MSTor 2023: A program for calculating partition functions, free energies, enthalpies, entropies, and heat capacities of complex molecules including torsional anharmonicity

MANUAL

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ABSTRACT. *MSTor* is a computer program for calculating gas-phase molecular partition functions and thermodynamic functions (standard state energy, enthalpy, entropy, free energy, and heat capacity at constant pressure) as functions of temperature by the multi-structural approximation with torsional anharmonicity (MS-T). The MS-T method is especially designed for the convenient treatment of molecules with many conformational structures generated by internal rotations (torsions). The default method in *MSTor* is the multi-structural approximation with torsional anharmonicity, a coupled torsional potential, and delocalized torsions, abbreviated as MS-T(CD), but the program also supports the older MS-T(U) and MS-T(C) methods, the multi-structural local harmonic (MS-LH) approximation, and the multi-structural local quasiharmonic (MS-LQ) approximation. The MS-T methods account for the coupling of torsions to one another and to overall rotation and, to some extent, the coupling between torsions and

other vibrational modes. By combining a redundant-internal-coordinate auto-generation procedure with torsional projection techniques, *MSTor* automates the identification of torsional vibrations and their separation from the other vibrational modes; this reduces the needed user input.

MSTor includes eight utility codes that can be used as stand-alone programs. One utility program calculates reduced moments of inertia by the method of Kilpatrick and Pitzer, one generates conformational structures, the third and fourth calculate volumes of torsional subdomains defined by Voronoi tessellation either analytically or by Monte Carlo sampling, the fifth and the sixth generates template input files, and the seventh calculates one-dimensional torsional partition functions using the torsional eigenvalue summation method. The final utility code is for computing dual level MS-T partition functions.

Table of contents

1. Introduction

The *MSTor* program is a computer program for calculating partition functions and thermodynamic functions of molecules by the multi-structural approximation with torsional anharmonicity (MS-T). It is especially designed for the convenient treatment of molecules with many conformational structures generated by internal rotations (torsions). There are three main variants of the algorithm:

- MS-T(U) method, which is an "uncoupled" approximation with respect to potential coupling between the torsional degrees of freedom.
- MS-T(C) method, which is a "coupled" approximation in that it includes an approximate treatment of the potential coupling between torsions.
- MS-T(CD) method using redundant internal coordinates for torsional identification

MS -T(U) came first, and it was originally called MS-AS and then called MS-T; now we use MS-T without the parenthetical addition to refer to any of the three methods when it is not necessary to distinguish between them.

MS-T(U) is now recommended only for legacy purposes since MS-T(C) is a more complete theory with essentially identical input and essentially the same computational cost.

The MS-T methods are designed to yield the harmonic-oscillator (HO) results in the low-temperature limit (the U scheme exactly reproduces this limit, whereas the C scheme retains a residual correction to the HO limit, which may be regarded as an approximate anharmonicity correction) and to yield free-rotor results for torsions in the high-temperature limit. All three methods approximately account for kinetic coupling between the torsions, for the coupling between the torsions and the remaining vibrational modes, and for coupling of the vibrations to overall rotation. The MS-T(U) method includes kinetic and potential energy coupling at low T and kinetic energy coupling at high temperatures, where the torsional potential eventually becomes negligible. However, aside from a sum over structures and the switch between harmonic coupling and locally uncoupled torsions, the MS-T(U) method does not include potential energy coupling of the torsions in the intermediate-temperature regime (it only considers the potentials along separable internal coordinates and separable normal-mode coordinates). The MS-T(C) method is an improved formulation that uses a coupled potential not only for normal-mode frequencies but also for an implicit estimation of the effective torsional barriers that are key elements of the computation at intermediate temperatures. Therefore, the uncoupled internal-coordinate approximation used in the MS-T(U) method is eliminated in the formulation of MS-T(C).

The MS-T method does not require assigning torsions to specific normal modes. Therefore, the *MSTor* program can handle cases in which the system has significant coupling between torsions or between torsions and other modes, even at the normal-mode level. The nonredundant-internal-coordinate representation plays an important role in the MS-T methods because internal coordinates are used to separate the torsional modes from the overall vibrational Hessian. However, the use of nonredundant internal coordinates requires each torsion to be described by a single dihedral angle, and for this reason, the construction of a useful

nonredundant representation is often a trial-and-error process. One drawback of using nonredundant internal coordinates to project coupled torsions is that the choice of a proper set of nonredundant coordinates is often not obvious and is difficult to automate for general cases.

The MS-T(CD) method provides a way to identify torsions in normal-mode vibrations automatically and accurately, as well as to simplify the required input for MS-T calculations. It uses the delocalized internal coordinates of Baker et al. to separate torsions from other vibrations by projection in redundant internal coordinates and does not involve any iterative calculations. Furthermore, the method is made conformer-independent by starting from a set of highly redundant internal coordinates, and it does not include any assumptions about the natures of the modes except for the user identification of the single bonds whose internal rotations are considered. The new strategy of MS-T(CD) circumvents the need in the original MS-T methods for the user to define nonredundant internal coordinates, and it can straightforwardly separate any number of coupled torsions from the primitive Hessian. The MS-T(CD) method is the default in this version of *MSTor.*

The *MSTor* package includes utilities that can help the user to generate the input files for the code or to generate comparison results. These utilities are explained in more detail in section 7. Most of the utilities are designed for working with output files and *fchk* files produced by the *Gaussian* electronic structure package. The utility codes that read from their corresponding input files (including *mcvorm.exe*, *vorm.exe*, *tes.exe*, *kpmoments.exe* and *symmetry.exe*) do not require any explicit operations on *Gaussian* files (although the automatic generation of the input files for *mcvorm.exe* and *vorm.exe* do require such operations).

2. Licensing

MSTor 2023 is licensed under the Apache License, Version 2.0.

The manual of *MSTor 2023* is licensed under CC-BY-4.0.

Publications of results obtained with the *MSTor 2023* software should cite the program and/or the article describing the program (see section 3 of this manual).

No guarantee is made that this software is bug-free or suitable for specific applications, and no liability is accepted for any limitations in the mathematical methods and algorithms used within. No consulting or maintenance services are guaranteed or implied.

The use of the *MSTor 2023* implies acceptance of the terms of the licenses.

3. Citations for the MS-T methods and the *MSTor* program

MS-T(U) method (based on an uncoupled torsional potential)

1. "Practical Methods for Including Torsional Anharmonicity in Thermochemical Calculations on Complex Molecules: The Internal-Coordinate Multi-Structural Approximation," J. Zheng, T. Yu, E. Papajak, I, M. Alecu, S. L. Mielke, and D. G. Truhlar, Physical Chemistry Chemical Physics **13**, 10885–10907 (2011). doi.org/10.1039/C0CP02644A

MS-T(C) method (based on a coupled torsional potential)

2. "Quantum Thermochemistry: Multi-Structural Method with Torsional Anharmonicity Based on a Coupled Torsional Potential," J. Zheng and D. G. Truhlar, Journal of Chemical Theory and Computation **9**, 1356-1367 (2013). doi.org/10.1021/ct3010722

Dual level MS-T method (which works for both coupled and uncoupled methods)

3. "Dual-Level Method for Estimating Multi-Structural Partition Functions with Torsional Anharmonicity" J. L. Bao, L. Xing, D. G. Truhlar, Journal of Chemical Theory and Computation. **13**, 2511-2522 (2017). doi.org/10.1021/acs.jctc.7b00232

MS-T(CD) method using redundant internal coordinates for torsional identification

4. "Identification of Torsional Modes in Complex Molecules Using Redundant Internal Coordinates: The Multistructural Method with Torsional Anharmonicity with a Coupled Torsional Potential and Delocalized Torsions," W. Chen, P. Zhang, D. G. Truhlar, J. Zheng and X. Xu, Journal of Chemical Theory and Computation **18**, 7671–7682 (2022). doi.org/10.1021/acs.jctc.2c00952

Note: one may also use redundant internal coordinates for torsional identification in conjunction with the uncoupled method: MS-T(U) or the dual level MS-T method.

MSTor program – original version, versions 2013 and 2017-B, and current version

5. J. Zheng, S. L. Mielke, K. L. Clarkson, and D. G. Truhlar, *MSTor* computer program, original version, University of Minnesota, Minneapolis, 2012.

Available from CPC Program Library in Mendeley Data

at: doi.org/10.17632/vbd4k8p3hs.1

or at: data.mendeley.com/datasets/vbd4k8p3hs

6. J. Zheng, S. L. Mielke, K. L. Clarkson, R. Meana-Pañeda, and D. G. Truhlar, *MSTor* computer program, version 2013, University of Minnesota, Minneapolis, 2013. Available from CPC Program Library in Mendeley Data
at: doi.org/10.17632/4xn7xw3pvz
or at: data.mendeley.com/datasets/4xn7xw3pvz

7. J. Zheng, S. L. Mielke, J. L. Bao, R. Meana-Pañeda, K. L. Clarkson and D. G. Truhlar, *MSTor* computer program, version 2017-B, University of Minnesota, Minneapolis, MN, 2017.

8. J. Zheng, W. Chen, S. L. Mielke, J. L. Bao, K. L. Clarkson, R. Meana-Pañeda, X. Xu, and D. G. Truhlar, *MSTor 2023*, Tsinghua University, Beijing and University of Minnesota, Minneapolis, 2023. To be available from CPC Program Library in Mendeley Data.

Articles about the *MSTor* program – original and new version announcements

9. "*MSTor*: A program for calculating partition functions, free energies, enthalpies, entropies, and heat capacities of complex molecules including torsional anharmonicity," J. Zheng, S. L. Mielke, K. L. Clarkson, and D. G. Truhlar, Computer Physics Communications **183**, 1803-1812 (2012). doi.org/10.1016/j.cpc.2012.03.007

10. "*MSTor* version 2013: A new version of the computer code for the multistructural torsional anharmonicity with a coupled torsional potential", J. Zheng, R. Meana-Pañeda, and D. G. Truhlar, Computer Physics Communications **184**, 2032-2033 (2013). doi.org/10.1016/j.cpc.2013.03.011

11. "*MSTor 2023*: A new version of the computer code for multi-structural torsional anharmonicity, now with automatic torsional identification using redundant internal coordinates," W. Chen, J. Zheng, D. G. Truhlar, and X. Xu, Computer Physics Communications, in preparation.

3. 1. Reference for incorporated code

1. The code for evaluating of the point group of symmetry of a structure is from Serguei Patchkovskii (http://www.cobalt.chem.ucalgary.ca/ps/symmetry) and is redistributed under GNU general public license in the *MSTor* package.

4. Distribution and installation

4. 1. Distribution

The distributed *MSTor* package, *mstor_2023.tar.xz*, contains the following directories and files:

exe: This is an empty directory in the distribution. After successful installation, this directory should contain eleven executable files as described in section 4.C.

doc: This directory contains the manual of the *MSTor* program.

hull: This has a subdirectory *src/* that contains the source code of the *hull* program.

install.pl: This is a Perl script that can be used for installation of the *MSTor* program.

src: This directory contains source code for the main program *mstor.exe*

symmetry: This has a subdirectory *src/* that contains the source code of the *symmetry* program.

