MULTIMODE 4.9.0
USER-GUIDE

This Section describes in some detail the facilities offered by MULTIMODE.
It should be read in conjunction with the two Sections 'Input Parameters'
and 'Sample Inputs and Outputs'. In the Section 'Input Parameters' all data
records are specified in full. In the Section 'Sample Inputs and Outputs'
various facilities of MULTIMODE are tested, and in particular, key input
parameters are highlighted. It will be seen that the test programs fall into
'two' basic categories:

1..SCF: This category demonstrates how VSCF (Vibrational SCF) calculations
are performed.

2..VCI: This category demonstrates the use of (orthonormal) virtual zpe
wavefunctions in near-variational CI calculations.

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Introduction

In order to run MULTIMODE, the user must supply a subroutine which returns
the value of the potential energy of his molecule for any arbitrary values
of the Cartesian coordinates of the atoms associated with the distortions from
equilibrium (see the Section 'User-Specific Routines'). It is advised that
a careful check of his routine is first carried out to establish the presence
of any spurious 'holes' which will play havoc with numerical integration of
the potential. If his potential appears to be well-behaved, then the routines
USERIN and GETPOT can be compiled in his 'user.xxx.f' module.

The next step is to choose a convenient size for the work array in the module
'memo.vscf.4.9.0.f' (see the Section 'User-Specific Routines'). This is done
by setting the size of MAXSIZ in the PARAMETER statement which appears in the
first line of MAIN. A recommended value is around 3000000. The value given
to MAXSIZ determines the size of the work array which is used to dynamically
allocate memory. If it is set too low, MULTIMODE will halt with a suggested
alternative value. But remember; if it is set far too high, space will still
be required on disc to hold unnecessary array space, and a excessive amount
of memory will be sought. Start with MAXSIZ as low as possible.

Since GETPOT is called many times during a run of MULTIMODE, it is advised to use the highest possible level of optimization supported by the FORTRAN compiler when compiling 'user.xxx.f'. Some SGI compilers produce incorrect results if 'memo.vscf.4.9.0.f' is compiled at -O2, however, and we strongly recommend that the option -O1 is used when compiling 'memo.f'. All remaining modules can be compiled at the highest level of optimization, and when all modules are linked, the user is ready to start. We recommend that he carries out test runs using the data files given in the Section 'Sample Inputs and Outputs' and which are summarized below. This will enable him to gain experience in setting up data files, as those in 'Sample Inputs and Outputs' will have to be modified for use with his choice of molecule. The following categories have been designed to cover features that the user would naturally wish to address in order to gain familiarity with MULTIMODE. The test examples are all for the 3-atom molecule H_2O, for which a potential in internal coordinates (IWHICH > 0) is supplied. In all cases, coupling of a maximum of three modes (ICOUPL = 3) in the potential and Coriolis terms is required.

Numerical Integration

All integration of matrix elements is carried out numerically, using Gauss Hermite quadrature to integrate the NBF harmonic-oscillator primitives, followed by optimized HEG (Harris-Engerholm-Gwynn) quadrature to integrate the NVF contracted functions. There is a Gauss rule which states that MBF points will exactly integrate a polynomial of degree no greater than 2*MBF-1. Hence, if MBF = NBF+1, this will be sufficient to exactly integrate the overlap matrix of the primitives. In order to integrate a matrix element which contains a potential term in (say) quartic would require the modified condition MBF = NBF+3 and so on. The user will be aware of the degree of his potential and he would then set the difference MBF-NBF accordingly in his input data file. These Gauss quadrature points are used to contract the basis, after which the optimized HEG points are used. If an SCF or SCFCI procedure is being undertaken the number of contracted quanta are input directly as NVF.

If a VCI run is being conducted, and the MAXBAS facility is being used (see Input.pdf), then the value in NVF is overwritten by the maximum quantum required for the VCI calculation in MAXBAS. Whichever procedure is being used, however, the algorithm used in order to establish the HEG integration points is as follows. The integration of the contracted functions is assumed to follow the same criteria as the integration of the primitives, namely that the excess of HEG points to contracted functions is again MBF-NBF. This means that there must be sufficient primitives (NVF+MBF-NBF) in order to establish the required HEG points, since these are formed from diagonalization of the Q-expectation value

matrix in the NBF*NBF matrix of optimized functions (the contracted functions are taken from the NVF lowest-energy subset of these optimized functions). If these conditions are not met, MULTIMODE attempts to recover, from a knowledge of NVF and the excess MBF-NBF.

