INITIAL PARAMETERS (2)

- $\begin{cases} ICI > 0: & \text{Number of specific VSCF states in VCI} \\ ICI < 0: & |ICI| \text{ quanta in VCI matrix} - \text{depends on NMAX} \end{cases}$

- $\begin{cases} NMAX > 0: & \text{Maximum sum-over-quanta in VCI basis} \\ NMAX = 0: & \text{Unrestricted sum-over-quanta (beware!)} \\ NMAX < 0: & \text{Maximum mode-coupling in VCI basis} \end{cases}$

- CUT : Cut-off energy for reported band origins

- EVALJ0 Reference zero-point energy

- NVALR: Number final rovibrational states (JMAX > 0)

- $\begin{cases} \text{KSTEP} > 0: & \text{Increment between successive K from 0 to } 2J+1 \\ \text{KSTEP} = 0: & K=0 \text{ fns. used for all K-blocks} \end{cases}$

- $\begin{cases} \text{IPRINT} > 0: & \text{Print largest coefficient in VCI; print all RPH output} \\ \text{IPRINT} = 0: & \text{Print limited output only} \\ \text{IPRINT} < 0: & \text{Print } |\text{IPRINT}| \text{ coefficients in VCI} \end{cases}$

- $\begin{cases} \text{MATSIZ} \neq 0: & \text{Print current VCI matrix size - terminate} \\ \text{MATSIZ} = 0: & \text{Print nothing and continue} \end{cases}$

- $\begin{cases} \text{IREACT} > 0: & \text{MM-RPH with half-integral torsion for odd K} \\ \text{IREACT} = 0: & \text{MM-SR run} \\ \text{IREACT} < 0: & \text{MM-RPH with integral torsion for odd K} \end{cases}$

- $\begin{cases} \text{MOLPRO} > 0: & \text{Fit ab initio potentials by polynomials} \\ \text{MOLPRO} = 0: & \text{Use standard potentials} \\ \text{MOLPRO} < 0: & \text{Interpolate ab initio potentials} \end{cases}$

- $\begin{cases} \text{MOLINC} \neq 0: & \text{Special features (see later)} \\ \text{MOLINC} = 0: & \text{Normal setting} \end{cases}$

PRELIMINARY INVESTIGATIONS (ISCFCI < 0)

- $\begin{cases} \text{MCHECK} > 0: & \text{Move to P.A. in } I_r \text{ representation } (A=Z, B=X, C=Y) \\ \\ \text{MCHECK} < 0: & \text{Search for minimum close to input reference;} \end{cases}$

  Fit 1-dim. potentials to $V(Q_{HEG})$;

  Move to $\underline{Q} = 0$

- IREACT $\neq 0$: Use IPRINT > 0 to print all RPH output

- $\begin{cases} \text{INORM} > 0: & \text{Obtain N. Coords. for minimum} \\ \\ \text{INORM} < 0: & \text{Obtain N. Coords. for Saddle point } (-\omega_i) \end{cases}$