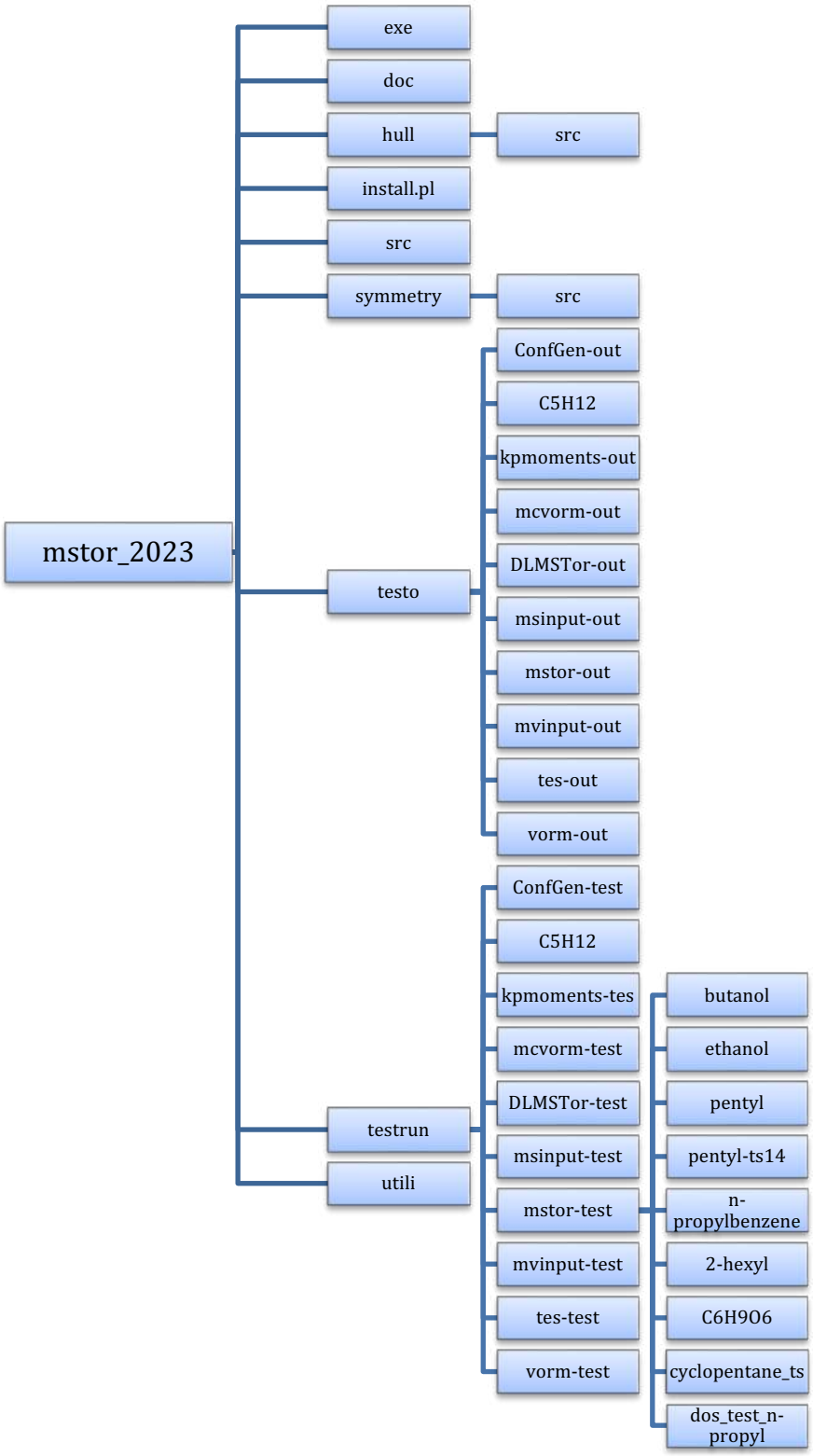
testo: This directory contains ten subdirectories: *C5H12*, *ConfGen-out*, *DLMSTor-out*, *kpmoments-out*, *mcvorm-out*, *msinput-out*, *mvinput-out*, *mstor-out*, *tes-out*, and *vorm-out*. The ten subdirectories contain output files of test runs for the *mstor.exe* program and the eight utility programs.

testrun: This directory contains ten subdirectories: *C5H12*, *ConfGen-test*, *DLMSTor-test, kpmoments-test*, *mcvorm-test*, *msinput-test, mvinput-test*, *mstor-test*, *tes-test*, and *vorm-test.* The ten subdirectories contain input files of test runs for the *mstor.exe* program and the eight utility programs.

The *mstor-test* subdirectory has nine subsubdirectories: *butanol*, *ethanol*, *pentyl*, *pentyl-ts14*, *n-propylbenzene*, *2-hexyl*, *C6H9O6*, *cyclopentane_ts*, *dos_test_n-propyl*. These contain test files for various molecules, including two saddle point tests.

utili: This directory contains the source code of the eight utility programs.

The directory structure is shown on the following page.


mstor_2023
exe
doc
hull
src
install.pl
src
symmetry
src
testo
ConfGen-out
C5H12
kpmoments-out
mcvorm-out
DLMSTor-out
msinput-out
mstor-out
mvinput-out
tes-out
vorm-out
testrun
ConfGen-test
C5H12
kpmoments-tes
mcvorm-test
DLMSTor-test
msinput-test
mstor-test
mvinput-test
tes-test
vorm-test
utili
butanol
ethanol
pentyl
pentyl-ts14
n-propylbenzene
2-hexyl
C6H9O6
cyclopentane_ts
dos_test_n-propyl

4. 2. Installation

The installation procedure consists of the following steps:

1) Copy the *mstor_2023.tar.xz* package to your home directory and then unzip and untar the package.

```
tar -xvJf mstor_2023.tar.xz <Return>
```

2) Go to the *mstor_2023/* directory and run the installation script

```
./install.pl <Return>
```

The *install.pl* script will search for available Fortran and C compilers and compile the *MSTor* code in the *mstor_2023/*src/ directory. It will also compile the *hull* code in the *mstor_2023/hull/* directory, and it will compile all utility codes in the *mstor_2023/utili/* directory.

3) If the install script runs successfully, the *mstor_2023/exe/* directory will contain eleven executables: *ConfGen.exe, kpmoments.exe*, *mcvorm.exe*, *mstor.exe*, *hull.exe*, *msinput.exe*, *mvinput.exe*, *symmetry.exe*, *tes.exe*, *vorm.exe*, and *DLMSTor.exe*.

4) To invoke these executables directly on the command line, please set environmental variables for *MSTor 2023* by adding the *mstor_2023/exe/* directory to your Linux/Unix PATH variable as follows:

```
echo "# Environment variable for MSTor_2023 ">>  ~/.bashrc
echo 'export PATH=$PATH:[your installation path]/mstor_2023/exe/' >>  ~/.bashrc
source ~/.bashrc
```

4. 3. Description of Executables

Executable	Description	Usage
mstor.exe	Main executable for calculating the MS-T partition function, the MS-LH partition function, and thermodynamic functions	*mstor.exe < mstor.inp > mstor.out*
vorm.exe	Utility code to calculate local periodicities (*M* values) using Voronoi tessellation by calling *hull.exe*	*vorm.exe < mvorm.inp > mvorm.out*
mcvorm.exe	Utility code to calculate local periodicities (*M* values) using the Monte Carlo method	*mcvorm.exe < mvorm.inp > mvorm.out*
msinput.exe	Utility code to generate a template input file for *mstor.exe.* If the *mvorm.out* file exists, the code also reads the local	*msinput.exe < all.fchk*

	periodicities from the *mvorm.out* file.	
mvinput.exe	Utility code to generate a template input file for *vorm.exe* and/or *mcvorm.exe*, and to pick out distinguishable structures (exclude mirror images)	*./mvinput.exe*
hull.exe	Computes the convex hull of a point set in general dimension. It is used by *vorm.exe* to calculate each Voronoi cell volume	see http://www.netlib.org/voronoi/hull.html for more details about using this as a standalone program.
symmetry.exe	Determines the symmetry point group of the molecular structure.	see http://www.cobalt.chem.ucalgary.ca/ps/symmetry for more details, and to use it as a standalone program.
ConfGen.exe	Utility code to generate a set of conformational structures by rotating user specified bonds in an input structure	*ConfGen.exe* < input
kpmoments.exe	Utility code to compute reduced moments of inertia by the method of Kilpatrick and Pitzer	*kpmoments.exe* < *input* > *output*
tes.exe	Utility code to calculate 1-D torsional partition functions using the torsional eigenvalue summation method	*tes.exe* < *input* > *output*
DLMSTor.exe	Utility code to create input *mstor.inp* for dual level MS-T calculations.	*./DLMSTor.exe*

5. Theoretical background

The total partition function is calculated here by

$$Q_{\text{total}} = Q_{\text{trans}} Q_{\text{elec}} Q_{\text{con-rovib}} \tag{1}$$

where Q_{trans} is the translational partition function, Q_{elec} is the electronic partition function, and $Q_{\text{con-rovib}}$ is the conformational–rovibrational partition function. Equation (1) assumes that the translational partition function and electronic degrees of freedom are separable from the other degrees of freedom. In all equations, the zero of energy for conformational–rovibrational partition functions is at the local minimum of the potential energy function, not at the lowest-energy vibrational state. Notice that this differs from the usual textbook convention (see section 5.9). We also place the zero of energy at the minimum of the potential energy function for thermodynamic quantities with units of energy.

The thermodynamic functions for the Gibbs free energy (G°), thermodynamic energy (E°), enthalpy (H°), and entropy (S°) are calculated analytically as

$$G^\circ = -\ln(Q)/\beta + k_B T \tag{2}$$

$$E^\circ = -\frac{\partial \ln(Q)}{\partial \beta} \tag{3}$$

$$H^\circ = E^\circ + P^\circ V \tag{4}$$

$$S^\circ = k_B \ln Q - \frac{1}{T}\left(\frac{\partial \ln Q}{\partial \beta}\right) \tag{5}$$

where $\beta = 1/k_B T$, k_B is the Boltzmann's constant, T is temperature, P is pressure, and V is volume. The degree symbol ($^\circ$) denotes standard state. The default for the standard state pressure is 1 bar, which equals 100 kPa or 0.987 atm.

Heat capacity at constant pressure (C_p°) is calculated using a four-point central finite differences formula

$$C_p^\circ(T) = \frac{H^\circ(T-2\delta T) - 8H^\circ(T-\delta T) + 8H^\circ(T+\delta T) - H^\circ(T+2\delta T)}{12\delta T} \tag{6}$$

where δT is a step size for temperature.

5. 1. Notation for the MS methods

The program calculates two MS approximations: MS-T (multistructural method for torsional anharmonicity) and MS-LH (multistructural local harmonic approximation). These methods were denoted in the original publication by other names as indicated in the chart below. The new names are recommended for future usage.

New name	Original or other name		
MS-T	MS-AS[a]	MS-AS-T[b]	
MS-LH	MS-HO[a]	MS-AS-HO[b]	MS-LQ[c]

[a] J. Zheng, T. Yu, E. Papajak, I. M. Alecu, S. L. Mielke, D. G. Truhlar, Phys. Chem. Chem. Phys. 13 (2011), 10885.

[b] T. Yu, J. Zheng, D. G. Truhlar, Chem. Sci. 2 (2011), 2199.

[c] When one uses scaled frequencies[1] in the MS-LH method, it is actually locally quasiharmonic (LQ or QH) because the scaling accounts not only for systematic errors in the electronic structure method but also for anharmonicity of the high-frequency modes. In such a case the method may still be called MS-LH, because the formulas are still based on the harmonic oscillator, or it may be called MS-LQ[2], where LQ denotes local quasiharmonic.