Since integration is carried out numerically, time and space can be saved in cases where symmetry exists, by only integrating over half of the total range of modes which do not transform as the totally symmetric irreducible representation of the point group of the molecule under investigation. If symmetry other than C1 is indicated by NVSYM, then the modes corresponding to such asymmetric irreducible representations (labelled by ISYM) should be echoed in MODINT with a value of MODINT(MODE)=2. All totally symmetric modes should be given the value MODINT(MODE)=1.

Basic Set-up Facilities

MULTIMODE Version 4.9.0 employs the Watson Normal Coordinate Hamiltonian for non-linear molecules, and therefore requires an input equilibrium geometry in Cartesian coordinates. The Watson Hamiltonian, however, requires that the input axes are the principal axes of rotation. If the molecule is in the principle axis frame, the users can just use the coordinate as the input geometry in MULTIMODE, and set MCHECK = 0 (see Input.pdf). Otherwise, users can input an equilibrium geometry (but not in principle axes), and instruct MULTIMODE to find these from the input geometry, by setting MCHECK > 0. The user inputs the NUCLEAR MASSES and corresponding EQUILIBRIUM CARTESIAN COORDINATES

MULTIMODE also requires the harmonic force constants of the potential (omegas) and the corresponding displacements of the atoms (the eigenvectors of FG). In the vast majority of cases, the user will rely on MULTIMODE to carry out the normal mode analysis. In this case he sets INORM > 0 (INORM < 0 for saddle points). It could well be that the user knows all of these quantities, and wishes to use them in a run of MULTIMODE. In this case, he sets INORM = 0, and at the same time, he must input 3N-6 values of omega (in cm-1) as IPOT,JPOT,CPOT. He must also input sets of NORMAL COORDINATE DISPLACEMENTS for each Normal Mode as x,y,z displacements for each atom in turn. Note: there MUST be consistency between the order of the NUCLEAR MASSES, EQUILIBRIUM CARTESIAN COORDINATES, NORMAL COORDINATE DISPLACEMENTS and the input omegas at IPOT,JPOT,CPOT. These two approaches are presented in the SCF examples (see next section).

Finally, the user may have a potential function for which the precise position of the equilibrium structure is not known exactly, but an approximate structure

is known. To obtain the correct Normal Coordinates, the principal axes must correspond to the true equilibrium, and to get MULTIMODE to find it set MCHECK < 0. To find the true position of the minimum, use is made of the integration points generated by the input parameters NBF,MBF,NVF. These may either be Gauss-Hermite or optimized HEG points as described above in 'Numerical Integration'. For each mode, in turn, the position of the minimum is moved to Q = 0 by first fitting the one-dimensional potential to a polynomial, using the three central integration points and finding the position of its minimum. This process is repeated with five, seven,... points until the integration points have been exhausted, in which case, the 'best' geometry is used to find the 'PRINCIPAL AXES COORDINATES'. Once the true equilibrium has been found, the resulting 'PRINCIPAL AXES COORDINATES' are transferred to the input EQUILIBRIUM CARTESIAN COORDINATES, taking into consideration any strict symmetry requirements.

1. Vibrational Self-Consistent Field (VSCF)

ISCFCI = 0 is the key parameter for VSCF calculations, and each state is found to an energy tolerance given by CONV. The SCF examples here are all to CONV = 1.D-2 cm-1. When any new system is being investigated, the potential and Coriolis terms must be established at the integration grids for all of the coupled modes demanded by ICOUPL. If ICOUPL > 0, REAL*8 grids are formed and written to disc if IDISC = 0. If disc space is short, REAL*4 grids can be used by setting ICOUPL < 0. For large systems, a large amount of time can be spent writing these grids to disc, but, providing that the final Normal Modes have been found (as in the AUX examples) and the optimum number of Gauss points and/or HEG points determined by the parameters NBF,MBF,NVF have been determined, these grids need only be written ONCE ONLY. Thereafter, setting IDISC > 0 will omit writing these grids, and use the existing ones already on disc.

