

Master Equation System Solver (MESS)

Program User Manual

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1. Purpose

The primary purpose of the program is to calculate temperature and pressure dependent rate coefficients for complex-forming reactions via solution of the one-dimensional master equation. Ancillary calculations of various quantities (e.g., stabilization probabilities for microcanonical initial distributions, microcanonical rate constants, partition functions, and related thermochemical information, time dependent propagation of species populations, etc.) are also available.

2. General Description

The master equation calculations proceed by first constructing the global relaxation matrix that describes both chemical transformations (bimolecular-to-complex reactions and internal isomerizations) and collisional energy relaxation, then finding the eigenstates of the relaxation matrix, and finally extracting from those the full set of phenomenological chemical rate coefficients.

The calculations are performed at the E-resolved (microcanonical) level, i.e., the one-dimensional master equation is solved. The chemical transformations are generally described with RRKM theory, although alternative expressions for the reactive flux may be incorporated through read options. A variety of models are available for evaluating the densities or numbers of states for barriers, wells, and bimolecular products. Similarly, collisional energy relaxation may be described with a variety of model energy transfer kernels.

The chemically significant eigenstate approach of Klippenstein and Miller [1,2] provides the basis for relating the eigenstates of the transition matrix to the phenomenological rate coefficients. The particular formalism employed here involves an irreversible rather than reversible treatment of bimolecular species, as described in a paper of Georgievskii et al. [3]. With this approach, the bimolecular products and reactants are treated on an equal footing, as sources and sinks and their concentrations are not included as variables in the global phase space. For each requested temperature and pressure the global relaxation matrix is constructed by appropriate discretization, the chemically significant eigenstates are found, analyzed, and used to evaluate all of the phenomenological rate coefficients.

3. Main Features

3.1. Solving the Master Equation

3.1.1. Calculation Method

There are currently two methods that are employed for the calculation of the thermal rate coefficients (keyword **CalculationMethod**):

- Direct diagonalization method (keyword **direct**), which diagonalizes the global relaxation matrix directly using LAPACK routines.
 - Advantages: gives full and accurate description of the full chemical and collision relaxation.
 - Drawbacks:
 - due to numerical limitations may not work at low temperatures.
 - numerically expensive (requires direct diagonalization).
- Low eigenvalue method (keyword **low-eigenvalue**) is based on assumption that chemical eigenvalues are much smaller than the relaxational ones.
 - Advantages:
 - very accurate for slow chemical modes
 - numerically cheap (requires only global relaxation matrix inversion)
 - works at low temperatures.
 - physically appealing.
 - quadruple precision is used to solve difficulties related to large span of eigenvalues
 - Drawbacks: not very accurate at high temperatures.

Recent modifications to the direct diagonalization method incorporate key elements of the low eigenvalue method for cases where the span of eigenvalues is too large. As a result, this method now appears capable of treating many low temperature cases, and has generally become our method of choice.

3.1.2. Well Truncation

To speed up the calculation, avoid low eigenvalue problems, and, in some cases, for consistency, some of the wells are occasionally truncated. The resulting rate coefficients are renormalized to the original non-truncated configuration.

3.1.3. Efficient Evaluation

Considerable attention has been devoted to reducing the clock time required for the evaluation of the thermal rate coefficients. Temperature dependent energy grids are employed in order to minimize the size of the matrix diagonalization. The requisite densities and number of states are pre-evaluated over a large energy scale and then the values for the specific T,P dependent grids are obtained through interpolation. The diagonalization of the transition matrix, which is generally the most time consuming step, runs in parallel for nodes with multiple threaded processors. This is largely accomplished through linking to the parallel MKL library, although some other aspects of the evaluations (such as various matrix multiplications) have also been parallelized. Sample calculations for a system with 20 wells and 30 barriers produces rate

coefficients in well under a 1 minute of wall time on a 16 core linux node.

3.2. Output Features

3.2.1. Automated Merging of Species

At high temperatures it is common for some of the species to rapidly equilibrate with each other or with bimolecular products. In this instance, the corresponding chemical modes merge with the energy relaxation pool and the effective number of chemical species should be reduced. A method that automates this reduction process has been developed and incorporated into the code.

When species reduction is necessary, it is important to know if some of the bound species are equilibrating with bimolecular products, and if so, with which ones. The kappa-matrix, which provides the coupling coefficients between the bound species and bimolecular products, provides this information and is calculated and printed in the log output file. Its elements should be close to unity for the pairs of bound species and bimolecular products that are in equilibrium with each other and close to zero otherwise. When multiple bimolecular products merge with the wells the situation may be more complex, but the kappa matrix, still provides a useful description of the couplings.

3.2.2. Product Energy Distributions

On request the code prints out the energy distribution for the bimolecular products (keywords are **PEDOutput** and **PEDSpecies**). Note, however, that the determination of the energy in a particular bimolecular product requires some further partitioning of this energy amongst the two products and their relative translation.

3.2.3. Direct Reaction Probabilities

The code can also evaluate (keyword **HotEnergies**) the probabilities that a reactive complex in a specific initial well with a particular energy is captured in one of the wells or directly dissociates to different bimolecular products.

3.2.4. Time Dependent Species Populations

The code can also print out (keyword **TimeEvolution**) the time dependent species populations for thermal or microcanonical distributions of any specific species.