The MS-T method can either be based on an uncoupled torsional potential or be based on a coupled torsional potential. For both the coupled and uncoupled MS-T method, there is also a dual-level version.[3] In addition, to further simplify the user input for MS-T calculations, the current version of the *MSTor* program provides a way to help users identify torsional modes using redundant internal coordinates.[4] To distinguish the methods, we use specific names as follows:

Name	Method
MS-T(U)	MS-T with uncoupled torsional potential
MS-T(C)	MS-T with coupled torsional potential (default)
Dual level MS-T	dual-level MS-T (works for both C and U)
MS-T(CD)	MS-T(C) with redundant internal coordinates

Note that one can also use redundant internal coordinates with the U and dual-level options.

[1] I. M. Alecu, J. Zheng, Y. Zhao, and D. G. Truhlar, J. Chem. Theory Comp. **6**, 2872-2887 (2010).

[2] E. Papajak, P. Seal, X. Xu, and D. G. Truhlar, J. Chem. Phys. **137**, article no. 064110 (2012).

[3] J. L. Bao, L. Xing, D. G. Truhlar, J. Chem. Theory Comp. **13**, 2511-2522 (2017)

[4] W. Chen, P. Zhang, D. G. Truhlar, J. Zheng and X. Xu, J. Chem. Theory Comp. **18**, 7671–7682 (2022).

5. 2. Translational partition function

The translational partition function for an ideal molecular gas is given by

$$Q_{\text{trans}} = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} V^\circ \tag{7}$$

where V° is the volume per particle in the standard state, k_B is the Boltzmann's constant, T is temperature, $\hbar$ is Planck's constant divided by 2π, and m is the molecule's mass. For an ideal gas, $V^\circ = k_BT/P^\circ$, where P° is the pressure in the standard state.

Often we quote the answer as a translational partition function per unit volume

$$\Phi_{\text{trans}} = Q_{\text{trans}} / V^\circ \tag{8}$$

Similarly, the total partition function per unit volume is

$$\Phi_{\text{total}} = Q_{\text{total}}/V^0 = \Phi_{\text{trans}} Q_{\text{elec}} Q_{\text{con-rovib}} \tag{9}$$

5. 3. Electronic partition function

The electronic partition function is calculated by

$$Q_{\text{elec}} = \sum_i d_i e^{-\varepsilon_i / k_BT} \tag{10}$$

where d_i and ε_i are the degeneracy and energy of the electronic state i, respectively. Here we set the ground electronic state energy as zero ($\varepsilon_1 = 0$). The partial derivative of Q_{elec} with respect to β is

$$-\frac{\partial \ln Q_{\text{elec}}}{\partial \beta} = \frac{1}{Q_{\text{elec}}} \sum_i d_i \varepsilon_i e^{-\varepsilon_i \beta} \tag{11}$$

where β is $1/k_BT$.

5. 4. Conformational–rovibrational partition function

5.4.1 MS-T(C) method

When torsions are coupled in the MS-T(C) scheme, we assume that each coupled torsion η for a structure j has the reference potential form, that is,

$$V_{j,\eta} = U_j + \frac{W_{j,\eta}^{(\text{C})}}{2}\left[1 - \cos M_{j,\eta}(\phi_{j,\eta} - \phi_{j,\eta,\text{eq}})\right]; \quad \frac{-\pi}{M_{j,\eta}} \le \phi_\eta - \phi_{j,\eta,\text{eq}} \le \frac{\pi}{M_{j,\eta}} \tag{12}$$

where U_j is the energy of structure j (where the global minimum is set to 0), $W_{j,\eta}^{(\text{C})}$ is effective coupled barrier height, $M_{j,\eta}$ is a local periodicity parameter, $\phi_{j,\eta}$ is torsional coordinate, and $\phi_{j,\eta,\text{eq}}$ is the torsional coordinate at equilibrium geometry.

For a molecule or a transition structure that has J distinguishable structures and t torsions, the conformational–rovibrational partition function according to the MS-T(C) method is

$$Q_{\text{con-rovib}}^{\text{MS-T(C)}} = \sum_{j=1}^{J} Q_{\text{rot},j} \exp\left(-\beta U_j\right) Q_j^{\text{HO}} \prod_{\eta=1}^{t} f_{j,\eta} \tag{13}$$

$$Q_j^{\mathrm{HO}} = \prod_{i=1}^{F} \frac{\exp(-\beta\hbar\omega_{j,i}/2)}{1-\exp(-\beta\hbar\omega_{j,i})} \tag{14}$$

where $Q_{\mathrm{rot},j}$ is the rotational partition function of structure j, β is $1/k_BT$, k_B is Boltzmann's constant, T is temperature, Q_j^{HO} is the usual normal-mode harmonic oscillator vibrational partition function calculated at structure j, $f_{j,\eta}$ is a factor that takes account of torsional anharmonicity, F is the number of degrees of freedom for the vibrational modes, and $\omega_{j,i}$ denotes the normal-mode vibrational frequency of mode i of structure j. Note that the zero of energy for Q_j^{HO} is at the local minimum of the potential energy function for structure j, not at the zero point level of structure j.

We use the classical expression for the rotational partition function for structure j

$$Q_{\mathrm{rot},j} = \frac{\sqrt{\pi}}{\sigma_{\mathrm{rot,j}}}\left(\frac{2}{\hbar^2\beta}\right)^{3/2}\sqrt{I_{\mathrm{A},j}I_{\mathrm{B},j}I_{\mathrm{C},j}} \tag{15}$$

where $\sigma_{\mathrm{rot},j}$ is the symmetry number of overall rotation, and $I_{\mathrm{A},j}$, $I_{\mathrm{B},j}$, and $I_{\mathrm{C},j}$ are the principal moments of inertia.

If the $f_{j,\eta}$ are set to unity, the partition function $Q_{\mathrm{con-rovib}}^{\mathrm{MS-T(C)}}$ reduces to the multi-structural local-harmonic (MS-LH) partition function. Note that the resulting method is called "local harmonic" but the result is actually quasiharmonic if one uses frequencies scaled to account for anharmonicity (and possibly also accounting for other factors). The scaling is described in footnote 1 of section 5.1.

Because the torsional anharmonicity correction is based on the coupled torsional potential, the individual $f_{j,\eta}$ is not meaningful and the product of the $f_{j,\eta}$ is the correction for torsional anharmonicity for the t coupled torsions,

$$\prod_{\eta=1}^{t} f_{j,\eta} = (2\pi\beta)^{t/2}\frac{\prod_{m=1}^{F}\omega_{j,m}}{\prod_{\bar{\bar{m}}=1}^{F-t}\bar{\bar{\omega}}_{j,\bar{\bar{m}}}}\frac{\sqrt{\det\mathbf{D}_j}}{\prod_{\tau=1}^{t}M_{j,\tau}}\prod_{\eta=1}^{t}\exp(-\beta W_{j,\eta}^{(\mathrm{C})}/2)I_0(\beta W_{j,\eta}^{(\mathrm{C})}/2) \tag{16}$$

where $\bar{\bar{\omega}}_{j,\bar{\bar{m}}}$ are torsion-projected normal mode frequencies, $\mathbf{D}_j$ are the Kilpatrick and Pitzer torsional moment of inertia matrices, $M_{j,\tau}$ are local periodicity parameters for uncoupled torsion τ, and I_0 is a modified Bessel function. Note that it is difficult to determine the coupled periodicity parameter $M_{j,\eta}$ so that we use the $M_{j,\tau}$ here instead of $M_{j,\eta}$.

To calculate the thermodynamic functions from the MS-T(C) partition function, we need the partial derivative of the logarithm of the partition function with respect to β:

$$-\frac{\partial}{\partial\beta}\ln Q_{\text{con-rovib}}^{\text{MS-T(C)}} = \frac{1}{Q_{\text{con-rovib}}^{\text{MS-T(C)}}}\sum_{j=1}^{J}\left(Q_{\text{rot},j}\exp\left(-\beta U_j\right)Q_j^{\text{HO}}\prod_{\eta=1}^{t}f_{j,\eta}\right)\left\{\frac{3}{2\beta}+U_j\right.$$
$$\left.+\sum_{m=1}^{F}\frac{\hbar\omega_{j,m}}{2}\left(\frac{1+e^{-\beta\hbar\omega_{j,m}}}{1-e^{-\beta\hbar\omega_{j,m}}}\right)+\sum_{\eta=1}^{t}\left[\frac{W_{j,\eta}^{(\text{C})}}{2}\left(1-\frac{I_1(\beta W_{j,\eta}^{(\text{C})}/2)}{I_0(\beta W_{j,\eta}^{(\text{C})}/2)}\right)-\frac{1}{2\beta}\right]\right\} \quad (17)$$

5.4.2 MS-T(U) method

In the MS-T(U) method, we assume each uncoupled torsion τ has a potential given by

$$V_{j,\tau} = U_j + \frac{W_{j,\tau}^{(\text{U})}}{2}\left[1-\cos M_{j,\tau}(\phi_{j,\tau}-\phi_{j,\tau,\text{eq.}})\right];\quad \frac{-\pi}{M_{j,\tau}} \le \phi_{j,\tau}-\phi_{j,\tau,\text{eq.}} \le \frac{\pi}{M_{j,\tau}} \quad (18)$$

where $W_{j,\tau}^{(\text{U})}$ is effective uncoupled barrier height, $\phi_{j,\tau}$ is the torsional coordinate, and $\phi_{j,\tau,\text{eq}}$ is the torsional coordinate at the equilibrium geometry

For a molecule that has *J* distinguishable structures and *t* torsions, the conformational-rovibrational partition function according to the MS-T(U) method is

$$Q_{\text{con-rovib}}^{\text{MS-T(U)}} = \sum_{j=1}^{J} Q_{\text{rot},j}\exp\left(-\beta U_j\right) Q_j^{\text{HO}} Z_j \prod_{\tau=1}^{t} f_{j,\tau} \quad (19)$$

where Z_j is a factor designed to ensure that the MS-T(U) partition function reaches the correct high-temperature limit, and $f_{j,\tau}$ is an internal-coordinate torsional anharmonicity function that, in conjunction with Z_j, adjusts the harmonic or quasiharmonic result of structure *j* for the presence of the torsional motion τ.

If the Z_j and $f_{j,\tau}$ are set to unity, the partition function $Q_{\text{con-rovib}}^{\text{MS-T}}$ reduces to the multi-structural local-harmonic (MS-LH) partition function.