When performing an SCF calculation, a discreet number of vibrational states are found. There are a variety of ways to indicate those states required. The simplest way is merely to determine the lowest -NSTAT vibrational levels, by setting NSTAT < 0. In this case, there are no SCF STATE DEFINITIONS, and use is made of the omegas to calculate the states required. Test programs SCF.1 and SCF.2 are examples for which ten such states are found. SCF.1 uses Normal Modes determined by MULTIMODE, and SCF.2 uses user-supplied Normal Modes.

If a more specific set of VSCF states are required, set NSTAT > 0 to indicate how many, and set the SCF STATE DEFINITION parameter. As in test program SCF.3, is initiated by setting the SCF STATE DEFINITION < 0. This is followed by NSTAT

records which define the SPECIFIC STATES. Each record consists of NMODE = 3*NATOM-6 integers which signify the specific number of quanta in ALL the modes for all the NSTAT states to be determined.

Test programs SCF.1 to SCF.3 all determine the VSCF states for zero total angular momentum (JMAX = 0). Test program SCF.4 calculates J=0 and J=1 VSCF states by setting JMAX = 1; J>0 energies for SCF states are obtained by using the adiabatic rotation approximation only. Currently, all J > 0 levels are assigned according to asymmetric top definitions of Ka, Kc.

2. Orthonormal Virtual zpe Functions in CI (VCI)

ISCFCI > 0 is the key parameter for all CI calculations, and signifies the number of vibrational (JMAX = 0) or rovibrational K-diagonal (JMAX > 0) energies required, subject to the print cut-off parameter in CUT. All CI energies are printed in cm-1 relative to the base energy given in EVLJ0, which is usually set to zero for J=0 calculations. In this case, the energies are printed out relative to the J=0 zero point. For J>0 calculations, EVLJ0 is usually input as the absolute zero point energy for J=0. In all the following examples, one hundred CI energies are required (ISCFCI = 100) subject to a cut-off of 2.0D+4 cm-1.

This is the most exact algorithm in the MULTIMODE package, and is initiated by setting ISCFCI > 0, and ICI < 0. NMAX is used to select the virtual states in the VCI calculation. The NMAX could be >= 0, but it is rarely used, so will not be described in this manual. When NMAX < 0, |NMAX| modes are allowed to be excited simultaneously in the VCI basis. For example, NMAX = -2 is similar to CISD and NMAX = -3 is CISDT. In MULTIMODE, singles, doubles, triples,... are referred to as 1-, 2-, 3-mode basis, etc. When NMAX < 0, user also needs to specify the parameters MAXSUM and MAXBAS. MAXSUM should have |NMAX| numbers, which restricts the sum of quanta in 1-mode, 2-mode, ... |NMAX|-mode basis. MAXBAS should be |NMAX|*NMODE, and the first line indicates the maximum quantum of excitation for each mode in 1-mode basis, the second line indicates the maximum quantum of excitation for each mode in 2-mode basis, and so on so forth.

The CI matrix size could be huge sometimes. It is advised to first run a job with MATSIZ > 0. This merely instructs MULTIMODE to work out the matrix size(s) and then STOP. If they appear to be manageable, he can continue by running the same data set with MATSIZ = 0. The example VCI.1 does this, and VCI.2 runs the VCI calculation and final CI states are printed in the output file.

Another parameter NCONT allows the total number of modes (NMODE=3N-6) to be

split into a maximum of two groups (say low-frequency and high-frequency). For this purpose NCONT=-2 must be used. The actual modes selected for each `scheme' is input in ICONT and JCONT. ICONT is the number of modes in each scheme, and JCONT is the actual modes, labeled by the normal mode analysis (INORM>0, INORM<0) or input by the user (INORM=0). Two individual VCI bases are set up in the standard way, and therefore a set of parameters MAXSUM must be input for each scheme. These two basis sets are then combined to form one complete VCI basis which covers the entire NMODE modes. (A future release with NCONT=+2 will carry out a VCI on each scheme in turn, and collect the number of eigenfunctions given by NVAL1 and NVAL2. These will then be re-combined in a conventional contraction scheme analysis). Since `multimode.4.9.0' only fully supports the case NCONT=-2 (or the original single scheme with NCONT=1), only a single VCI is carried out, and only NVAL1 is required. This is equivalent to ISFCI>0, and will override any setting of ISCFCI if set non-zero. If NVAL1=0, the number of eigenfunctions specified by ISCFCI will be used.