- $\begin{cases} \text{MOLPRO} > 0: & \text{Fit 'ab initio' potentials} \\ \\ \text{MOLPRO} < 0: & \text{Interpolate 'ab initio' potentials} \end{cases}$
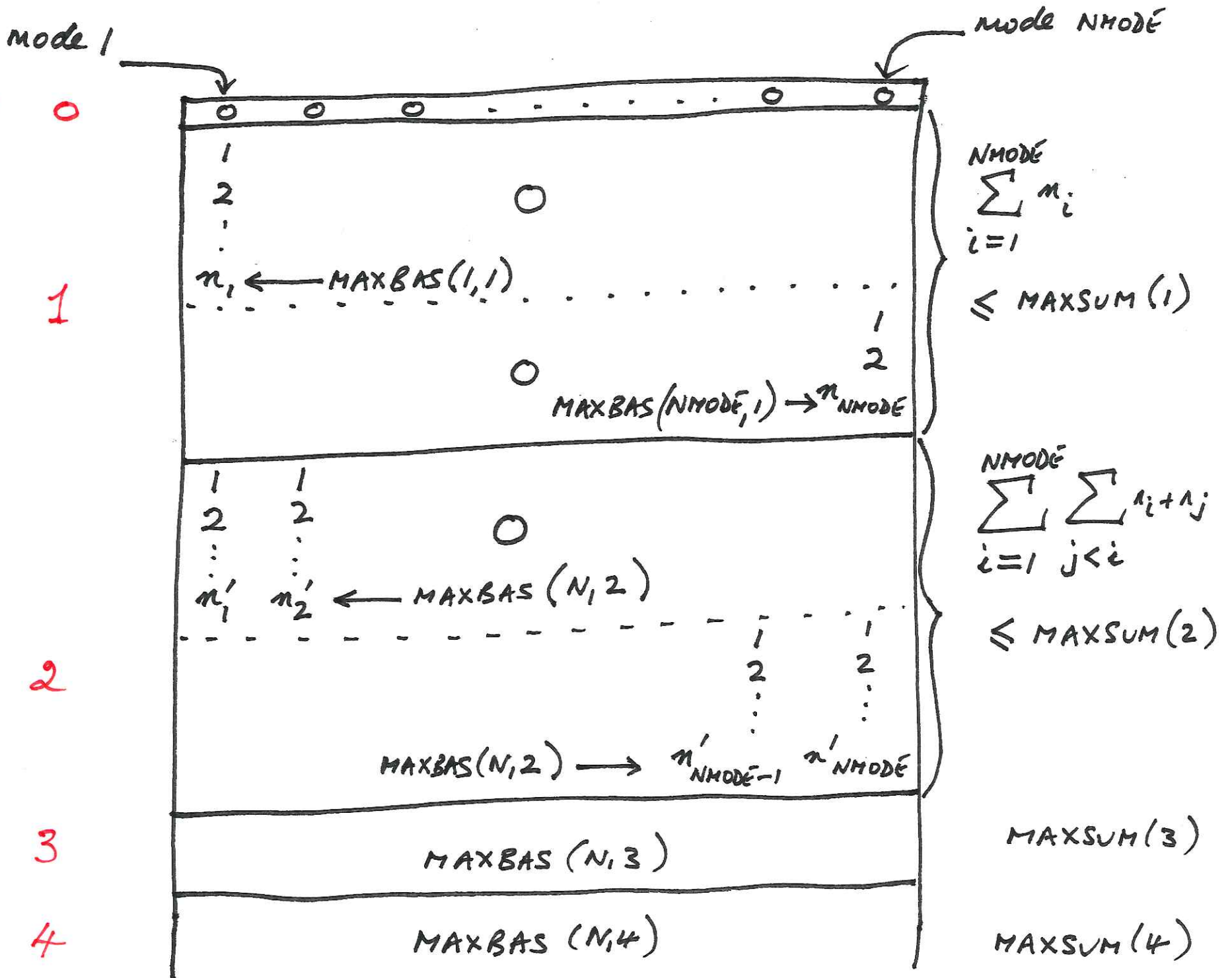
SPECIFIC FEATURES

● 1. MAXBAS/MAXSUM/NMAX

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

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*NATOM - 6.

mode 1

mode NMODE

0

1

$n_1 \leftarrow$ MAXBAS$(1,1)$

MAXBAS$($NMODE$,1) \rightarrow n_{\text{NMODE}}$

$\sum_{i=1}^{\text{NMODE}} n_i$

$\leq$ MAXSUM(1)

2

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

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

$\sum_{i=1}^{\text{NMODE}} \sum_{j<i} n_i + n_j$

$\leq$ MAXSUM(2)

3

MAXBAS$(N,3)$

MAXSUM(3)

4

MAXBAS$(N,4)$

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-mode e-functions (>0) or 3-mode functions (<0) to retain

- TOLCUT: Tolerance of 2nd-order terms with remaining elements

- LANCYC: Number final e-values/e-vectors required (cf ISCFCI)