The torsional anharmonicity function using the uncoupled internal-coordinate approximation for torsion τ at structure *j* is given by

$$f_{j,\tau} = \frac{\bar{\omega}_{j,\tau}\sqrt{2\pi\beta I_{j,\tau}}}{M_{j,\tau}}\exp(-\beta W_{j,\tau}^{(\text{U})}/2) I_0(\beta W_{j,\tau}^{(\text{U})}/2) \quad (20)$$

where $\bar{\omega}_{j,\tau}$ is an internal-coordinate torsional frequency, $I_{j,\tau}$ is the torsional moment of inertia calculated by Pitzer's method without coupling between torsions, $M_{j,\tau}$ is a local periodicity parameter, and $W_{j,\tau}^{(\text{U})}$ is an uncoupled effective barrier height. These parameters are interrelated as

$$W_{j,\tau}^{(\text{U})} = \frac{2I_{j,\tau}\bar{\omega}_{j,\tau}^2}{M_{j,\tau}^2} \quad (21)$$

The factor Z_j is given by

$$Z_j = g_j + (1-g_j)Z_j^{\text{int}}Z_j^{\text{coup}} \quad (22)$$

where Z_j^{int} replaces the normal-mode vibrational partition function in the high-T limit by internal-coordinate ones, and Z_j^{coup} replaces the uncoupled moments of inertia for individual torsions by values that account for their coupling. $g_j \to 1$ at low T where the effects of rotational-vibrational coupling are minimal, and $g_j \to 0$ at high T. The Z_j^{int} are given by

$$Z_j^{\mathrm{int}} = \frac{\prod_{m=1}^{F-t} \overline{\overline{\omega}}_{j,m}^{-1} \prod_{\tau=1}^{t} \overline{\omega}_{j,\tau}^{-1}}{\prod_{m=1}^{F} \omega_{j,m}^{-1}} \tag{23}$$

where F is the number of vibrational degrees of freedom, $\omega_{j,m}$ is the frequency of normal mode m. The factors Z_j^{coup} are equal to

$$Z_j^{\mathrm{coup}} = \left(\frac{\left| \det \mathbf{D}_j \right|}{\prod_{\tau=1}^{t} I_{j,\tau}} \right)^{1/2} \tag{24}$$

The expression used for g_j to enforce the correct limits is

$$g_j = \left(\prod_{\tau=1}^{t} \tanh \frac{\sqrt{2\pi k_{j,\tau} \beta}}{M_{j,\tau}} \right)^{1/t} \tag{25}$$

where $k_{j,\tau}$ is the force constant for torsion τ at structure j in internal coordinates.

The partial derivative of the MS-T partition function with respect to β is

$$-\frac{\partial}{\partial \beta} \ln(Q_{\text{con-rovib}}^{\text{MS-T(U)}}) = \frac{1}{Q_{\text{con-rovib}}^{\text{MS-AS}}} \sum_{j=1}^{J} \left\{ e^{-\beta U_j} Q_{\mathrm{rot},j} Q_j^{\mathrm{HO}} Z_j \prod_{\tau=1}^{t} f_{j,\tau} \left(\frac{3}{2\beta} + U_j \right.\right.$$

$$+ \sum_{m=1}^{F} \frac{\hbar \omega_{j,m}}{2} \frac{1 + e^{-\beta \hbar \omega_{j,m}}}{1 - e^{-\beta \hbar \omega_{j,m}}}$$

$$- \left(g \frac{(1 - Z_j^{\mathrm{int}} Z_j^{\mathrm{coup}})}{2t\sqrt{\beta} Z_j} \left\{ \sum_{\tau=1}^{t} \frac{\overline{\omega}_{j,\tau} \sqrt{2\pi I_{j,\tau}}}{M_{j,\tau}} \frac{\operatorname{sech}^2 \left(\overline{\omega}_{j,\tau} \sqrt{2\pi I_{j,\tau} \beta} / M_{j,\tau} \right)}{\tanh \left(\overline{\omega}_{j,\tau} \sqrt{2\pi I_{j,\tau} \beta} / M_{j,\tau} \right)} \right\} \right)$$

$$\left. \left. + \sum_{\tau=1}^{t} \left(\frac{I_{j,\tau} \overline{\omega}_{j,\tau}^2}{M_{j,\tau}^2} - \frac{1}{2\beta} - \frac{I_{j,\tau} \overline{\omega}_{j,\tau}^2}{M_{j,\tau}^2} \frac{I_1(\beta I_{j,\tau} \overline{\omega}_{j,\tau}^2 / M_{j,\tau}^2)}{I_0(\beta I_{j,\tau} \overline{\omega}_{j,\tau}^2 / M_{j,\tau}^2)} \right) \right) \right\} \tag{26}$$

Note that the zero-point energy corresponding to the MS-T partition function is

$$E_0^{\text{MS-LH}} = \min_j \left\{ E_{j,0}^{\mathrm{HO}} + U_j \right\} \tag{27}$$

where $E_{j,0}^{\mathrm{HO}}$ is the harmonic oscillator zero-point energy of structure j with the zero of energy at its local minimum, which is given by

$$E_{j,0}^{\mathrm{HO}} = \frac{\hbar}{2}\sum_{m=1}^{F}\omega_{j,m} \qquad (28)$$

5. 5. Treatment of rotational symmetry and mirror images

Special care is needed when considering rotational symmetry for systems that exhibit torsional motion. To calculate the classical partition function for such a system, either one could integrate exp(-βV) over only the symmetry unique portion of configuration space or one could integrate exp(-βV) over all of configuration space and divide the result by a *structure-independent* symmetry number. However, it is convenient to consider only the *J* fully-distinguishable structures (i.e., structures that are distinguishable after considering both torsional and rotational symmetry) in the structure summation of equations such as Eq. 13 or Eq. 19. When doing so, we use structure-specific rotational symmetry numbers, $\sigma_{\mathrm{rot},j}$, because we are then using a hybrid approach whereby we are accounting for rotational symmetry partly via the use of symmetry numbers and partly by omitting certain regions of configuration space that we recognize as symmetrically equivalent to other regions.

For many systems, the observed structures occur as pairs of mirror images (sometimes a structure is its own mirror image); mirror images are distinguishable, but because they have equal contributions to the overall partition function it is convenient to perform explicit calculations for only one member of each pair and to weight this structure by a factor of 2 in the final results (see WEIGHT keyword in section 7.1.G). The various utility codes included in the software package identify mirror images in order to make the calculation more efficient, for example by reducing the required number of harmonic frequency calculations.

It is important to note that the Voronoi tessellation codes that calculate *M* parameters for strongly coupled torsions do not explicitly consider rotational symmetry; thus, one needs to provide structure information to these routines for all structures that would be distinct *without* accounting for rotational symmetry (see section 5.6 below).

The case of pentane is a useful illustration of how we treat rotation and mirror images. Pentane has four torsions: C1-C2, C2-C3, C3-C4, and C4-C5. If we considered only the two non-methyl torsional degrees of freedom (i.e., C2-C3 and C3-C4, each of which has a torsional symmetry number equal to 1), we would find 11 structures before accounting for symmetry. A plot of these structures using the data reported in R. A. Scott and H. A. Scheraga, J. Chem. Phys., 44, 3054 (1966) is given in Figure 5.1.

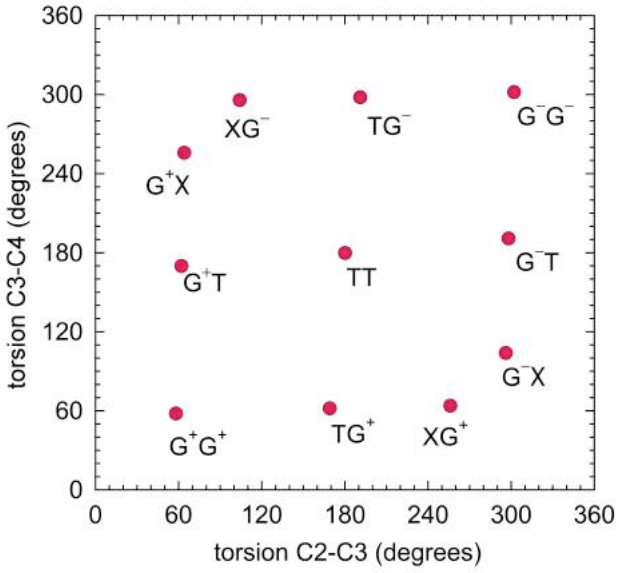


Figure 5.1. Structures for pentane.

We might have naively expected to find nine uniformly distributed structures in Fig. 5.1, but steric effects lead to finding two structures, G^+X and XG^-, nearby to (60, 300) where we might have expected to find one structure, and, similarly, two structures, XG^+ and G^-X, nearby to where we might have expected a single structure at (300, 60). For this system, three (TT, G^+G^+, and G^-G^-) of the 11 structures have $\sigma_{\mathrm{rot},j} = 2$; the eight remaining structures have $\sigma_{\mathrm{rot},j} = 1$, but overall rotation maps each of these structures onto one of the other eight structures (for example, G^+T is related by an overall rotation to TG^+ as shown in Fig. 5.2), so only four of these eight are distinct after accounting for overall rotation. Of the seven distinct structures which should be included in the calculations of MS-T partition functions (i.e. $J = 7$ in eq 13 and eq 19), one (TT) is its own mirror image and the remaining six occur as three pairs of mirror images (for example, G^+T and G^-T); thus, in the actual treatment, we can perform frequency calculations for only four structures (for example, TT, G^+G^+, G^+T, and G^+X) and then only include the four structures in the *mstor.inp* file by setting the WEIGHT keyword of TT, G^+G^+, G^+T, and G^+X as 1, 2, 2, and 2 to obtain the final MS-T partition functions.

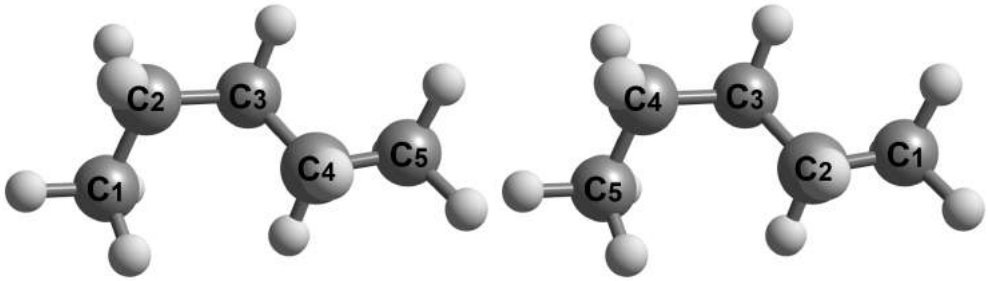


Figure 5.2. Structures G^+T and TG^+.

The correct way to handle the issues raised in this subsection is revisited in section 6.

5. 6. Voronoi tessellation scheme for *M* values

When torsions are strongly coupled together, it is sometimes impossible to assign integer $M_{j,\tau}$ values for each torsion. We divide the *t* torsions into two types: nearly separable (NS) and strong coupled (SC). We use the notation $\mathrm{NS:SC} = t_{\mathrm{NS}} : t_{\mathrm{SC}}$ to denote that t_{NS} torsions are treated as nearly separable and t_{SC} torsions are treated as strongly coupled. In general, the strongly coupled coordinates may be further partitioned into two or more subspaces, with each subspace involving only those coordinates that are strongly coupled to each other.

Each of the strongly coupled subspaces is treated by Voronoi tessellation separately. Voronoi tessellation divides a space into cells around a discrete set of points. In the applications considered here, the space to be tessellated is described by the dihedral angles $\phi_{1,}\phi_2,\cdots,\phi_{t_{\mathrm{SC}}}$, and the points correspond to structures. Each cell corresponds to a specific structure and consists of all torsional configurations closer to this structure than to any other structure when only the t_{SC} strongly coupled degrees of freedom are considered.

Next we define the concept of torsional symmetry number σ_τ for torsion τ; if there are *t* torsions in a molecule, there will be *t* torsional symmetry numbers, each of which corresponds to one torsion in the molecule. The symmetry number for torsion τ can be determined by treating the least symmetric of the two rotating fragments as a fixed frame and counting the number of identical structures obtained when the more symmetrical top is rotated from 0 to 360 degrees with respect to the torsional bond *t* and relaxed. For example, the symmetry numbers for C-O torsion in methanol, C-N torsion in nitromethane, and C-C torsion in 1,2 dichloroethane are 3, 3, and 1, respectively.