Transition state as the reference geometry

It is sometimes necessary to centre the Principal Axes on a transition state, rather than at equilibrium (cf ammonia, where the coordinate origin is the planar transition state). Unless otherwise indicated, the normal mode analysis will assume that the first (lowest) six eigenvalues and eigenvectors are associated with the three translations and three rotations. For such an analysis performed at a saddle point there will be at least one imaginary frequency, and this situation is indicated by setting INORM < 0.

Sometimes (see INORM<0) the origin of the normal coordinates is not on the minimum of the potential, and the preliminary one-dimensional contraction of the primitive harmonic-oscillator basis will take place with all coordinates except the one under contraction set to zero. This means that the contractions may take place at a saddle point. Since the quantization of the global potential will ultimately refer to the equilibrium (minimum) of the potential, it is desirable to contract the basis with respect to an `effective' potential which `sees' the effect of the global minimum. For example, if the imaginary frequency in ammonia is labelled as mode number one (1), the values of MEFF(MODE) for MODE>1 to be given the values MEFF(MODE)=1, with MEFF(1)=0. This will result in the one-dimensional potential for mode MODE>1, for each point Q(MODE), being minimised with respect to the complete range of MODE=1.

Iterative diagonalization

Sometimes the CI matrix could still be too large so the Davidson/Liu (Lanczos-like) diagonalization scheme is used at the CI stages, each diagonalization performing a maximum of NCYCLE iterations for a tolerance of TOLLAN in the eigenvalues. The Hamiltonian matrices are built up in a half-size work matrix whose order is LANMAX.

There is sometimes a problem with such diagonalization, depending on the operating system (eg Linux before Mark 8), in that the maximum file-size allowed is 2GB. To attempt to overcome this, the Lanczos files can be spread over 5 disc files by setting the parameter LAN20 to the maximum size of a single disc file < 2GB. A further function of this parameter is to allow the diagonalization procedure (for a single symmetry species, see MVSYM) to be restarted if any problems occur with the installation etc. Providing that the message `Calculating Lanczos' has appeared on `fort.2', it is safe to kill the job and restart setting LAN20 = -LAN20. All files created during the job with LAN20 > 0 will have to be saved so that they can be re-read during the job with LAN20 < 0.

"Direct Dynamics" calculations

MOLPRO is the key parameter in the new `Direct Dynamics' feature of `multimode.4.9.0'. The method of M-mode coupling offers a solution to the problem of generating global potentials for large molecules. If, for example, 3-mode coupling is all that is required, then only 1-mode, 2-mode and 3-mode grids of the potential are required....anything greater than this will never be used, and therefore need not be constructed. Potentials are invariably obtained these days from ab initio packages such as `Molpro', and files can be produced to interface with such ab initio packages.  The ab initio data are then fed back into `multimode.4.9.0' to produce the required M-mode grids. There are two possible ways of creating potentials corresponding to these grids. The first way is to fit the ab initio data to a polynomial form (MOLPRO > 0) and then use these fits to generate the potential along these grids, as required. The second way is to store potentials and first derivatives at the M-mode grid points, and then to use a Hermite interpolation in order to generate the potential, as required. As an aside, it is even possible to re-determine a potential which already exists in functional form (it may contain `wiggles' or some other feature that requires `smoothing out').

But assume that it is required to investigate the spectroscopy of a molecule

for which nothing is known. The following procedure can be adopted to fit the various M-mode grids. The first thing that must be done is to obtain the position of the equilibrium structure ab initio, and then to carry out a standard Wilson FG Normal Coordinate analysis within the ab initio package. The `fort.1' data file for `multimode.4.9.0' is then set up with IWHICH = 0, ISCFCI < 0, INORM = 0 and NPOT = 3N-6. The normal coordinate harmonic potential (3N-6 values of omega) is then input as IPOT,JPOT,CPOT, together with the parameters SYMBOL, XM, X0 and XL (see Input.pdf), where XL are the mass-weighted displacement vectors arising from the Wilson FG analysis. Now set ICOUPL = ICOUPC = 1 and MOLPRO = 1 and run. A file `fort.4' will be produced with a series of Cartesian geometries (Angstroms), corresponding to one-mode Gauss quadrature grids; in particular, a line of `**********' will appear for each geometry. This line must be replaced by a line containing a single value of the ab initio energy (all other lines must remain intact) and the new file must be transferred to `fort.3'.  Now amend `fort.1' by setting MOLPRO = 2 and re-run. A file `fort.4' will again be produced, but this time it will contain the fitted one-mode potentials in the order required by `multimode.4.9.0' (the number of Gauss quadrature grid points generated in this scheme will be fixed by the input parameter MBF). This file, preceded by a suitable single-record header such as C**ONE-DIMENSIONAL FITS should now be appended to the `fort.1' input file.