- TOLMAT: $H_{rs} = 0$ if $\underline{H_{rs} < TOLMAT}$
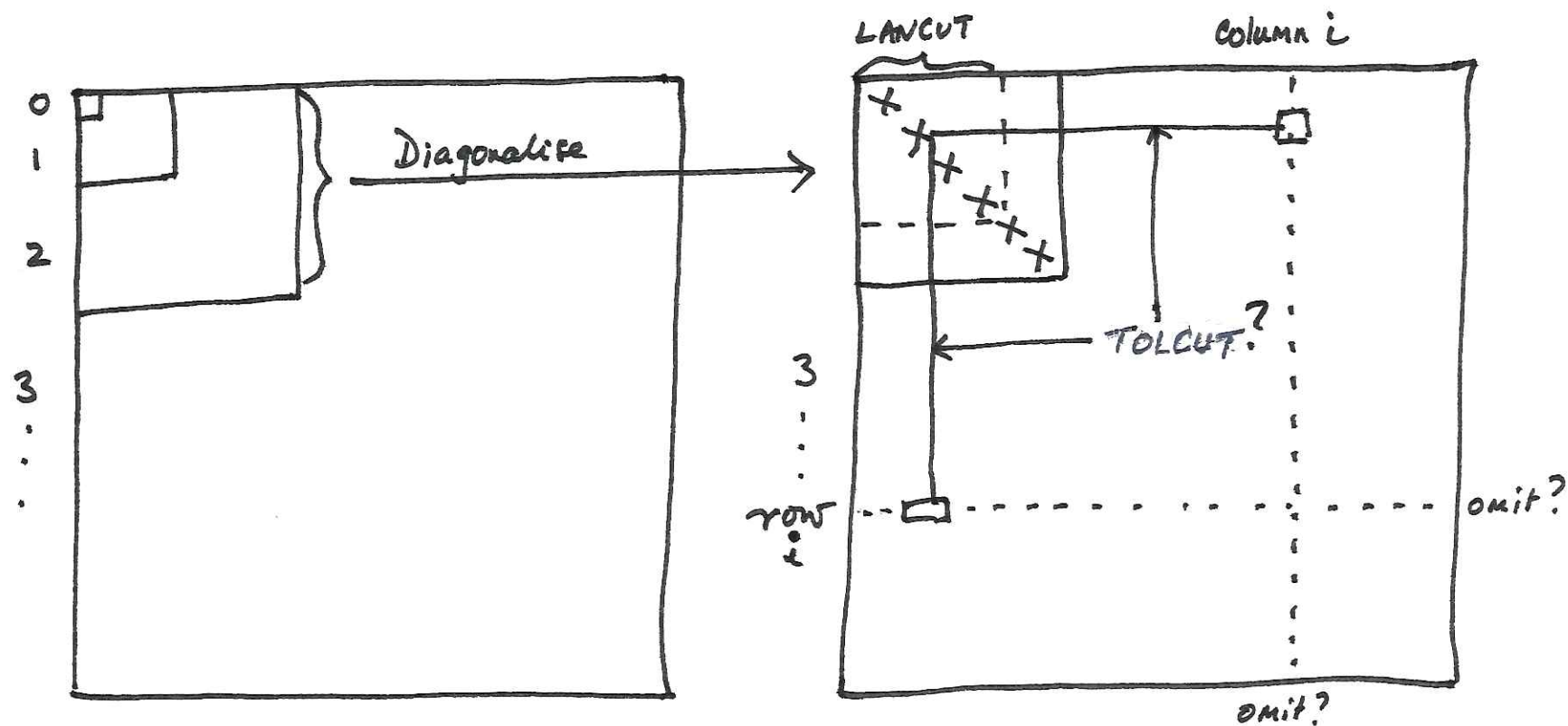
METAANOL

Full matrix	2-dim matrix	LANCUT	TOLCUT	Final matrix
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 modes with symmetry NWSYM

- ISYM (NSYM(NWSYM)): Specific modes with symmetry NWSYM

- MVSYM: Number blocks required; MWSYM: Specific blocks required

- MXDIP: IRs of MX, MY, MZ (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 $\sin\left(m\tau/2\right)$ if RPH