The tessellation code (*mcvorm.exe*) properly accounts for torsional symmetry according to the input torsional symmetry numbers σ_τ in the MC sampling (see equation 29), but the current version does not exploit torsional symmetry efficiently to reduce the statistical uncertainty (which does not affect the computed *M* values). The code also does not use rotational symmetry to reduce the domain of configurations it must consider, so for systems exhibiting rotational symmetry (e.g., linear alkanes), besides the distinguishable structures after considering all possible symmetries, structures that would be indistinguishable under consideration of both rotational and torsional symmetries but are distinguishable under *only* torsional symmetry **must** be included in its input file (*mvorm.inp*). Note that the utility code *mvinput.exe* automatically includes the additional structures in the generated template *mvorm.inp* file that are required provided that they were obtained in the prior structure search step. When the input contains pairs of structures that are mirror images of each other, and/or rotationally related to each other, the code will use this information to reduce the statistical uncertainties.

In this manual we will refer to the total number of fully distinguishable structures (i.e., distinguishable after considering all possible symmetries) as *J*, and we will refer to the number of

structures that would be distinguishable without considering rotational symmetry (but fully accounting for torsional symmetry) as $\tilde{J}$. (There may be places in previous writing where these two quantities were not carefully distinguished. For the case of pentane that we have discussed earlier and for which only the two non-methyl torsions are included in the calculations, we would have $J = 7$ and $\tilde{J} = 11$.) The volume of the SC torsional subspace is then given by

$$\Omega^{\mathrm{SC,tot}} = \sum_{j=1}^{\tilde{J}} \Omega_j^{\mathrm{SC}} = \frac{(2\pi)^{t_{\mathrm{SC}}}}{\prod_{\tau=1}^{t_{\mathrm{SC}}} \sigma_\tau} \tag{29}$$

where t_{SC} is the number of torsions in the strongly coupled space. Whenever we use Voronoi tessellation, we assume that the torsional subspace is so strongly coupled that we cannot assign $M_{j,\tau_{\mathrm{SC}}}$ by considering each torsion separately; then we replace all $M_{j,\tau_{\mathrm{SC}}}$ for strongly coupled torsions of a given j by a single M_j^{SC} equal to

$$M_j^{\mathrm{SC}} = \frac{2\pi}{\left(\Omega_j^{\mathrm{SC}}\right)^{1/t_{\mathrm{SC}}}} \tag{30}$$

5. 7. Low-temperature limits

In this section, we use the common thermodynamics convention where temperature is written as a subscript. Then

$$G_T^\circ = -\ln(Q)/\beta + k_B T \tag{31}$$

$$E_T^\circ = -\frac{\partial \ln(Q)}{\partial \beta} \tag{32}$$

$$H_T^\circ = E_T^\circ + PV = E_T^\circ + RT = \varepsilon(T) + RT \tag{33}$$

$$S_T^\circ = k_B \ln Q - \frac{1}{T}\left(\frac{\partial \ln Q}{\partial \beta}\right) \tag{34}$$

Consider the low-temperature limit ($T \to 0$), where only the ground state, with energy ε^{G} and degeneracy d_0, is important. Note that if the structure that has the lowest zero-point-inclusive energy is the same as the structure that has the lowest zero-point-exclusive energy, then ε^{G} is the zero-point vibrational energy of that structure. Otherwise ε^{G} is given by eq. (18). Then, where all arrows refer to the limit as temperature goes to zero, we have:

$$Q \to d_0 \exp\left(-\beta\varepsilon^{\mathrm{G}}\right) \to 0 \tag{35}$$

Therefore

$$\ln Q \to -\beta\varepsilon^{\mathrm{G}} + \ln d_0 \tag{36}$$

$$-\frac{\partial}{\partial\beta}\ln Q \to \varepsilon^{\mathrm{G}} \tag{37}$$

Substituting eqs. (35)–(37) into eqs. (31)–(33) yields the following low-T limits:

$$G_T^\circ \to \varepsilon^{\mathrm{G}} \tag{38}$$

$$E_T^\circ \to \varepsilon^{\mathrm{G}} \tag{39}$$

$$H_T^\circ \to \varepsilon^{\mathrm{G}} \tag{40}$$

Note that most statistical mechanics textbooks use a different zero of energy, at the ground-state level. We label partition functions with that choice as $\tilde{Q}$ where

$$\tilde{Q} \equiv Q\exp\left(\beta\varepsilon^{\mathrm{G}}\right) \tag{41}$$

and we note that the limits of eqs. (31)–(33) would be different with that different choice of the zero of energy. The zero of energy used here is more convenient when working with electronic-structure input data.

Equation (34) yields

$$S_T^\circ \to \ln d_0 \tag{42}$$

in the low-temperature limit, which is consistent with the third law of thermodynamics.

5. 8. Transition structures

Throughout this manual we use the language of stable structures. The code can also be applied to transition structures. A transition structure is a first-order saddle point on a transition state dividing surface that separates reactants from products. A first-order saddle point is one that has $3N - 7$ real frequencies and one imaginary frequency, where N is the number of atoms. Sometimes, especially in the older literature, transition structures are called transition states. (A transition state is a dividing surface containing an infinite number of geometries, whereas a transition structure is a single geometry.)

Each stable structure has $3N - 6$ real frequencies, whereas calculations for transition structures are based on the $3N - 7$ real frequencies of each transition structure (i.e., each saddle point that is classified as a transition structure). Note that saddle points for torsional transitions (i.e., saddle points where the imaginary-frequency normal mode is a torsional coordinate connecting two different torsional structures rather than connecting reactants to products) should not be called transition structures in this context; they are not used in *MSTor* calculations.

The code determines whether the system is at a stable structure or a transition- structure based on the number of imaginary frequencies. Note, though, that the code cannot know if a transition structure connects reactants to products. The user should on their own determine if a transition structure connects reactants to products.

5. 9. Thermodynamics convention

For thermodynamic calculations based on electronic structure theory, the most convenient zero of energy is the lowest equilibrium (zero-point-exclusive) one. This choice is used throughout the manual and the code. However, almost all textbooks and compilations of thermodynamic data in the literature set the zero of energy at the zero-point level. With this convention the partition function goes to the degeneracy of the ground electronic state at 0 K and enthalpy and free energy go to 0 at 0 K. For the convenience of users, we print all of the calculated quantities (Q, E, H, and G) with this thermodynamic convention. The default is to compute thermodynamic functions at 1 bar.

6. Guidelines of MS-T calculations

6. 1. Overview

To run MS-T calculations with the *MSTor* program, the user first needs to prepare two input files, one is the *mstor.inp* file (which includes all the information of the distinguishable conformers except their Hessians), and the other is the Hessian input file with a fixed name, *hess.dat* file. The user should put them both in the same working directory. Then the user should run the executable file *mstor.exe*.

mstor.exe < *mstor.inp* > *mstor.out*

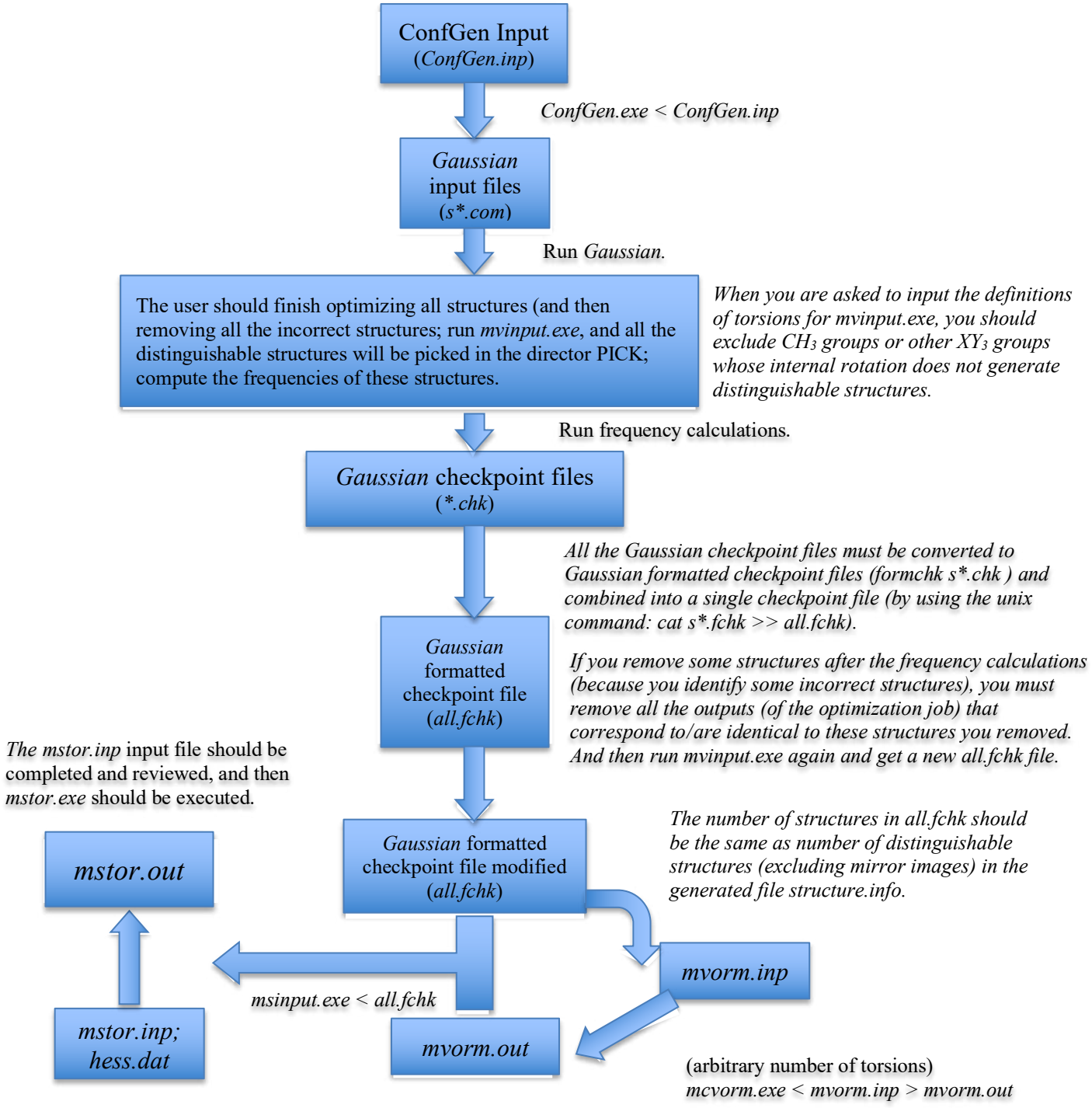
The details of the required information and format for the two input files are given in section 7.1.