To continue with the fitting of two-mode grids, set ICOUPL = ICOUPC = 2, MOLPRO = 3, and MOLINC = 1 if all HEG points are to be used to construct the grids, or MOLINC = 2 if alternate HEG points are to be used. The number of HEG points generated will be governed by NVF from the algorithm NVF+(MBF-NBF), where the number of points is always ensured to be EVEN. Then set MOLPRO = 4 and transfer `fort.4' to `fort.3', with the line of `**********' replaced by ab initio energies and re-run to obtain the 2-mode potentials.

This process is repeated for 3-mode and 4-mode potentials if required, noting that the number of ab initio calculations will grow rapidly from 2-mode through 4-mode grids, and so careful manipulation of the number of HEG points (using NVF and MOLINC) is suggested.

Full symmetry of the system is used such that no point will be generated twice, so NVSYM and the remaining symmetry parameters should be set if appropriate. This procedure can first be tested by the user on a molecule for which he has a global potential. Such a test on the 6-mode molecule H2CS is supplied with multimode.4.9.0' (see TESTS section below).

On completion of the fitting procedure, an enlarged `fort.1' will exist which contains the potential parameters for the M-mode cuts appended in sequence. In order to use these potentials, set up the remaining parameters required for a VCI calculation with IWHICH < 0 (keeping MOLPRO > 0). A complete sequence

of `fort.1' files is included in the test programs that accompany this release
of multimode.4.9.0' which should act as a guide.

A related method can be performed, except that MOLPRO < 0 is set in the above
procedure. This is the indication that the potential is to be interpolated
between grid points. At the input of `fort.3' with `even' MOLPRO, not only
is the potential required, but the derivatives with respect to the mass-weighted
normal coordinates Q. For an M-mode grid, the order of the first derivatives
in the input line `**********' is: V, dV/dQ(k), dV/dQ(l), dV/dQ(n), dV/dQ(m),
where k > l > n > m. The actual modes are output to 'fort.3' to make sure that
the correct ordering can be guaranteed. How the derivatives are obtained,
however, is another matter; it may be possible to obtain derivatives with
respect to x,y,z directly from the ab initio package, and then the normal
coordinate vectors can be used to convert these to derivatives with respect
to the Q. Other ways might be to obtain the derivatives by finite differences
in the ab initio cycle, or even to fit the potentials to polynomials and then
differentiate these. This method of `Direct Dynamics' is however more
cumbersome than that described above for the M-mode fits, and should possibly
be avoided.

XTANPM input has been introduced to assist in the fitting of M-mode grids when
using the `Direct Dynamics' facility. For each of the 3N-6 normal modes, a
parameter XTANPM(MODE) is input such that, if the extreme Gauss quadrature
point is G(max) = -G(-max), a variable Y is defined as Y = gamma.Q (Q is a
mass-weighted normal coordinate), such that Y = XTANPM(MODE) at Q = G(max).
The variable tanh(Y) is then used in the potential. This parameter behaves
like a Morse function at large displacements and the input parameter XTANPM(MODE)
sets the asymptotic value. In most cases, a value XTANPM(MODE) = 1.0 will be
appropriate, but this can be varied if required.

MOLINC is another input introduced for the `Direct Dynamics' facility. Its
allowed values are 1 & 2, and is used to stipulate the number of HEG integration
points used to generate M-mode grids which are used to define the points at
which abinitio calculations are required. MOLINC = 1 implies that every HEG
point will be used, whilst MOLINC = 2 implies every other HEG point will be
used.

