USER MANUAL

This Section describes in some detail the facilities offered by MULTIMODE. It should be read in conjunction with 'Input_parameters.pdf' and 'User_subroutines.pdf'. In 'Input_parameters.pdf' all data records are specified in full.

We provide two sample input files generated with mmhelper.py for VSCF+VCI calculations on formaldehyde (H_2CO) as a quick start, one for full-dimension calculations with all normal modes, and the other for reduced-dimensional calculations by excluding two lowest-frequency modes. The inputs and corresponding outputs can be found in the folder 'examples'. In both cases, MULTIMODE will find the harmonic frequencies (in cm-1) and normal coordinate displacements. The user can copy the inputs to the folder where the executable "mm.x" locates, and run as follows:
./mm.x fort.1.XXX fort.2.XXX

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 'User_subroutines.pdf'). 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.XXXX.f' module.

The next step is to choose a convenient size for the work array in the module 'memo.VSCF.X.f' (see User_subroutines.pdf). 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 260000000 (corresponds to 2GB). 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 an 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 optimisation supported by the FORTRAN compiler when compiling 'user.f'. Some SGI compilers produce incorrect results if 'memo.f' is compiled at -O2, however, and we strongly recommend that the option -O1 is used when compiling 'memo.vscf.X.f'. All remaining modules can be compiled at the highest level of optimisation, 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 summarised 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 4-atom (NATOM = 4) Molecule H2CO, for which a PIP potential (IWHICH > 0) is supplied. In all cases, coupling of a maximum of three modes (ICOUPL = 3) in the potential and two modes (ICOUPC = 2) in the Coriolis terms is used.

Numerical Integration

All integration of matrix elements is carried out numerically, using Gauss hermite quadrature to integrate the NBF harmonic-oscillator primitives, followed by optimised 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 optimised 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_parameters.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 optimised functions (the contracted functions are taken from the NVF lowest-energy subset of these optimised functions).   If these conditions are not met, MULTIMODE attempts to recover from a knowledge of NVF and the excess MBF-NBF.

1. Basic Set-up Facilities

These test examples are mainly concerned with features relating to the Normal Coordinates and are terminated after initial tests have been performed by setting ISCFCI < 0. For these initial test examples, many of the input parameters are ignored. Only those relevant to the specific test under discussion are highlighted below.

MULTIMODE employs the Watson Normal Coordinate Hamiltonian for non-linear molecules and therefore requires an input equilibrium geometry in Cartesian coordinates, the harmonic force constants of the potential (omegas) and the corresponding displacements of the atoms (the eigenvectors of FG). It could well be that the user knows all of these quantities and wishes to

use them in a run of MULTIMODE. The user inputs the NUCLEAR MASSES and corresponding EQUILIBRIUM CARTESIAN COORDINATES and indicates that he wishes to use his own Normal Coordinates by setting INORM=0. The user must input NPOT=3*NATOM-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. It is most common when running an FG analysis to choose a 'convenient' cartesian coordinate system to describe the equilibrium configuration (one axis along a bond with an atom at the origin is common**). The Watson Hamiltonian, however, requires that the input axes are the principal axes of rotation (specifically, the Ir system Z~a, X~b, Y~c, with 'a', 'b', and 'c' denoting the axes corresponding to minimum, intermediate, and maximum moments of inertia, respectively), and to instruct MULTIMODE to find these from the input geometry, set MCHECK > 0.**

In the vast majority of cases, the user will rely on MULTIMODE to carry out his Normal Coordinate analysis. In this case he sets INORM > 0. There are now NPOT = 0 values of omega to input at IPOT, JPOT, CPOT and the NORMAL COORDINATE DISPLACEMENTS are omitted.

2. Vibrational Self-Consistent Field (SCF)

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. If a more specific set of VSCF states are required, set NSTAT > 0 to indicate how many, and set the SCF STATE DEFINITION parameter. Two types of setting are supported. The first 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. The second first sets the SCF STATE DEFINITION to a default value (usually 0) and then inputs

NSTAT-1 records which indicate number of quanta in corresponding mode, respectively. This default method is really only desirable for setting up fundamentals and overtones.

3. Non-orthogonal VSCF Functions in CI (SCFCI)

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. An SCFCI calculation is indicated by setting ICI > 0, and this is the number of VSCF states to mix in the non-orthogonal CI basis.