Users can prepare the needed information in their own way to generate the two input files manually. Alternatively, one can use utility codes that are provided in the *MSTor* package to generate the *MSTor* input files in combination with the *Gaussian* software package.[5] The procedure for doing this is summarized in the following:

1. Search for and optimize all distinguished conformers. This procedure will use the *ConfGen.exe* and *mvinput.exe* utilities: the former is for generating a list of *Gaussian* optimization input files with different initial conformational guesses; the latter examines the *Gaussian* optimization output files to pick up the distinguishable structures.
2. Perform *Gaussian* frequency calculations for these optimized distinguished structures. Combine all the formatted *Gaussian* check files (*.fchk*) of these frequency calculations into a single checkpoint file with a fixed name *all.fchk* for later use.
3. Calculate the periodicity parameter $M_{j,\tau}$ required in *mstor.inp* by using the *mvinput.exe* and *mcvorm.exe* utilities. The *mvinput.exe* utility can generate the *mvorm.inp* input file for the *mcvorm.exe* utility; the *mcvorm.exe* utility calculates $M_{j,\tau}$ values defined by Voronoi tessellation of the torsional space by Monte Carlo sampling.
4. Generate a draft of the *mstor.inp* file and the *hess.dat* file with the *msinput.exe* utility.
5. Complete and review the *mstor.inp* file carefully. In early versions of *MSTor*, the user needed to define nonredundant internal coordinates manually in the *mstor.inp* file. Beginning with *MSTor 2023*, the program will apply the MS-T(CD) method by default. The MS-T(CD) method uses redundant internal coordinates, and the program will automatically construct the redundant-internal-coordinate set required in MS-T(CD) calculations. Therefore, there is no longer a need for users to provide the nonredundant internal coordinates. More information about this can be found in section 7.1.E;
6. Execute the *mstor.exe* code to get final results.

[5] Frisch, M. J. *et al. Gaussian 03/09/16*; Gaussian, Inc.: Wallingford, CT, 2003/2009/2016

The following flowchart shows one process that the user may follow:



6. 2. Detailed procedure

In this section, we give a more detailed description of the process shown in the above flowchart. In the first step, the user should carry out a search of all conformations that can be obtained by internal rotation of the various fragments of the initial structure. Using the Cartesian coordinates of the initial structure and the definition of each torsion angle as an input file (denoted in the flowchart as *ConfGen.inp*), the *ConfGen* utility generates the *Gaussian* input files of starting guesses for the different conformers and puts them in the working directory. The generated structures, obtained by all possible combinations of the values of the dihedral angles specified by the user in the input file, should then be optimized by running the *Gaussian* software package, and the output files will go in the working directory.

In the second stage, all the optimized structures should be analyzed, and the user should remove from the working directory the *Gaussian* output files for all the incorrect structures (those converged to a structure that is not what the user wanted – for instance, a torsional saddle point where a reaction saddle point was sought or any other kind of wrong transition structure). If you remove an incorrect structure, you should remove *all* the output files (from geometry optimization) that contain the identical (incorrect) structure. Note, at this point, if all has gone well, the conformational search will have yielded all $\tilde{J}$ structures needed for the tessellation, though the actual number of optimized structures is much larger than $\tilde{J}$ due to the duplication.

After removing all incorrect structures from the working directory, the user can leave all remaining output files (geometry optimization files, whose file names are sXXXXXX.out, of which the *Gaussian* inputs are automatically generated by the conformational search utility *ConfGen.exe*) in the working directory, and then run *mvinput.exe* by typing "./*mvinput.exe*" and choosing option 1 in the interactive dialog. This will pick out distinguishable structures (excluding mirror images or structures related by overall rotation) for you, and these output files are copied to the automatically created directory PICK. (Note that PICK is the directory containing the structures for which frequencies need to be calculated.) For example, for the case of pentane, which was discussed in detail in section 5.5, four files will be located in the PICK directory. The *mvinput.exe* code will also generate an information file called *structure.info*, which includes a summary of all distinguishable structures (excluding mirror images) and all indistinguishable rotationally related structures (excluding mirror images).

Finally, the *mvinput* utility also generates a template input file, *mvorm.inp*, for the code that computes the M_j values (*mcvorm.exe* and/or *vorm.exe*). This *mvorm.inp* file should include all $\tilde{J}$ structures required for the tessellation, which consists of all $\boldsymbol{J}$ distinguishable structures considering all possible symmetries (including those non-superimposable mirror images) and all indistinguishable rotationally related structures. One of the features of the *mvinput.exe* code is that it partially corrects for deficiencies in the structure search. In particular, it will find and remove duplicate structures, and it will identify structures that should have a mirror image and rotationally and indistinguishable structures. In the above step of creating PICK directory, the *mvinput.exe* code excludes all mirror images and rotationally and torsionally indistinguishable structures for calculational efficiency, but in this step for generating the template *mvorm.inp* file,

if that mirror image is missing in the set of found structures, it will be added, i.e., all ***J*** distinguishable structures considering all possible symmetries (including non-superimposable mirror images) and those rotationally indistinguishable structures found in the structure search are included in the template *mvorm.inp*. Note carefully that the *mvinput.exe* code is not able to identify missing rotationally related structures that will be needed in the tessellation code so, if the system exhibits rotational symmetry, the user should be especially careful to ensure that the conformational search accounts for these needed structures. The user must always be very careful when using this *mvorm.inp* file because there are some cases that deserve special attention (e.g., chiral systems). These cases are discussed in further detail in section 7.6.

In the next step, the frequencies of the conformations that were placed in the PICK directory, (which, as stated above, include only the conformers that are distinct after fully accounting for both torsional and overall rotational symmetry and after the removal of one structure from each pair of mirror images) should be calculated and the *Gaussian* checkpoint file (including the Cartesian coordinates, the energy, and the Hessian) should be saved and subsequently formatted using the command *formchk s*.chk*.

Once all *Gaussian* formatted checkpoint files from the frequency calculations are generated, the user must combine all of these formatted checkpoint files into a single file named *all.fchk* (using, for instance, the unix command: *cat s*.fchk >> all.fchk*), and this *all.fchk* file should be located in the same working directory as used in the second stage; this file is used by the utility called *msinput* to generate the *MSTor* input file (denoted as *mstor.inp*). The number of structures contained in *all.fchk* should be the same as the number of distinguishable structures (excluding mirror images) that is documented in *structure.info*. If, after the freq. calculation, the user removed some structures (probably because the user has identified additional incorrect structures (for instance a TS that is not what you are looking for), you need to remove *all* the output files (*Gaussian* geometry optimization) which contain the identical (incorrect) structures, and then run *mvinput.exe* again. You can check the information in *structure.info* to help you identify what distinguishable structures (excluding mirror images) you had in a previous run.

The automatically generated *mstor.inp* file by *msinput.exe* cannot be used directly as an input file for the *MSTor* program also because many parameters are not included, e.g., the definition of the internal coordinates) and some parameters are assigned temporary values (e.g., the temperatures); also, in *mstor.inp* one should include all the torsions (including $–CH_3$), but some torsions (for instance $–CH_3$) should not be included in *mvorm.inp* (i.e., not included in Voronoi tessellation because they are treated as nearly separable torsions), the user needs to add the *M* values of these torsions (for instance for $–CH_3$, $M = 3.0$), and the order of the *M* values in *mstor.inp* should be consistent with the order of the definitions of the torsions in the $INTDEF section in *mstor.inp* **.**

7. Input files

7. 1. Input files for *mstor.exe* executable

Two input files are required for running the *mstor.exe* executable. One file contains all the information except Hessians, and the other one has the Hessians of all structures. The former will be referred to as the main input file and the latter as the Hessian input file. Note that the name of the Hessian input file is fixed as *hess.dat*.

The main input file consists of several sections. Each section name begins with the symbol $. At the end of each section, a keyword "END" must be given to indicate the end of this section. Each section consists of several keywords. All keywords and section names are case insensitive and any lines beginning with # symbols are comment lines.

Note that each line of the input files should be equal or less than 80 characters and characters after column 80 are ignored by the program.

7. 1. A. Description of sections of the main input file

Section Name	Description
$General	General data to describe the system
$Intdef	Defines the internal coordinate
$Temp	List of temperatures
$Structure #	Gives the geometry, energy, M values, and weight for each structure. Here # is an integer to label the structure

7. 1. B. Glossary of keywords in $GENERAL section

The section $GENERAL is for the general information about the system, e.g., the number of atoms, the number of structures, and so on. The following keywords can be used in this section.

ATM

ATM is a keyword to use 1 atmosphere pressure for the standard state pressure. By default, if ATM is not specified, the program uses 1 bar.

BAR

BAR is a keyword to use 1 bar for the standard state pressure. This is the default, and the specification of defaults in the keyword list is optional.

COUPLED

COUPLED is a keyword to use the MS-T(C) method that is based on coupled torsional potential. This is default.

DELTAT

DELTAT is a keyword for specifying the temperature interval (in degrees Kelvin) of eq. (6) for calculating the heat capacity by using the four-point central finite difference formula. The default value is 1 K.

Example:

```
DELTAT      1
```

ELEC

ELEC is a keyword for specifying the degeneracy of the electronic states and their corresponding energies (in hartrees), which are used for calculating the electronic partition function. The ground electronic state has been chosen as the zero of energy. If low-lying excited states exist, they need to be included. We assume that all conformational structures have the same electronic partition function.

Example:

```
ELEC
  1  0.0
END
```

This example indicates that the ground electronic state is a singlet state and that this molecule has no low-lying excited states.

The example below shows a doublet ground electronic state with a low-lying doublet excited state (higher in energy than the ground state by 0.00064 hartrees).

Example:

```
ELEC
  2  0.0
  2  0.00064
END
```

The default, if ELEC is not specified, is “1 0.0”.

EMAX

EMAX is a keyword for turning on the calculation and printing of the density of states in the standard *MSTor* output file and for specifying the maximum energy of the energy levels used for calculating the density of states. The unit is kcal/mol. The default value is 400 kcal/mol. EMAX should be large enough to converge the thermodynamic properties.

Example:

EMAX 400

ESTEP

ESTEP is a keyword for turning on the calculation and printing of the density of states in the standard *MSTor* output file and for specifying the energy step used in calculating the density of states. The unit is kcal/mol. The default value is 2.859114E-3 kcal/mol (1 cm^{-1}).

Example:

ESTEP 2.859114E-3

FREQSCALE

FREQSCALE is a keyword for specifying a frequency-scaling factor. This factor scales all the frequencies used in the calculation. The default value is 1.0. The scale factor that the user should use in thermochemistry is the ZPE scale factor, which can be found from the scale factor database (https://comp.chem.umn.edu/freqscale/version3b2.htm) for different electronic structure methods. When frequencies are scaled, the harmonic approximation becomes quasiharmonic, but the results are still labeled LH because the H in LH denotes the use of harmonic formulas, not necessarily harmonic frequencies. The way that the current *MSTor* code does this is to read in the Hessians and scale the Hessians by the square of FREQSCALE; this is equivalent to scaling the harmonic frequencies by FREQSCALE (but this is not the way that *MSTor* does it).

Example:

FREQSCALE 0.970

MTUMME

MTUMME is a keyword for turning on the calculation and printing the density of states to a separate output file named *mtumme.out* in a format readable by the TUMME[6] master equation software. This option is convenient for TUMME 2023 and later.

Note that any one of the MTUMME, EMAX, or ESTEP keywords will turn on the calculation of density of states (DOS), but only MTUMME print the DOS in a separate output file, which is a

[6] "TUMME: Tsinghua University Minnesota Master Equation program," R. M. Zhang, X. Xu, and D. G. Truhlar, Computer Physics Communications **270**, article no. 108140 (2021). doi.org/10.1016/j.cpc.2021.108140

convenient procedure for users of TUMME 2023 and later. Users of earlier versions of TUMME (version 3.1 or earlier) can use EMAX and ESTEP to print the DOS to the standard *MSTor* output file (which makes the *MSTor* standard output file very long, but the earlier versions of TUMME can read the *MSTor* standard output file to obtain the DOS).

NATOMS

NATOMS is a keyword for specifying the number of atoms in the system. There is no default; NATOMS must be specified.