Reaction Path calculations

IREACT is the key parameter in the `Reaction Path' feature of `multimode.4.9.0'.
IREACT labels the torsional mode at the starting value of `tau' (the Reaction
Path coordinate) selected by the user. This will be the order of the torsional
mode in a Wilson FG analysis performed at the starting configuration. If

IREACT > 0, a global potential function must be supplied, and if IREACT < 0, files obtained from ab initio packages must be supplied. For IREACT > 0, two variants are available. The first satisfies the Eckart conditions between successive points along the path, whilst the second uses successive geometries which are aligned along principal axes. For IREACT < 0, the non-Eckart procedure is used. For all `Reaction Path' studies, the user must provide a subroutine REACT (see User.pdf). If all `Reaction Path' diagnostics are required, set IPRINT > 0, ISCFCI < 0. This will stop after the construction of the `Reaction Path', when the user can investigate the many tests pertaining to the accuracy/validity of the path. Once satisfied, set IPRINT < 0 and ISCFCI > 0, plus the remaining parameters required for a conventional VCI run (see Input.pdf and RPH in TESTS section below).

Corresponding to the mode denoted by IREACT, the parameters NBF,MBF,NVF will be set, bearing in mind the curvilinear nature of the `Reaction Path' coordinate. MBF = 90 or higher is usually sufficient for the number of integration points spanning `tau' = 0 to 360 degrees. NBF is the number of primitive (both sin(n.tau) and cos(n.tau)), and something in the range 30 to 60 is reasonable. The reason for so many torsional primitives is that convergence along the `Reaction Path' is slow for such functions.

Dump-restart

There is also a research facility for VCI calculations (ICI < 0) whereby it is possible to dump information about wavefunctions to a disc file for further scrutiny, for example the study of transition moments, etc.

IDUMP is the key parameter in the `Dump & Restart' feature of `multimode.4.9.0'. The idea is to be able to carry out a vibrational analysis and then to calculate properties relating to these vibrational wavefunctions. Currently, this feature is not available for `Reaction Path' studies. Furthermore, only the evaluation of dipole moment matrix elements is available.

If IDUMP > 0, then IDUMP VCI wavefunctions will be saved, as it is for these functions that the property is to be calculated. To calculate the dipole moment matrix elements, the program can be restarted with LDUMP = 1. The user must provide a routine to evaluate the dipole moment components (as for the equivalent routine for the potential); if IWHICH > 0, the internal coordinate routines GETPOT (potential) and GETDIP (dipole) must be supplied. If IWHICH < 0, the equivalent normal coordinate routines GETQPT (potential) and GETQDT (dipole) must be supplied. The 'Dump & Restart' facility is not (yet) supported for the black-box normal coordinate potential and dipole indicated by IWHICH

= 0. Dipole moment components are input in the sequence A1,B2,B1(A2) if C2v; A',A" if Cs, etc..

TESTS

The additional test programs supplied with `multimode.4.9.0' are inside the folder TESTS. They are intended to augment those water examples in such a way as to give examples of the majority of features now at the user's disposal. These tests are grouped into five distinct directories H2CS, HOOH, FURAN, RPH and MOLPRO.

1. H2CS: This directory is mainly a hard copy of all allowed permutations of the potential integration coupling (ICOUPL) and the Coriolis integration coupling (ICOUPC) for standard VCI runs using a potential in internal coordinates (IWHICH>0). For all cases except ICOUPL=5 and ICOUPL=6, these tests include both J=0 and J=1. The reason for this complete set is straightforward; should the user modify the code in any way (incorrectly), the test programs should be repeated, starting with ICOUPL=1, ICOUPC=0, followed by ICOUPL=1, ICOUPC=1, etc. until such time that the results corresponding to the relevant `fort.2' file are no longer reproduced. This may help in locating the suspect routine. The user is, however, NOT encouraged to make changes to the code in any way before prior consultations with myself. All test input/output files which contain the word `test' are single-scheme (NCONT=1) VCI calculations, for which `fort.1.H2CS.test' is the master input file, set up with ICOUPL=4, ICOUPC=4, JMAX=0, EVLJ0=0.0. These parameters alone need to be changed to run all the examples bearing the word `test'. Standard `multimode' is reported in Theor. Chem. Accts., 100, 191 (1998); J. Phys. Chem., A104, 2443 (2000); Int. Rev. Phys. Chem., 22, 533 (2003) and references therein.