3.3. Transition Matrix Features

3.3.1. Coupled Internal Rotations

An essential feature of the program is the ability to calculate the density or number of states and statistical weight for the group of coupled internal rotations and vibrations whose frequencies depend on torsion angles. For energies below a certain limit the quantum energy levels are calculated by direct diagonalization of the Hamiltonian for the complex with zero angular momentum and in the ground vibrational state. To reduce the number of matrix elements in the Hamiltonian that need to be calculated one can prune both the potential and the kinetic energy terms (keywords are **PotentialPruningTolerance** and **MassPruningTolerance**). To approximately include external rotations the quantum state average of the square root of the

inverse product of principal inertia moments is calculated and used to generate the (external) rotational density or number of states for each internal quantum state. The overall quantum density or number of states in the ground vibrational state is obtained by summation of the individual (external) rotational densities or numbers of states over all internal quantum states. The so obtained quantum density or number of states in the ground vibrational state is used to obtain the quantum correction to the classical density or number of states for the internal rotations mixed with external rotations and torsion-dependent vibrations. As an option, there is a possibility to generate quantum levels for all energetically relevant vibrational population configurations. A statistical weight is calculated using the path integral approach with a local quadratic approximation for the potential. Comparison with the statistical weight generated with a full quantum treatment demonstrates excellent agreement down to the 100 K temperature range. It is also possible (keyword **AngularMomentumMax**) to calculate quantum energy levels for coupled internal and external rotations, however this calculation is often computationally very expensive.

3.3.2. Anharmonic Umbrella Modes

Anharmonic umbrella mode treatments may be incorporated through the specification of the anharmonic potential (keyword **Umbrella** in **RRHO** section).

3.3.3. IR Radiative Transitions

For the harmonic oscillator portion of the **RRHO** model (see below) one can include doubly harmonic radiative transitions (keyword **InfraredIntensities** in **RRHO** section) within the energy relaxation kernel.

3.3.4. External Reactants

To describe fast bimolecular reactions of hot isomers with external reactants it is possible to provide an optional exit channel from each well [keyword **Escape**] with a predefined pseudo first order energy-resolved escape rate.

3.3.5. Automated Connectivity

For each barrier the user specifies via species labels which pair of wells and/or bimolecular products it separates. A connectivity scheme is then set up automatically.

3.3.6. Collisional Energy Transfer Kernel

Several model forms of collisional energy transfer kernel are available:

- The standard exponential form for downward transitions. Utilizing this form in conjunction with an energy-independent collision frequency may lead to unphysical negative transition probabilities at low energies. To avoid this problem one must truncate the corresponding well. As an alternative, the following two forms provide a means to avoid this problem or at least to ameliorate its effect.
 - Exponential form for upward transitions.
 - The collisional energy transition probability is represented by the product of the final density of states and the standard exponential down factor.
- Each of these collisional models may be extended to a sum of exponentials.
- The collisional model may be set up to consider multiple colliders (e.g., for a mixture of

N₂ and O₂).

- Distinct collisional models may be employed for the different wells.

3.3.7. Models

The program is built around the evaluation of objects that we call *statistical species*, which are the density or number of states as a function of energy and/or a statistical weight as a function of temperature. A variety of models for evaluating the statistical species for stable species, transition states, and bimolecular products are available:

- The most common statistical species (keyword **RRHO**) considers a multidimensional complex with external and internal rotations, vibrations, umbrella modes, etc. It consists of a core (keyword **Core**), several uncoupled one-dimensional motions (keyword **Rotor**), tunneling factor (keyword **Tunneling**), constant harmonic frequencies (keyword **Frequencies[1/cm]**), and electronic levels (keyword **ElectronicLevels[1/cm]**). The core represents those degrees of freedom that are inextricably coupled to external rotations of the complex. The following cores are currently available:
 - Rigid rotor (keyword **RigidRotor**).
 - Several coupled internal rotations (keyword **MultiRotor**). This core may also include a set of vibrations whose frequencies depend on the torsion angles.
 - Number of states for transitional modes of two rigid fragments forming a transition state complex, which are obtained from variable reaction coordinate flux (VaReCoF) calculation (keyword **Rotd**).
 - Phase space theory model for barrierless transition state complex (keyword **PhaseSpaceTheory**).

The following one-dimensional uncoupled motions are currently available (as qualifiers to the **Rotor** keyword) for convolution with the core density or number of states:

- One-dimensional free rotor (keyword **Free**).
- One-dimensional hindered rotor (keyword **Hindered**).
- One-dimensional umbrella mode: out of plane motion in an arbitrary well-like potential (keyword **Umbrella**).

The following tunneling models are currently available (as qualifiers to the **Tunneling** keyword):

- Parabolic barrier (keyword **Harmonic**).
- Eckart barrier (keyword **Eckart**).
- Quartic/Cubic potential barrier (keyword **Quartic**).
- A union of several statistical species (keyword **Union**) may be considered. Its density or number of states is a sum of the densities or numbers of states of its constituents.
- The density/number of states may be read from a file (keyword **Read**). The code will interpolate and, as needed, extrapolate from the user specified grid of data.
- A variational barrier treatment (keyword **Variational**) evaluates the minimum of the numbers of states of its constituent RRHO's at each given energy.
- A separate treatment for atoms (keyword **Atom**) is also provided.

The input for each of these models is described in detail in Section 5 below.

4. Input File Structure

Dimensional parameter keywords have units attached to the parameter name in the square parentheses. Composite parameters end with an **End** keyword. In general, the keywords associated with a particular composite parameter can go in any order. Sometimes there are several groups of keywords associated with a specific composite parameter. Then the keywords in the same group can go in any order but they should stay together as a group.

Comments can be inserted more or less anywhere and should start with a # or ! character. Everything after these characters to the end of the line is considered as a comment. The primary exception is that a comment cannot be inserted between a parameter keyword and its value, which must go on the same line. After the parameter value, everything to the end of the line is considered as a comment. Another notable exception is the atom definitions in the **Geometry** subsection. No comments are allowed on the atom definition lines.