Example:

NATOMS 15

NSTR

NSTR is a keyword for specifying the number of structures included in the calculation. This number must be equal to the number of $Structure sections in the input file.

Example:

NSTR 15

There is no default; NSTR must be specified.

NTOR

NTOR is a keyword for specifying the number of torsions treated with torsional corrections. Note that NTOR can be smaller than the total number of torsions in the studied molecule if one wants to treat some of them using a harmonic approximation.

Example:

NTOR 4

There is no default; NTOR must be specified.

UNCOUPLED

UNCOUPLED is a keyword to use the MS-T(U) method (the original MS-T method based on an uncoupled torsional potential).

7. 1. C. Description of $FRAMECHAIN section

The section $FRAMECHAIN is an optional section that specifies how the frames in a molecule are connected to each other. The presence of this section and the (also optional)

$FRAMEDEF section that is discussed next allow KP moments of inertia to be calculated by the algorithm of Kilpatrick and Pitzer, which ensures correct results. If these sections are omitted, the det **D** is calculated from the determinant of the inverse of the $\mathbf{G}_{tor}$ matrix, but this only yields correct results for well-chosen sets of torsional angles in the $INTDEF section (see section 7.1.E). Given the ease with which it is possible to select a set of torsional coordinates that does not yield a correct **D** matrix, users are strongly urged to include these optional sections. Here 1-butanol is taken as an example of the $FRAMECHAIN input.

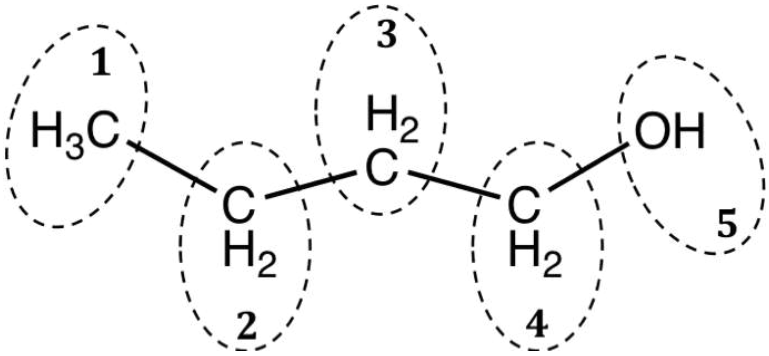


Fig 7-1. Definition of frames for 1-butanol. The group of atoms in each dashed-line circle is defined as a frame.

If frames are defined as in Fig. 7-1, we can define the $FRAMECHAIN section as

Example:

```
$FRAMECHAIN
        1   2
        1   2     3
        1   2     3     4
        1   2     3     4     5
    END
```

Each line in $FRAMECHAIN begins with frame 1 and ends with the destination frame, and it includes all intervening frames. One can number the frames and specify their connectivity in various ways. For example, an alternative definition of the frames for 1-butanol is given in Fig 7-2.

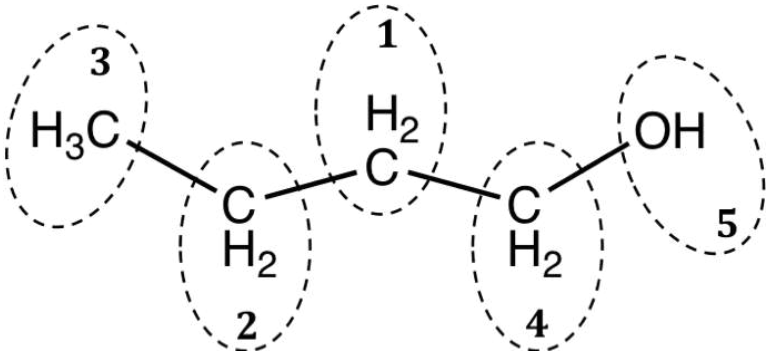


Fig. 7-2 Alternative definition of frames for 1-butanol.

If the frames are labeled as in Fig. 7-2, we can define the $FRAMECHAIN section as

Example:

```
$FRAMECHAIN
        1    2
        1    2        3
        1    4
        1    4        5
END
```

7. 1. D. Description of $FRAMEDEF section

The section $FRAMEDEF is an optional section that specifies the atom numbers in each frame. When this section is used together with the also optional $FRAMECHAIN section discussed in 7.1.C, the code will calculate the det(**D**) using the algorithm of Kilpatrick and Pitzer, which ensures correct results. If these sections are omitted, the det **D** is calculated from the determinant of the inverse of the $\mathbf{G}_{tor}$ matrix, but this only yields correct results for well-chosen sets of torsional angles in the $INTDEF section (see section 7.1.E) Ethanol, shown in Fig. 7-3, is taken as an example.

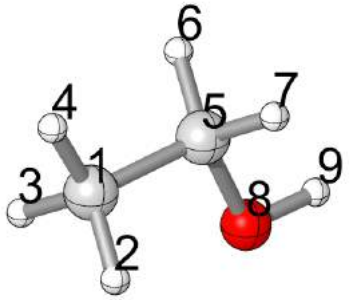


Fig. 7-3. Ethanol molecule.

Example:

```
$FRAMEDEF
        1 : 1 2 3 4
        2 : 5 6 7
        3 : 8 9
END
```

In each line, the number before the colon is the frame number, and the numbers after the colon specify the atom labels of the atoms in the particular frame. Note that the colon should be separated from the numbers by spaces.

7. 1. E. Description of $INTDEF section

The section $INTDEF defines the internal coordinates. In *MSTor 2023*, only the torsions being treated in the MS-T calculations need to be defined in this section. Each torsion should be represented by one (and only one) dihedral angle (*i*-*j*-*k*-*l*) where *i*, *j*, *k*, and *l* are atom labels. For example, for ethanol as shown in Fig. 7-3, if the torsions around the 1–5 and 8–5 rotatable bonds need to be considered, users can indicate this as follows:

Example:

```
$INTDEF
4-1-5-8 9-8-5-1
END
```

The program will then automatically generate a highly redundant internal coordinate set for the investigated species and use the MS-T(CD) method for calculating the partition functions and thermodynamic properties. This is the recommended procedure.

The following are for the users with their own preferences.

If users prefer to use the original MS-T methods, which require a self-defined non-redundant internal coordinate set, or to do MS-T(CD) calculations with a self-defined redundant internal coordinate set, a complete non-redundant internal coordinate set (with 3*n*-6 internal coordinates, where *n* is the number of atoms of the species) or a redundant internal coordinate set (with more than 3*n*-6 internal coordinates) should be defined manually in the section $INTDEF. The allowed types of internal coordinates are stretches (*i*-*j*), bends (*i*-*j*-*k*), linear bends (*i*=*j*=*k*), and dihedral angles (*i*-*j*-*k*-*l*), where *i*, *j*, *k*, and *l* are atom labels.

For a nonredundant internal coordinate set, each torsion being considered should be represented by only one dihedral angle, and these dihedral angles must be at the end of the

internal coordinate list. The following example shows how to define the non-redundant internal coordinates for the ethanol molecule shown in Fig. 7-3.

Example:

```
$INTDEF
   2-1 3-1 4-1 5-1 6-5 7-5 8-5 9-8
   2-1-4 2-1-3 2-1-5 3-1-4 4-1-5 1-5-6 1-5-7
   6-5-7 6-5-8 7-5-8 5-8-9
   4-1-5-8 9-8-5-1
END
```

For a user-defined redundant internal coordinate set, the NTOR torsions that need to be treated with torsional corrections are denoted by the final group of NTOR dihedral angles placed at the end of the internal coordinate list. The following example shows the user-defined redundant internal coordinates for the ethanol molecule shown in Fig. 7-3.

Example:

```
$INTDEF
2-1 3-1 4-1 5-1 6-5 7-5 8-5 9-8
2-1-4 2-1-3 2-1-5 3-1-4 4-1-5 1-5-6 1-5-7
6-5-7 6-5-8 7-5-8 5-8-9
3-1-5-8 9-8-5-7     ! for redundancy
4-1-5-8 9-8-5-1     ! Torsions around the 1–5 and 8–5 bonds will be corrected.
END
```

Note that the program detects the type and the number of internal coordinates given in $INTDEF to automatedly determine the intention of users. If only NTOR dihedral angles are given in this section (*which is highly recommended*), the MS-T(CD) method will be used with the redundant internal coordinates automatedly generated by the program. If the 3*n*-6 non-redundant internal coordinates are detected in this section, the program will perform the original MS-T calculations with the user-defined non-redundant internal coordinate set. If more than 3*n*-6 internal coordinates are detected in this section, the program will perform the MS-T(CD) calculations with the user-defined redundant internal coordinate set. The program will print an error and exit when more than NTOR but less than 3*n*-6 internal coordinates are detected in this section.

---

7. 1. F. Description of $TEMP section

The section $TEMP specifies a list of temperatures. Each line can list multiple temperatures (using integer or floating point format) and this section can have multiple lines. Note that the maximum number of temperatures allowed in this section is 100.

Example:

```
$TEMP
   200 298.15 300 400 600 1000
   1500 2000 2400 3000
END
```

7. 1. G. Description of $STRUCTURE section

The section $STRUCTURE specifies the information about each structure involved in the MS-T treatment. The number of $STRUCTURE sections must be the same as that specified by the NSTR keyword in the $GENERAL section. For each $STRUCTURE section, a number must follow $STRUCTURE to distinguish it from the other $STRUCTURE sections, i.e., $STRUCTURE 1. The following keywords can be used in these sections.

ENERGY

ENERGY is a keyword to specify the relative energy of the structure in kcal/mol. The global minimum is usually set to the zero of energy. Note that this energy is zero-point exclusive. The default value is zero.

Example:

```
ENERGY 0.077
```

GEOM

GEOM is a keyword to specify the Cartesian coordinates of the structure. The unit of the Cartesian coordinates is Ångstroms.

Example:

```
GEOM
6       -1.206324   -0.240211   -0.020995
1       -1.264318   -0.787854   -0.963519
1       -1.258873   -0.958451    0.795948
1       -2.072624    0.416915    0.056016
6        0.082734    0.557582    0.046385
1        0.126121    1.277301   -0.769964
1        0.133157    1.122438    0.982766
8        1.230304   -0.257043   -0.105397
```

```
1        1.235647   -0.918227    0.589594
END
```

Note that the first number in each line is the atomic number. For each structure, the order of the atoms should be the same.

One can specify an isotopic mass (in amu) after the coordinates for an atom. If there is nothing after the coordinates, the program uses the default mass, which is the mass of the most abundant isotope. One only needs to specify non-default isotopic masses in the first structure, and anything after the coordinates in the other structures will be ignored. Below is an example for specifying the deuterium mass in the CH_3CH_2OD molecule.

Note that an amu is a universal atomic mass unit equal to 1/12 the mass of a carbon-12 atom. The program uses the following conversion factor: 1 amu = 1822.888 atomic units of mass, where an atomic unit is the mass of an electron.

Example:

```
GEOM
6       -1.206324   -0.240211   -0.020995
1       -1.264318   -0.787854   -0.963519
1       -1.258873   -0.958451    0.795948
1       -2.072624    0.416915    0.056016
6        0.082734    0.557582    0.046385
1        0.126121    1.277301   -0.769964
1        0.133157    1.122438    0.982766
8        1.230304   -0.257043   -0.105397
1        1.235647   -0.918227    0.589594        2.014101777
END
```

MTOR

MTOR is a keyword to specify the $M_{j,\tau}$ values. The order of values should be consistent with the order of the dihedral angles defined in the $INTDEF section.