Two further tests are supplied which illustrate the `Dump & Restart' facility (see also FURAN below) for a potential and dipole in internal coordinates (IWHICH>0). In `fort.1.H2CS.dump' IDUMP=20 indicates that 20 VCI wavefunctions are to be saved for future use on `fort.60' whilst in `fort.1.H2CS.restart' dipole matrix elements between these functions are calculated by setting LDUMP=1 (the only LDUMP property supported to date). In order to calculate the three components of the dipole (A1, B2, B1) which will be integrated using the same integration points as those used to integrate the potential, a grid of geometries must be generated in the Eckart frame at which the X,Y,Z components of the dipole must be calculated and subsequently fit. The input file `fort.1.H2CS.eckart' can be run to generate such a grid. In theory, all displacements from the reference, which are determined by the normal coordinate vectors should already be in the Eckart frame, but this may not be guaranteed

due to rounding errors, etc. if external normal coordinates are input (INORM=0). This feature is a safeguard against this occurring. In `fort.1.H2CS.eckart', MDUMP=-4 is set to use 4 central (HEG) grid points and terminate after generating the Eckart frame grid. Both Cartesian coordinates and bond distances are given at each point in the grid. The `Dump & Restart' tests are reported in Phys. Chem. Chem. Phys., 3, 508 (2001). A second `Dump & Restart' test is similar to the above, but the VCI basis is constructed for two separate schemes (NCONT=-2) before recombination to give the required VCI basis which spans all 3N-6 modes. Data for this test are in `fort.1.H2CS.-C.dump' and 'fort.1.H2CS.-C.restart'. More information on `Dump & Restart' can be obtained from the Dump-Restart section above.

For all tests, the routine `user.H2CS.F' is supplied. USERIN reads all parameters necessary to evaluate the potential and dipole, whilst GETPOT and GETDIP calculate the instantaneous values of the potential and LDIP components of the dipole, respectively. The remaining routines in `user.H2CS.F' are not used but must be present as dummy routines. The potential (plus dipole) parameters are appended to `fort.1.H2CS.dump' and `fort.1.H2CS.restart', respectively.

2. HOOH: This directory is a hard copy of all allowed permutations of the potential integration coupling (ICOUPL) and the Coriolis integration coupling (ICOUPC) for `Reaction Path' VCI runs using a potential in internal coordinates (IWHICH>0). For all cases, these tests include both J=0 and J=1. The choice of `Reaction Path' is that for which each point along the path, separated from the previous point by a torsional (HOOH) angle of 0.5 degrees, satisfies the Eckart conditions with respect to the previous point. The parameter IREACT>0 points to the curvilinear mode number in a Wilson FG analysis at equilibrium. The user-supplied routine `react.XXX.eckart.f' that is needed to generate such a path is detailed in User.pdf (see also RPH below). The routine `user.HOOH.F' is supplied, which inputs all necessary parameters in USERIN, evaluates the potential energy using internal valence coordinates (IWHICH>0) in GETPOT, and determines the structure corresponding to the minimum energy for a given torsional angle in MINPOT. The HOOH `Reaction Path' tests are reported in J. Chem. Phys., 113, 987 (2000) and Spectrochimica Acta, in press (2004) for J=0 and J=1, respectively.

3. FURAN: The test in this directory covers two new aspects of `multimode.4.9.0'. The first is the use of potential (and dipole) functions, created free-standing by the user in mass-weighted normal coordinates, denoted by IWHICH<0 and MOLPRO=0 in `fort.1' (note that the choice of coordinate Y=gamma.Q is not adopted in this test, although the parameters XTANH must be input as dummy since IWHICH<0). The second aspect covered by this test is the `Dump & Restart' facility, and in `fort.1.FURAN.dump' the Dump facility is initiated by setting

IDUMP=20 to indicate 20 VCI wavefunctions will be saved for future use on `fort.60'. In `fort.1.FURAN.restart' the evaluation of dipole matrix elements (the only property supported at the moment) is prompted by LDUMP=1. The relevant routines in User.pdf are supplied in `user.FURAN.F'. Routine USERIN inputs all parameters necessary to evaluate the potential and dipole, whilst GETQPT evaluates the potential which has been constructed by differentiation of an ab initio PES and converted to mass-weighted normal coordinates as an independent exercise. Similarly, the three components of the dipole (A1, B2, B1) are evaluated in GETQDT, depending on the parameter IDIP. The remaining routines in `user.FURAN.F' are not used but must be present as dummy routines. The potential (plus dipole) parameters are appended to `fort.1.FURAN.dump' and `fort.1.FURAN.restart', respectively. The FURAN tests are reported in Spectrochimica Acta, A59, 1881 (2003) and Phys. Chem. Chem. Phys., 6, 340 (2004). More information on `Dump & Restart' can be obtained from the Dump-Restart section above.