All parameters belong to one of two groups: the **global** (unnamed) section, which goes first, and the **model** section (keyword **Model**). The **Model** section consists of the statistical species definitions for each of the wells, the bimolecular products, and the barriers. The **Model** section ends with an **End** keyword. No input will be read after the **Model** section ends.

The remainder of the manual provides line-by-line descriptions of the input options and protocol. These descriptions may be used to generate a complete input file. However, it is probably better to produce input files through suitable modification of the numerous examples provided in the distribution. These descriptions should be used more as a reference to the possibilities and as a guide in debugging. Note that the log file generally provides a clear indication of what part of the input file is creating input errors.

5. Global Keywords

5.1. Condition Parameters

- **TemperatureList[K]**: a list of temperatures should follow this keyword on the same line. This parameter is compulsory.
- **PressureList[Unit]**: a list of pressures should follow this keyword on the same line. This parameter is compulsory. **Unit** = **bar**, **torr**, or **atm**.

5.2. Method Parameters

- **CalculationMethod**: possible values are either **direct** or **low-eigenvalue** (cf. Sec. 3.1.1). This parameter is compulsory.
- **SpeciesReductionMethod**: the method used to reduce the number of species when some of the species are rapidly equilibrated. Each of these methods provides an alternative approach for determining the best partitioning of the species in terms of the chemical eigenvector subspace. Currently available methods: **threshold** (default), **sort_out**, **incremental**, and **sequential**. The **sort_out** method considers all possible well merging scenarios in determining the partitioning that provides the greatest projections on the chemical subspace. While being the most accurate, it depends on the number of species in a factorial manner, and as result it becomes too costly for systems with many wells. The **threshold** method uses a preevaluation of the projection of the chemical subspace on the well population vectors to restrict consideration to a limited subset of possible merging scenarios. It is both accurate and fast and should be used in most situations. The **incremental** approach adds species one at a time to the core set (of same dimension, S , as the reduced chemical subspace) of species with maximal projection in the chemical subspace. The **sequential** approach populates the species definition one by one according to whether or not they increase the projection on the chemical subspace. The **incremental** and **sequential** approaches have largely been superseded by the **sort_out** and **threshold** methods, but for debugging purposes all still provided.
- **WellProjectionThreshold**: a parameter for the **threshold** species reduction method, which determines which wells will be considered when evaluating the initial possible merging scenarios. Small values imply more complete consideration of the possible merging scenarios, but too small a value may be unfeasible. Its physical meaning is the minimal value of the single well projection onto the whole chemical subspace required for inclusion of the well. Any well with a value larger than this parameter is considered in the further analysis of the well partitioning. The default value is 0.2, which is based on the assumption that a typical maximum spreading of the chemically significant eigenvector is across 5 species.
- **ReductionNumber**: number of best possible reduction schemes to print. Note, however, that only the supposed best reduction scheme is employed in the rate analysis. The default is 5.
- **DefaultReductionScheme**: optional parameter describing a default reduction scheme, which will be enforced. On the same line this keyword is followed by several tokens describing equilibrated groups of isomers. Each token should contain all equilibrated isomers names. If the isomer equilibrates with bimolecular products its name should not be present in any token.
- **LowEigenvalueRateReductionMethod**: refers to the method employed in generating the phenomenological rates for the merged species for the low eigenvalue method only. Possible

values are **diagonalization** or **projection**. The diagonalization method is more accurate but it will not work if the range of chemical eigenvalues is too large. The default value is **projection**.

5.3. Energy Grid Parameters

- **EnergyStepOverTemperature**: ratio of the discretization energy step in the global relaxation matrix to the temperature.
- **EnergyStep[1/cm]**: discretization energy step in the global relaxation matrix. One should specify either this parameter or the preceding one.
- **ExcessEnergyOverTemperature**: Ratio of the highest energy in the global relaxation matrix to the temperature. This energy is counted from the highest barrier in the model.
- **ReferenceEnergy[Unit]**: highest energy in the global relaxation matrix. One should specify either this parameter or the preceding one. **Unit** = 1/cm, kcal/mol or kJ/mol.
- **ModelEnergyLimit[kcal/mol]**: highest energy that will ever be used in the partition function evaluations. Extremely large values will slow the calculation somewhat, while too small a value will lead to errors. Typically a value of 400 kcal/mol is appropriate. This parameter is compulsory.
- **Reactant**: bimolecular species whose ground energy will be used as a reference. If defined, all energies will be shifted so that the ground energy of this species will be zero.

5.4. Cutoff Parameters

- **ChemicalEigenvalueMax**: If < 1 then maximal projection of the eigenvector onto the collisional relaxation subspace. If > 1 then minimal ratio of the lowest collision relaxation to the chemical eigenvalue one. Its value separates chemically significant modes from others. If negative the ratio of successive eigenvalues is explored from top down until until the ratio lies below the threshold.
- **ChemicalEigenvalueMin**: Minimal ratio of the chemical eigenvalue to the lowest collision relaxation one for which the direct diagonalization method will be used. Eigenstates with smaller eigenvalues will be calculated with the low eigenvalue method. The default value is 10^{-7} . This keyword is applicable to the direct diagonalization method only.
- **WellCutoff**: This well truncation parameter defines the maximal ratio of the dissociation limit (for the lowest barrier height relative to the bottom of the well) to the temperature. For each well, all energy states below that limit will be truncated and the corresponding populations will be assumed to be Boltzmann. If it is negative, no user requested cutoff will be applied (there may still be a cutoff caused by the collisional transition kernel consistency problem, see above). By default it is negative.
- **GlobalCutoff[Unit]**: this parameter can be used to remove low-energy wells and barriers for highly exothermic reactions. The energies below the value of this parameter are not included into the master equation. The value of this parameter is assumed to be measured relative to the zero of energy (i.e., the reactants reference energy). This parameter is optional. **Unit** = 1/cm, kcal/mol, or kJ/mol.
- **MicroRateMax[1/sec]**: maximum value of the microscopic isomerization and dissociation rate coefficients. This optional parameter allows for the qualitative examination of effects due to limitations in intramolecular vibrational relaxation rates, for example.
- **TunnelingActionCutoff**: for tunneling action bigger than this parameter the tunneling coefficient is set to 0. The default value is 40.