- MODINT (NMODE): Totally symmetric (1) or otherwise (2) for NMODE modes

SPECIFIC FEATURES

- 5. TWO-GROUP BASIS/CONTRACTION SCHEME

  - $|NCONT| = 1$: Single basis

  - $|NCONT| = 2$: Two-group basis or contraction scheme

  - $|ICONT(|NCONT|)|$: Number modes in group $|NCONT|$

    - $ICONT > 0$: Contraction scheme $(NVAL1, NVAL2)$

    - $ICONT < 0$: Two group basis $(ISCFCI)$

  - $JCONT(|NCONT|)$: Specific modes in group $|NCONT|$

  - $NCOUPL(|NCONT|), NCOUPC(|NCONT|)$: 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 $3N-6$ modes

- $|NCONT| = 2$: Two individual bases established via MAXBAS for $|ICONT(|NCONT|)|$ modes 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

- ICONT (|NCONT|) > 0: Two VCI calculations performed for each basis in turn, storing NVAL1, NVAL2 functions $\Psi(1)$ and $\Psi(2)$

- NCONT > 0: Final stage involves two-dimensional basis $\Psi(1) \cdot \Psi(2)$ of size NVAL1 $\cdot$ NVAL2

- NCONT < 0: Terminates after initial two-group VCI calculations of NVAL1, NVAL2 functions $\bar{\Psi}(1)$, $\bar{\Psi}(2)$

SPECIFIC FEATURES

- 6. FITS/INTERPOLATIONS/INTRINSICS

  - IWHICH ≥ 0, MOLPRO > 0: Fit intrinsic potentials

    MOLPRO < 0: Interpolate full potentials

  - $|\text{MOLPRO}| = 1$: Produce 1-dim grid from GAUSS pts. (ω_e)

    $+2$: Fit $V^{(1)}(Q_K)$

    -2: Save $V(Q_K)$ and $\dfrac{\partial V(Q_K)}{\partial Q_K}$

    3: Produce 2-dim grid from HEG pts.

    $+4$: Fit $V^{(2)}(Q_K, Q_\ell) = V - \sum_K V^{(1)}(Q_K)$

    -4: Save $V(Q_K, Q_\ell)$ and $\dfrac{\partial V}{\partial Q_K}$, $\dfrac{\partial V}{\partial Q_\ell}$

- IWHICH < 0, MOLPRO > 0: Build fitted intrinsics $V^{(m)}(\underline{\varphi})$

  MOLPRO < 0: Build total interpolated $V(\underline{\varphi})$

- XTANPM: Asymptotic value of γ/φ_{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 GETPOT. 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 k_a uses half-integral $\sin \frac{m\tau}{2}, \cos \frac{m\tau}{2}$

< 0: All k_a use integral $\cos m\tau, \sin m\tau$

$ISYMT$: I.R. of $\sin \frac{m\tau}{2}$ in chosen point group

PROPERTIES

- $IDUMP = 0$: Dump data if $KDUMP(NVSYM) \neq 0$

    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 rovibrational 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 NVSYM

USER-WRITTEN MODULES

- **REACT:** Obtain minimum-energy Reaction Path for torsion (cf HOOH) from $\tau = 0$ to $\tau = 2\pi$ in intervals of $\frac{1}{2}$ 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
  <u>ONCE ONLY</u>

- **GETPOT:** Calculate V for any $\underline{X}$

- **GETDIP:** Calculate $\underline{\mu}$ for any $\underline{X}$

- **GETPRP:** Calculate P for any $\underline{X}$

OTHER FEATURES

- EFFECTIVE POTENTIALS

$$MEFF(NMODE,1) = N: \text{if mode NMODE optimised to } N$$
$$= 0: \text{if no optimisation required}$$

$$MEFF(NMODE,2) = M: \text{if mode NMODE optimised to}$$
$$\text{both } N \text{ and } M$$

- SCALING POTENTIALS

$$XMOD\varphi(NMODE) = X: (\text{default value } 1.0).$$
$$\text{Define } \varphi(NMODE) = X.\varphi(NMODE)$$

- POTENTIAL CHECK

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