4. Orthonormal Virtual Functions in CI (VCI)

This is the most exact algorithm in the MULTIMODE package and is initiated by setting ISCFCI > 0 (as above), and ICI < 0. If NMAX > 0 or NMAX = 0, then -ICI means the maximum quantum of excitation (in ALL modes) in the VCI basis. If NMAX > 0, the VCI basis is restricted to a sum of quanta of NMAX. The fact that a VCI run is in progress curtails the VSCF procedure after the initial state has been determined, and the zpe virtual functions are therefore used in the VCI. If, for some reason, the user thinks that some other VSCF would be more appropriate for his VCI basis, he should use the NSTAT > 0 facility (see SCF above) and input his preferred choice of VSCF state as the initial SPECIFIC STATE. There is 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.

If NMAX = 0, the VCI basis is unrestricted, but this may lead to extremely large CI matrices, especially as the number of modes increases. 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.

5. New Features of `multimode.4.9.0'
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1. ICOUPL: It is now possible to extend the mode-coupling of the potential to six (6) modes.

2. ICOUPC: It is now possible to have a different mode-coupling for the Coriolis terms than that for the potential. For large(ish) systems, the `multi-mode' coupling becomes relatively more important for the potential than for the Coriolis terms. ICOUPC = 0, ..., ICOUPL are the allowed ranges of the new parameter ICOUPC which can be used to verify this for the case under

investigation. Much computing time and space can be saved by minimizing the value of ICOUPC, particularly for high values of ICOUPL. Currently, the maximum value of ICOUPC = 4.

3. INORM: 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.

4. NMAX: The maximum mode-coupling of the VCI basis has been extended to 5 (See also MAXSUM and MAXBAS).

5. NCONT: In `multimode3.4` the composition of the VCI basis is governed by the three sets of parameters NMAX, MAXSUM and MAXBAS. The parameters MAXBAS are mode-dependent, whereas NMAX and MAXSUM are common to all modes. In order to allow more flexibility into the construction of the VCI basis, a new parameter NCONT has been introduced into `multimode.4.9.0'.  This parameter 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 facility with NCONT=+2 will be introduced in a future release of `multimode.4.9'). 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.

6. MODINT: 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 (labeled 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.

7. MEFF: 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 libeled 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 minimized with respect to the complete range of MODE=1.

8. NVSYM: It is now possible to extend the number of irreducible representations to eight (8). This is for pseudo D_{2h} symmetry, where a centre of symmetry is added to C_{2v}; hence the species A_{1g}, A_{1u} ... etc. are all allowed.

9. LAN20: For very large VCI matrices, it is probably most convenient to use the Davidson-Liu (Lanczos-like) iteration diagonalization (see NCYCLE). 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.

10. SYMBOL: This input has been introduced to interface with ab initio packages when using the `Direct Dynamics' facility (see MOLPRO below). The NATOM atomic symbols are input in the order used in the Normal coordinates that has been chosen by the user. This parameter is ALWAYS required.

11. XTANPM: This input has been introduced to assist in the fitting of M-mode grids when using the `Direct Dynamics' facility (see MOLPRO below). 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 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.

12. MOLINC: This input has been introduced for the new `Direct Dynamics' facility (see MOLPRO below). Its allowed values are 1 & 2 and are used to stipulate the number of HEG integration points used to generate M-mode grids which are used to define the points at which ab initio calculations are required. MOLINC = 1 implies that every HEG point will be used, whilst MOLINC = 2 implies every other HEG point will be used.

13. MOLPRO: This 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.DOC), 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 proceeded 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 (unlike `multimode.3.4') 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 Part B 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 a `fort.1' file 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.

14. IREACT: This is the key parameter in the new `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_subroutines.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.DOC and RPH in Part B 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.

15. IDUMP: This is the key parameter in the new `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 but will be introduced in a future release of `multimode.4.9'. Furthermore, only the

evaluation of dipole moment matrix elements is available, but I welcome any further suggestions that you may have for future implementation. 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 A_1, B_2, B_1 (A_2) if C_{2v}; A', A" if C_s, etc.

6. Additional Features added in `multimode.5.X'

See "Additional_Notes.pdf"