- **AtomDistanceMin[Unit]**: minimal interatomic distance. This parameter is used for geometry checking. The default value is 1.5. **Unit** = **bohr** or **angstrom**.

5.5. Output Parameters

Optional parameters to specify filenames for various ancillary output.

- **RateOutput**: output file for rate coefficients. If not defined the program will construct the rate output file name from the input file name. This file contains the calculated phenomenological rate coefficients for the full set of temperature and pressures organized in a variety of ways to facilitate perusal and plotting.
- **LogOutput**: file name for log file. If not defined the program will construct the log output file name from the input file name. This file contains a variety of intermediate outputs. These outputs are useful in debugging the input and in exploring the intermediate partition functions, particularly for torsional motions. When errors in the input are encountered the last few lines in this output will provide some indication of where the errors occurred.
- **PEDOutput**: file name for printing various product energy distributions and probabilities. Product steady-state energy distributions for well-to-bimolecular-product processes, for predefined pairs of bimolecular reactants and products in a chemically activated process (see next keyword **PEDSpecies**), and for well escape channels (see **Escape** keyword in **Well** section), will be printed in this file. In addition, hot energy product species probabilities (see **HotEnergies** keyword) can be printed here. If not provided no product energy distributions will be printed.
- **PEDSpecies**: pairs of bimolecular reactants and products for which the product energy distribution at the transition state will be printed. It is followed by several tokens on the same line. Each token represents a pair of reactants and products and should contain their names.
- **HotEnergies[Unit]**: parameter to print the probabilities that the reactive complex in the specific initial well with the specific initial energy will be captured in one of the wells or will dissociate to the different bimolecular products. This parameter requires multiple additional input lines. First, it must be followed by the number of subsequent lines on the same line. Then, each subsequent line has the following format: the name of the initial well is followed by one or more initial energies for which the capture probabilities should be calculated. **Unit** = **1/cm**, **kcal/mol**, or **kJ/mol**
- **MicroRateOutput**: the name of the file to which the microscopic rate coefficients will be printed. If not specified, the microscopic rates will not be printed.
- **MicroEnerMax[kcal/mol]**: maximal energy for microscopic rate output.
- **MicroEnerMin[kcal/mol]**: minimal energy for microscopic rate output.
- **MicroEnerStep[kcal/mol]**: energy step for microscopic rate output.
- **EigenvalueOutput**: eigenvalue output file name. If not defined no eigenvalues will be printed. When specified, this output contains the chemically significant eigenvalues and a limited number of relaxational eigenvalues as specified by **EigenvectorNumber** (cf. description below).
- **EigenvectorOutput**: eigenvector output file name. If not defined no eigenvectors will be printed. When specified, this output contains the chemically significant eigenvectors and a limited number of relaxational eigenvectors as specified by **EigenvectorNumber** (cf. description below).
- **EigenvectorNumber**: the number of relaxational eigenvectors to be printed in addition to the chemical eigenvectors. The default value is 0.

- **TimeEvolution:** parameter to print out the time evolution of an initially thermal distribution of some specified reactant for a given time period. This parameter requires that the following keywords be provided followed by an **End** statement.
 - **Start[s]:** initial time in seconds for output of time evolution.
 - **Finish[s]:** final time in seconds for output of time evolution.
 - **Size:** number of logarithmic time steps in time evolution.
 - **Reactant:** label specifying the species for the initial thermal population.
 - **TimeOutput:** filename for output of time evolution.

6. Model

In **Model** section the following keywords can be used:

- **EnergyRelaxation**: defines default (each well can also have their own separate kernels) collisional energy relaxation kernel for each buffer gas. It should be repeated for as many buffer gas molecules as you have. This keyword is compulsory. However, if any well specific collisional energy relaxation kernels are provided they will override these values. Currently the only possible energy relaxation model is:
 - **Exponential**: assumes a multiple exponential form for the transition probability as a function of energy difference between initial and final energies. Possible parameters of the model are:
 - **Factor[1/cm]**: $\Delta E_{down}^{(0)}$ at standard temperature $T_0 = 300$ K. The factor can be repeated multiple times according to the number of exponentials.
 - **Power**: the power n in the expression $\Delta E_{down} = \Delta E_{down}^{(0)} \times (T/T_0)^n$. The power can be repeated multiple times according to the number of exponentials.
 - **Fraction**: If there is more than one exponential then this keyword should be provided to define the fraction for each exponential. The fractions should add to unity.
 - **ExponentCutoff**: maximum value for the ratio $\Delta E/\Delta E_0$ in the exponential form, where ΔE_0 is the value of ΔE_{down} at the given temperature. If $\Delta E/\Delta E_0$ exceeds this value the transition probability is assumed to be zero. The default value is 10.
- **EnergyRelaxationFlag**: optional energy relaxation kernel modifier. There may be several instances of this parameter. The corresponding values will be logically combined. Possible values are:
 - **up**: predefined (exponential or other) form is assumed for the upward transitions.
 - **density**: a proportionality to the final density of states, $P(E \rightarrow E') \propto \rho(E')$ is added (multiplicatively) to the the presumed transition probability.
 - **notruncation**: no well truncation is performed even when the constant collision frequency condition cannot be satisfied (typically, near the bottom of the well). The collision frequency at the particular energy is adjusted to satisfy the population conservation principle.
- **CollisionFrequency**: collisional frequency model. This keyword is compulsory. It can be repeated for as many buffer gas molecules as you have. Currently the only available collisional frequency model is:
 - **LennardJones**: collisional frequency model based on Lennard-Jones potential. Possible parameters are:
 - **Epsilons[1/cm]**: $\epsilon_{1,2}$ parameters.
 - **Sigmas[angstrom]**: $\sigma_{1,2}$ parameters.
 - **Masses[amu]**: masses of the buffer gas molecule and the complex.
- **BufferFraction**: Set of buffer gas fractions. The number of buffer gas fractions, collision frequency models, and energy relaxation models should be the same.
- **OutputTemperatureStep[K]**: optional output grid step for partition function and thermodynamic data. The default value is 100 K.
- **OutputTemperatureSize**: optional output grid size for partition function and thermodynamic data. The default value is 20.