4. RPH: This directory contains tests for the three supported versions of the `Reaction Path' facility, and is sub-divided into three further directories (ECKART, NONECKART, ABINITIO).

ECKART contains a test similar to those in HOOH above, and the user is also referred to that directory. The benefit of satisfying the Eckart conditions between successive points along the path is that the successive structures form a smoothly-varying path. The (slight) drawback is that very small numerical errors become enlarged at points along the path as they become more distant from the starting point, and it may become necessary to `tidy up' a structure of high symmetry (for example for HOOH it is necessary to ensure that the `cis' and `trans' structures are strictly planar, due to the fact that the rotations required to obey successive Eckart conditions lead ultimately to slightly off-planar structures - the user can handle this difficulty as he/she feels fit, but it is pointed out here as something to beware of).

NONECKART overcomes this difficulty in so far as successive points along the path are rotated to a principal axis coordinate system only. In this case however, it can not be guaranteed that the coordinate systems for successive points along the path have not undergone axis-interchange due to over-rotation. A test must therefore be included to ensure that the path remains smooth. The user-supplied routine `react.XXX.noneckart.f' that is needed to generate such a path is detailed in User.pdf.

ABINITIO goes about the `Reaction Path' problem in a completely different way, since now it is assumed that no potential is available for the molecule in question. In this sense, the approach is more one of `direct dynamics' in which everything is evaluated by some ab initio package (GAUSSIAN, MOLPRO,..).

Specific data files must be generated corresponding to specific path points, and therefore it is important to know the starting point of the path (usually some high-symmetry structure such as `cis' or `trans') and the torsional interval between successive points. This process is outlined in detail for `react.XXX.abinitio.f' in User.pdf where the path is constructed as in NONECKART above. The test example supplied is for a harmonic methanol potential, reported in Molec. Phys., 101, 3513 (2003), and the parameter IREACT<0 points to the curvilinear mode in a Wilson FG analysis at equilibrium.

All test programs supplied in the RPH directories give full output (IPRINT>0) at each step during the development of the path (the determination of the path, the derivatives of the path structures, the projection out of the `Reaction Path' coordinate, the derivatives of the 3N-7 normal coordinate vectors). More information on `Reaction Path' can be obtained from IREACT in "Reaction Path calculations" above, and in the document User.pdf.

5. MOLPRO: This directory contains tests for the construction of the M-mode cuts of the potential, and is sub-divided into two further directories (FITS, HERMITE).

FITS contains test data for fitting 1-mode to 5-mode cuts in the potential, by mimicking an ab initio package with the use of an internal coordinate potential (IWHICH>0). The potential cuts produced at each stage are successively appended to the various data files in `fort.1.H2CS.fit.M.V', where `M' is the M-mode cut in question. These fitted cuts are then used in evaluation of the vibrational energy levels with `fort.1.H2CS.test.fit.V', where ICOUPL and ICOUPC can be varied at the user's discretion (See "Direct Dynamics" calculations section above). The test example supplied is reported in Chem. Phys. Lett., 352, 1 (2002).

HERMITE contains equivalent data for interpolation of the M-mode cuts of the potential used in FITS above. The interpolation data (potential plus first derivatives) produced at each stage are successively appended to the various data files in `fort.1.H2CS.herm.M.V', where `M' is the M-mode cut in question. These cuts are then used in evaluation of the vibrational energy levels with `fort.1.H2CS.test.herm.V', where ICOUPL and ICOUPC can be varied at the user's discretion (see "Direct Dynamics" calculations section above). The test example supplied is reported in Chem. Phys. Lett., 342, 636 (2001).

More information on `Direct Dynamics' can be obtained from "Direct Dynamics" calculations above. In particular, details on how to construct potential cuts from ab initio data are given.