- **OutputReferenceEnergy[kcal/mol]**: Optional reference energy for partition function. The default is 0.
- **ThermodynamicDataOutput**: optional name of file for outputting thermodynamic data. If not provided the thermodynamic data will not be generated.
- **RelativeTemperatureIncrement**: Relative temperature step size for evaluating derivatives of the partition function.
- **Well**: isomer model. A unique name should follow this keyword on the same line. It is a composite parameter that consists of the following objects:
 - **EnergyRelaxation**: collisional energy relaxation kernel, which is specific for the given isomer. This keyword is optional and has the same meaning as the **EnergyRelaxation** keyword in the **Model** section.
 - **Species**: Density of states model. Possible models are common for wells, barriers, and fragments in bimolecular products. They are described below. This parameter is compulsory.
 - **Escape**: optional pseudo-first-order escape channel for the well. Its possible values are:
 - **Constant**: energy-independent pseudo-first-order escape rate coefficient. It consists of a single parameter:
 - **PseudoFirstOrderRateConstant[1/sec]**: its value is the rate constant value in seconds.
 - **Fit**: energy-dependent pseudo-first-order escape rate coefficient, which will be spline fitted. It consists of a single parameter:
 - **RateDataFile[kcal/mol,1/sec]**: its value is the name of the file with the rate data. The file should have two columns. In the first column are the energies in kcal/mol and in the second column are the corresponding rate coefficients in 1/s. For energies greater than the highest value in the file a constant rate coefficient corresponding to that at the maximal energy will be used. Similarly for energies below the minimal one the rate coefficient corresponding to the minimal energy will be used.
- **Bimolecular**: model for bimolecular products or reactants. A unique name should follow this keyword on the same line. Available keywords are:
 - **Fragment**: models for a bimolecular fragment are described below. There should be exactly two fragment keywords in the bimolecular description. The fragment name should follow this keyword on the same line.
 - **GroundEnergy[Unit]**: total absolute energy for both fragments. Both fragment energies, which are defined inside the corresponding fragment sections, should be set to zero. Depending on whether or not the fragment zero-point energies have been included into the ground energy, one should use **ZeroEnergy** or **ElectronicEnergy** keywords (see below) for the fragment energies. **Unit** = 1/cm, kcal/mol, kJ/mol, or au.
 - **Dummy**: should be used for dummy bimolecular products. This parameter does not have any value associated with it. Of course, if specified this channel cannot be treated as a reactant.
- **Barrier**: transition state model. This keyword should be followed on the same line with a unique name for the barrier and then the names of the two species it connects: either two wells or the well and bimolecular products/reactants. Possible models are described below.

There are several possible models (**RRHO**, **Variational**, **Union**, **Read**, **Atom**) for each of the stable species (well), transition states (barrier), and bimolecular fragments. Detailed descriptions of the keywords for these models are provided below. Each of these models should immediately be followed by one of the keywords (**Geometry[Unit]**, **Stoichiometry**, and **Mass[amu]**). For conciseness, we describe these keywords only for the RRHO model.

6.1. RRHO

RRHO: this is the most common model both for a stable species and for a transition state. It is probably better labeled as extended rigid-rotor-harmonic-oscillator model. Available keywords are:

- **Geometry[Unit]**: provides the cartesian coordinates (**Unit** = **angstrom** or **au**) and atom name of all constituent atoms. The center of mass will be shifted to the origin of the reference frame. This keyword, if present, should go first, immediately after the **RRHO** header line. The number of atoms should follow this keyword on the same line. Atoms are defined one per line. No comments are allowed within the atom definition. Possible atom definition formats are
 - Atom name, isotope number, and three Cartesian coordinates.
 - Atom name and three Cartesian coordinates. The most abundant isotope number is used.
- **Mass[amu]**: This keyword provides an alternative means for entering the species mass in cases where the geometry is not provided (e.g., **RotD**, **Read**, or **Atom**).
- **Stoichiometry**: provides the stoichiometric coefficients in the form “C_xH_yO_z...” where x, y, z, etc., are numbers. This keyword also provides an alternative means for entering the mass in cases where the geometry is not provided.
- **Core**: represents the external rotation degrees of freedom and those degrees of freedom that cannot be separated from them. This keyword should appear once and only once. The following cores are available:
 - **RigidRotor**: available keywords are:
 - **RotationalConstants[Unit]**: provides an alternative way to specify the rotational constants. If the geometry is specified then this is unnecessary. The rotational constants should follow this keyword on the same line. The number of rotational constants will be interpreted to imply a particular rotational dimensionality. One rotational constant would imply a linear complex. Two rotational constants also imply a linear complex and should be the same. Three rotational constants imply a non-linear complex. **Unit** = **1/cm** or **GHz**.
 - **SymmetryFactor**: The effective symmetry number σ_{eff} for external rotation and enantiomers. I.e., $\sigma_{\text{eff}} = \sigma_{\text{rot}} / m$, where σ_{rot} is the symmetry number for external rotation and m is the number of enantiomers. The default is 1.
 - **MultiRotor**: represents several internal rotations (coupled with overall rotations) and, optionally, some harmonic vibrational modes whose frequencies depend on torsion angles. The fully coupled internal and external rotations are typically treated semiclassically. Full quantum treatments of both sets of modes, or of just the internal rotations, are also possible. The vibrational modes are treated adiabatically. The following keywords are available:

- **InternalRotation**: defines internal rotation. This keyword can be repeated as many times as required. At least one internal rotation definition should be present. There are two groups of keywords for this composite parameter. In each group parameters can go in any order but they should stay together as a group. The available keywords in the first group, which should go first, are:
 - ◆ **Group**: indices of the atoms in the moving group. They should follow this keyword on the same line. The index of the atom that belongs to the rotation axis should not be included. This parameter is compulsory.
 - ◆ **Axis**: two atomic indices describing the rotation axis. They should follow this keyword on the same line. This parameter is compulsory.
 - ◆ **Symmetry**: internal rotation symmetry number. The default is 1.
 Available keywords in the second group of keywords are:
 - ◆ **MassExpansionSize**: number of mass expansion Fourier harmonics. It should be positive and odd. This keyword is compulsory.
 - ◆ **PotentialExpansionSize**: number of potential expansion Fourier harmonics. It should be positive, odd, and not exceed the number of potential samplings in the potential energy surface file plus one. If it is not defined the corresponding sampling dimension from the potential energy surface file will be used.
 - ◆ **GridSize**: the grid size for the statistical weight calculation. This keyword is compulsory.
 - ◆ **HamiltonSizeMin** and **HamiltonSizeMax**: window for quantum phase space dimension. If provided they should be positive and odd. The code tries to figure out the optimal dimension itself. These parameters provide lower and upper bounds for it. If not defined no restrictions will be used.
- **PotentialEnergySurface[Unit]**: its value is the name of the file that defines the (multidimensional) potential energy surface and (optionally) variable vibrational frequencies. The structure of the file is as follows. The first line defines potential sampling dimensions for all internal rotations in the same order as they appear in **MultiRotor** section. The second line provides the indices of the vibrational frequencies to be used (in the order they appear on a sampling line). The third line is a comment line. Subsequent lines represent individual sampling points. The number of these lines should correspond to the number of sampling configurations. For each line sampling indices go first followed by the potential energy value and optionally by the set of vibrational frequencies. Sampling configurations should belong to an equidistant mesh. No points are repeated. The angle range for a given internal rotation is from 0 to $360/\text{Symmetry}$. This keyword is compulsory. **Unit** = 1/cm or kcal/mol or kJ/mol.
- **SymmetryFactor**: the effective symmetry factor (σ_{eff} , see above) for the coupled internal and external rotation system, excluding that part which has already been included in the internal rotation definitions. The default is 1.
- **QuantumLevelEnergyMax[Unit]**: defines the maximal energy up to which the quantum energy levels will be calculated. It is counted from the multi-rotor potential energy minimum. If it is negative, which is the default, no quantum levels will be calculated. **Unit** = 1/cm or kcal/mol or kJ/mol.

- **WithoutExternalRotation**: this parameter assumes no value. If it is provided, external rotation will not be included in the density/number of states and/or weight calculation.
- **InterpolationEnergyMax[Unit]**: maximal energy up to which the density/number of states will be actually calculated. Above it a simple power extrapolation will be used. It is counted from the ground energy. This parameter is required for wells and barriers. It is not used for bimolecular fragments. **Unit** = **1/cm** or **kcal/mol** or **kJ/mol**.
- **InterpolationEnergyStep[1/cm]**: the grid step for energy and rounding error for potential energy and vibration frequencies. The default value is 1 cm^{-1} .
- **ExtrapolationStep**: logarithmic backwards energy step for use in estimating the power exponent for the power extrapolation of the density or number of states at the maximal energy. Its default value is 0.1.
- **FullQuantumTreatment**: this parameter assumes no value. If provided the quantum levels will be calculated for all relevant vibrational population configurations.
- **AngularMomentumMax**: this keyword allows one to calculate the quantum rotational energy levels for the coupled external and internal rotations up to a maximal value of the total angular momentum. The default is 0.
- **PotentialPruningTolerance**: this parameter allows one to remove harmonics with small coefficients from the potential and/or vibrational frequencies (pruning). If it is positive, the smallest terms whose relative cumulative contribution to the potential/vibrational frequencies does not exceed the value of this parameter are removed from the potential/vibrational frequencies Fourier expansion. The default is negative.
- **MassPruningTolerance**: the control for pruning internal mobility matrix and external rotation factor fourier expansions (see the description for the previous keyword). The default is negative.
- **Rotd**: reads number of states for the transitional modes from a specified file. This number of states is typically obtained from variable reaction coordinate flux (VaReCoF) evaluations. Available keywords are:
 - **File**: its value is the name of the file containing the transitional mode number of states. This keyword is compulsory.
 - **SymmetryFactor**: the effective symmetry factor (σ_{eff} , see above) for the transitional modes. The default value is 1.
- **PhaseSpaceTheory**: provides phase space theory estimate for the number of states. Available keywords are:
 - **FragmentGeometry[Unit]**: there should be exactly two of these unless two subsequent keywords (**FragmentMasses** and **RotationalConstants**) are present. The format is the same as in **Geometry** subsection of **RRHO**. **Unit** = **angstrom** or **au**.
 - **FragmentMasses[amu]**: alternative way to provide fragments masses. The masses should follow the keyword on the same line.
 - **RotationalConstants[1/cm]**: alternative way to provide the rotational constants for the fragments. The rotational constants should follow the keyword on the

same line. The number of rotational constants should correlate with the cumulative rotational dimensionality of the fragments.

- **SymmetryFactor**: the effective symmetry factor (σ_{eff} , see above) for the transitional modes. The default value is 1.
- **PotentialPrefactor[au]**: The prefactor, C_n , in the power law expansion of the potential energy as a function of distance, $V = -C_n/R^n$. This value must be provided in au and is for R in bohr. This parameter is compulsory.
- **PotentialPowerExponent**: The distance power exponent, n, in the potential energy expression. This parameter is compulsory.
- **Rotor**: uncoupled one-dimensional motion. This keyword is optional. Possible values are:

➤ **Free**: one-dimensional free rotor model. There are two groups of keywords. The keywords in the same group can go in any order but they should go together. The first group is common for all possible types of rotors:

- **Geometry[Unit]**: optional. It is needed for the cases when a common geometry is not available, for example, phase space theory with separate internal rotational treatments for one or both of the fragments. The format is the same as in **Geometry** subsection of **RRHO**. **Unit** = **angstrom** or **au**.
- **HamiltonSizeMin** and **HamiltonSizeMax**: window for quantum phase space dimension. The code figures out the dimension itself. These parameters provide lower and upper bounds for it. Their default values are 99 and 999, respectively. These parameters and subsequent ones are actually not used in the free rotor model. They are important though for other types of rotors.
- **LevelNumberMin**: minimal allowed number of quantum energy levels. Its default value is 10.
- **GridSize**: discretization size for the statistical weight calculation. Its default value is 1000.
- **ThermalPowerMax**: maximal exponent power in the Boltzmann factor for the statistical weight calculation. Its default value is 10.

The keywords in the second group are also common to the hindered rotor model. They have the same meaning as the ones in the **InternalRotation** subsection of **MultiRotor** section:

- **Group**: atomic indices in the moving group. They should follow this keyword on the same line. The index of the atom that belongs to the rotation axis should not be included into the group. This parameter is compulsory.
- **Axis**: two atomic indices that define the axis of rotation. They should follow this keyword on the same line. This parameter is compulsory.
- **Symmetry**: The symmetry number for the given internal rotation. The default value is 1.

➤ **Hindered**: hindered rotor model. It has the same keywords as the free rotor model and the following additional keywords, which should follow the free rotor model keywords:

- **Potential[Unit]**: The potential for the internal rotational motion is assumed to be sampled equidistantly. No points are repeated. The angle range is $360/\text{Symmetry}$. The number of sampling points follows the keyword on the same line. Potential

values start on the next line. Either this keyword or the next one should be present. **Unit** = kcal/mol, 1/cm, or kJ/mol.

- **FourierExpansion[Unit]**: This keyword provides an alternative procedure for describing the internal rotational potential. The number of Fourier harmonics in the input follows the keyword on the same line. Harmonics are defined one per line in the following format: harmonic index, then harmonic amplitude (coefficient in front of sin or cos term). Harmonic indices are defined as follows: constant term has index zero, first sin – 1, first cos – 2, second sin – 3, second cos – 4, etc,

$$V(x)=V_0 + V_1*\sin(s*x) + V_2*\cos(s*x) + V_3*\sin(2*s*x) + V_4*\cos(2*s*x) + \dots$$

One can put any number of harmonics in the input in any order. For example, a potential $V(x)=1+100*\cos(x)+10*\sin(3*x)$ can be described with three lines:

```
0 1
2 100
5 10
```

Unit = 1/cm, kcal/mol, or kJ/mol.

- **Umbrella**: calculates quantum levels of the out-of-plane mode in the arbitrary well-like potential. It shares the first group of keywords with the free rotor model and has the following additional keywords, which should follow the free rotor model keywords:
 - **Group**: atomic indices of the moving group. They should follow this keyword on the same line. This parameter is compulsory.
 - **Plane**: The umbrella plane is specified in terms of three atomic indices. The indices should follow this keyword on the same line. Either this keyword or the **Direction** keyword should be present.
 - **ReferenceAtom**: atom to which moving atoms are coupled.
 - **Direction**: provides an alternative way to define the umbrella plane in terms of the normal to it. The Cartesian cosines should follow this keyword on the same line.
 - **Potential[Unit]**: the number of potential sampling points follows this keyword on the same line. Individual samplings follow, one per line with the format: coordinate value, then potential value. If a **ReferenceAtom** is defined, the coordinate in the coordinate variation of the potential definition is assumed to be in degrees. Otherwise, the coordinates are assumed to be in angstroms.
 - This parameter is compulsory. **Unit** =1/cm, kcal/mol, or kJ/mol.
- **Tunneling**: provides a one-dimensional tunneling correction to the number of states. Valid only for barriers. This keyword should appear only once (i.e., it should not be repeated in a variational calculation) and is optional. Possible values are:
 - **Harmonic**: parabolic barrier model. Available keywords are:
 - **CutoffEnergy[kcal/mol]**: provides the energy window for the convolution of the number of states with the tunneling density. This parameter is compulsory for a harmonic barrier and optional for Eckart and quartic barriers (see below). It should be positive. **Unit** = 1/cm, kcal/mol, or kJ/mol.
 - **StatisticalWeightTolerance**: the ratio of the energy discretization step to the temperature in the statistical weight calculation. The default value is 10^{-2} .

- **ImaginaryFrequency[1/cm]**: this parameter is compulsory and should be positive.
- **Eckart**: Eckart model for tunneling factor. It uses the same keywords as the parabolic barrier model, which should go first, and the additional keyword:
 - **WellDepth[Unit]**: its value should be positive and greater than the cutoff energy. This keyword should appear exactly twice – once for the depth of the well relative to the barrier on each side of the barrier. **Unit = 1/cm, kcal/mol, or kJ/mol.**
- **Quartic**: model for tunneling through the quartic potential barrier. It uses the same keywords as the parabolic barrier model, which should go first, and the following additional keywords:
 - **WellDepth[Unit]**: should appear either once or twice. If it appears only once a cubic potential is assumed. **Unit = 1/cm, kcal/mol, or kJ/mol.**
 - **CoordinateTolerance**: tolerance for the potential minimum search. The default value is 10^{-10} , which is fairly sound.
 - **CoordinateDiscretizationStep**: action integration grid step. The default value is 10^{-3} .
 - **ActionInterpolationSize**: The default value is 50.
- **ElectronicEnergy[Unit]**: electronic energy; **Unit = 1/cm, kcal/mol, kJ/mol, eV, or au.** Either this keyword or the **ZeroEnergy** keyword (see below) should be present.
- **ZeroEnergy[Unit]**: electronic energy corrected with vibrational zero-point energy; **Unit = 1/cm, kcal/mol, kJ/mol, eV, or au.**
- **Frequencies[1/cm]**: describes harmonic oscillator frequencies. The number of frequencies should follow this keyword on the same line. The frequencies values should start on the next line. This keyword is optional.
- **InfraredIntensities[km/mol]**: adds radiative transitions to the energy relaxation model. The infrared intensities, if provided, should correlate with the harmonic oscillator frequencies. The structure of the input is the same as the one for harmonic frequencies. This keyword is optional.
- **ElectronicLevels[Unit]**: number of electronic levels follows this keyword on the same line. Electronic energies are presumed separable from the rovibrational energies. The energy levels are defined in terms of one level per line. The format is: energy level relative to the ground level followed by the electronic degeneracy number. This keyword is optional. **Unit = 1/cm, kcal/mol, kJ/mol, eV, or au.**
- **InterpolationEnergyMax[kcal/mol]**: maximum energy relative to the ground energy for which the density or the number of states will be actually calculated. This parameter is optional. If not provided, the global model energy limit will be used to figure out its value.
- **InterpolationEnergyStep[1/cm]**: the energy discretization step and vibrational frequencies rounding error. The default value is 1 cm^{-1} .
- **ExtrapolationStep**: Value of the logarithmic step back in energy used to estimate the exponent power in the power extrapolation expression for the density or number of states for energies above the maximal interpolation energy. The default value is 0.1.

6.2. Variational

Variational: represents a variational approach to the evaluation of the transition state number of states. It is valid only for barriers. Available keywords are:

- **RRHO:** extended RRHO model. The format is the same as that of the standalone **RRHO** section. It is repeated as many times as needed. No tunneling should be included inside of each such section. Instead that subsection should be provided as a separate model outside the RRHO model.
- **OuterRRHO:** extended RRHO model for the outer part of the transition state in the two-transition-states model. No tunneling is allowed in this part of the transition state. This parameter is optional.
- **2TSMETHOD:** the method to calculate the effective number of states, N_{eff} , for the two-transition-states model. Possible values are **statistical** and **dynamical**. For the **statistical** method N_{eff} is evaluated as $1/N_{\text{eff}} = 1/N_1 + 1/N_2$, where N_1 and N_2 are the two transition state number of states. For the **dynamical** method N_{eff} is evaluated as the minimum of N_1 and N_2 . The default is **statistical**.
- **Tunneling:** tunneling model for the tight part of the transition state. Possible values are the same as for the **Tunneling** subsection of the standalone **RRHO** section. This parameter is optional and should appear only once.
- **InterpolationEnergyMax[kcal/mol]:** the maximal energy, counted from the ground energy, at which the number of states will be calculated. If it is not provided, the global model energy limit will be used to determine its value.
- **InterpolationEnergyStep[1/cm]:** the discretization energy step used in the number of states calculation. Its default value is 1 cm^{-1} .
- **ExtrapolationStep:** The value of the logarithmic step back in energy used to estimate the effective power exponent in the simple number of states extrapolation as a power function of energy. Its default value is 0.1.

6.3. Union

- **Union**: sum of the density or number of states of the constituent species, which are read from the input in the same format as described above and ended by **End** keyword.

6.4. Read

- **Read**: represents species whose density/number of states are read from an input file. Available keywords are:
 - **File**: its value is the name of the file from which the density or the number of states is read.

6.5. Atom

- **Atom**: represents an atomic fragment. Valid only as part of bimolecular products/reactants. Available keywords are:
 - **Mass[amu]**: atomic mass. Either this keyword or the next one should be present.
 - **Name**: alternative way to specify the atom mass. Possible formats are:
 - Atom name. (Assumes most abundant isotope.)
 - Atom name and isotope number.
 - **ElectronicLevels[Unit]**: the format is the same as in **ElectronicLevels** subsection of **RRHO** section. This keyword is optional. **Unit** = 1/cm, kcal/mol, kJ/mol, eV, or au.

References

¹ **From the Time-Dependent, Multiple-Well Master Equation to Phenomenological Rate Coefficients**, Stephen J. Klippenstein and James A. Miller, *J. Phys. Chem. A*, **106**, 9267-9277 (2002).

² **Master Equation Methods in Gas Phase Chemical Kinetics**, James A. Miller and Stephen J. Klippenstein, *J. Phys. Chem. A*, **110**, 10528-10544 (2006).

³ **Reformulation and Solution of the Master Equation for Multiple-Well Chemical Reactions**, Yuri Georgievskii, James A. Miller, Michael P. Burke, and Stephen J. Klippenstein, *J. Phys. Chem. A*, **117**, 12146-12154 (2013).