Example:

```
MTOR
  3     3
END
```

If several torsional modes are strongly coupled, one could use Voronoi tessellation to determine the $M_{j,\tau}$ values by using the utility code *vorm.exe* or *mcvorm.exe.* One runs the utility code separately and then inputs the noninteger $M_{j,\tau}$ values here.

Example:

```
MTOR
  2.532   2.532      3       3
END
```

Note that there is no default value for this keyword.

ROTSIGMA

ROTSIGMA is a keyword to specify the symmetry number of overall rotation for the structure given in the $STRUCTURE section. The default value is 1.

Example:

```
ROTSIGMA  2
```

WEIGHT

WEIGHT is a keyword to specify the number of structures that have the same energy and vibrational frequencies as that specified in GEOM. For example, if the geometry given in GEOM has a mirror image structure, one can specify a weight of 2 and only include one of the structures. The default value is 1.

Example:

```
WEIGHT 2
```

7. 1. H. Description of the *hess.dat* input file

The *hess.dat* file contains Hessians for the structures given in the $STRUCTURE sections in the main input file. The only section name is $HESS in *hess.dat* file. Each $HESS should be numbered consistently with the $STRUCTURE sections in the main input file. The Hessian should be given as in upper triangular packed form in unscaled Cartesian coordinates in hartree/bohr^2. Note carefully the ordering of the matrix elements. Each line can have an arbitrary number of elements except that each line cannot exceed 80 characters.

Example:

$HESS 1
F11 F12 F22 F13 F23 F33
F14 F24 F34 F44 F15 F25
F35 F45 F55 F16 F26 F36
F46 F56 F66
END

7. 2. Input files for the *ConfGen.exe* executable

The executable *ConfGen.exe* generates a list of conformational structures by rotating a set of user-specified bonds of an input structure over a specified grid. The program writes each generated structure to a file in *Gaussian* input format.

Example:

```
19      2       ! number of atoms and rotating bonds
C       -10.440384  -1.363155  -2.523127 ! Cartesian coordinates
……
# TORSION 1 DEFINITION (COMMENT LINE)
5 8     !define rotation axis as the bond between atom 5 and atom 8
7       !number of atoms in one fragment
1 2 3 14 5 6 7  ! atom numbers of this fragment
3               ! number of values that the dihedral angles take
0.0 120.0 -120.0        ! angle values by which the torsion will be rotated
#TORSION 2 DEFINITION (COMMENT LINE)
8 11    !define rotation axis as the bond between atom 8 and atom 11
10      !number of atoms in one fragment
 1 2 3 14 5 6 7 8 9 10   ! atom numbers of this fragment
3                       ! number of values that the dihedral angles take
0.0 120.0 -120.0        ! angle values by which the torsion will be rotated
%nproc=8                ! number of processors for Gaussian job
%mem=600mb              ! memory
# Method/Basis          ! route section
0 1                     ! charge and multiplicity
Extbasis                ! line at the end of the Gaussian input file for other options
(such as using external basis sets)
```

Note that this utility code removes all the generated structures that show an interatomic distance smaller than a specific tolerance, currently set at 0.5 Å. (If users wish to use a different tolerance, they will need to modify the parameter "smalldist" that appears in the module "confgen_param" listed at the top of the ConfGen.f90 file and then recompile.)

7. 3. Input files for the *kpmoments.exe* executable

The executable *kpmoments.exe* calculates reduced moments of inertia by the method of Kilpatrick and Pitzer (KP). The input file for *kpmoments.exe* is illustrated by the following example.

Example: (1-butanol)

```
15 5          ! number of atoms and number of frames
0.00000000   0.00000000   0.00000000  1.00782503207     1
0.00000000   0.00000000   0.95000000  15.99491461956    1
1.32452586   0.00000000   1.40960337  12.0              2
2.11134566   1.20846054   0.96134036  12.0              3
3.52426612   1.22340239   1.50755872  12.0              4
4.31853757   2.43052798   1.05637017  12.0              5
5.32525047   2.41970290   1.46196246  1.00782503207d0   5
1.26090910  -0.01952514   2.49366282  1.00782503207d0   2
1.83970151  -0.91390364   1.10583534  1.00782503207d0   2
 1.58023648   2.10625129   1.27164940 1.00782503207d0   3
 2.14464785   1.23080044  -0.12912254 1.00782503207d0   3
 4.03977823   0.31375819   1.20306619 1.00782503207d0   4
 3.48797307   1.19751170   2.59554571 1.00782503207d0   4
 3.84329672   3.35364351   1.37650469 1.00782503207d0   5
 4.39964721   2.46369549  -0.02679096 1.00782503207d0   5
1 2 0 0 0    !  connectivity of frame chain
1 2 3 0 0    ! connectivity of frame chain
1 2 3 4 0    ! connectivity of frame chain
1 2 3 4 5    ! connectivity of frame chain
2 3          !start rotation axis
3 4
4 5
5 6
```

Lines 2–16 give the Cartesian coordinates (in Å) in the first three columns for each atom, the mass of each atom in the fourth column, and the label of the frame in the fifth column. Lines 17–20 give the connectivity of the frames that is explained in Sect. 7.1.C and 7.1.D. Lines 21–24 define the rotation axis for each torsion; the numbers in these lines are the numbers of the atoms, not the frame numbers.

7. 4. Input files for the *mcvorm.exe* executable

The executable *mcvorm.exe* calculates $M_{j,\tau}$ values defined by Voronoi tessellation of the torsional space by Monte Carlo sampling. This program can handle cases of arbitrary dimensionality.

The input file (*mvorm.inp*) for *mcvorm.exe* is illustrated by the following example.

Example:

```
2        !number of torsions (dimensions)
5        !number of structures in the input
0.005    !Monte Carlo standard error
2  1     !symmetry number for each torsion
-152.3      65.1   ! values of the dihedral angles for the first structure
 159.7     178.8   ! values of the dihedral angles for the second structure
  84.3    -180.0   ! values of the dihedral angles for the third structure
 152.3     -65.1   ! values of the dihedral angles for the fourth structure
-159.7    -178.8   ! values of the dihedral angles for the fifth structure
```

The text after the ! symbol is an optional comment that explains the input of that line. Starting from the fifth line, each line lists the dihedral angles of the torsions for each structure.

7. 5. Input files for the *msinput.exe* executable

The *msinput.exe* is a utility program to generate a template main input file (named *mstor.inp*) and *hess.dat* input file by extracting the needed information from *Gaussian* formatted checkpoint files. All the *Gaussian* formatted checkpoint files must be combined into a single file and this single file is the input file of the *msinput.exe* program.

Note that the generated *mstor.inp* file cannot be used directly as an input file of the *mstor.exe* program because many parameters are not assigned, and some of them are assigned to some temporary numbers (e.g., the internal coordinates are not written). The Cartesian coordinates (in Å) and relative energies (in kcal/mol with the lowest energy set to 0) in the *mstor.inp* file and the Hessians in the *hess.dat* file are taken from the checkpoint file.

If the output *mvorm.out* file from *mcvorm.exe* is given, this utility code will take the M_j values from the *mvorm.out* file (do not rename the *mvorm.out* file name). However, if the Voronoi tessellation calculation only includes a subset of the torsions, which is often the case, the user needs to input other *M* values for uncoupled torsions manually in the *mstor.inp* file.

This program uses the *symmetry.exe* code to determine the weight and the symmetry number of overall rotation of each structure.

7. 6. Running the *mvinput.exe* executable

The *mvinput.exe* is a utility program to generate a template input file, named *mvorm.inp*, for the *vorm.exe* and/or *mcvorm.exe* programs by extracting the information from *Gaussian* optimization output files or formatted checkpoint files. Users have two ways to run the utility program *mvinput.exe* to check and prepare the input file for *mcvorm.exe* program (Voronoi tessellation):

(1)The user can be asked to provide the necessary information interactively. The number of coupled torsions included should *exclude* $–CH_3$ groups or any other $–XY_3$ groups in which the group has C_{3v} symmetry. The definition of the torsions to specify a dihedral angle between the *abc* plane and the *bcd* plane should be in the form: *a b c d*. For instance:

```
Please provide necessary information...

 Input total number of coupled torsions:
 (Excluding -XH3 (X = C, Si etc.)!!)
5
 Input definitions of these torsional angles:
 (Define one dihedral angle at each line)
18 17 15 16
17 15 16 5
15 16 5 13
16 5 13 14
1 5 6 9
```

If you have included nearly planar $–CH_2$ groups (or, in general, nearly planar $–XY_2$) in the above definition, the code will ask you to input further information. For instance, in the above definition, the first and the fourth dihedral angles are $–CH_2$ groups. In this case you respond as follows to some additional questions:

```
Did you include any nearly-planar -XH2 or tetrahedron -XH3 in the above definitions?
 (yes/no)
yes
 Total number of -XH2 or -XH3 you included in the above definitions is?
2
 And these are:
 (If the j-th defined torsion is -XH2 or -XH3, input: j)
 (Define one j value at each line)
1
4
```

(2) The user can also combine all *fchk* files of geometry optimizations into a single file. The user should put the number of structures on the first line of the file and the four atom numbers to define the torsions on each of the following lines. This single combined file can be used as the input file of *mvinput.exe*, i.e., *./mvinput.exe input_file_name.*

The program uses the *symmetry.exe* code to determine the symmetry point group of each structure and in certain cases, as outlined below, it adds missing mirror image structures. However, if in the interactive dialogue, the program was told that the molecule has a chiral center, no images are added. This is because the mirror images (enantiomers) of a molecule with a chiral center cannot be interconverted via internal rotations, so only one of the enantiomers should be included in the tessellation (the one that has the same chiral-atom configuration that the user used in the initial configuration generation step). If a structure of a molecule lacking a chiral center has no S_n (*n*-fold improper rotation axis), that is, it may be chiral, the values of the dihedral angles corresponding to its mirror images are automatedly included in the output file (*mvorm.inp*). But, in some unusual circumstances this can lead to two different enantiomers being present in the output file. In general, for chiral molecules, only structures corresponding to one enantiomer should be included in the tessellation calculations—even if there is sufficient energy for enantiomer interconversion—unless these enantiomers are converted via a treated torsional motion. In these circumstances, user must manually remove some structures before running vorm.exe or mcvorm.exe codes. In some rare cases (for instance, substituted allenes), in which the molecule does not contain any chiral atom but the molecule is itself a chiral molecule, and the enantiomers cannot be interconverted via internal rotations, the user should also answer "yes" to the question "Is there any chiral atom in the molecule?" when running the *mvinput.exe* utility, in order to prevent the code from automatically adding spurious mirror images.

Again, we want to stress that the *mvinput.exe* utility code does not check for missing structures that are related by an overall rotation to input structures; all such structures need to be included in the tessellation and it is the user's responsibility to make sure that they are accounted for. Actually, the user does not need to worry about this issue as long as an exhaustive conformational search is carried out.

In all cases the generated *mvorm.inp* file must be checked carefully by the user before using it. For example, the symmetry numbers for all torsions in the generated file are always set to 1 and must be reset appropriately by the user.

7. 7. Input files for the *tes.exe* executable

The *tes.exe* executable is a utility program to calculate 1-D torsional partition functions using the torsional eigenvalue summation (TES) method. The TES method is described in: B. A. Ellingson, V. A. Lynch, S. L. Mielke, and D. G. Truhlar, Journal of Chemical Physics **125**, 84305/1–17 (2006). Here is a brief description of the method.

A Fourier cosine series is used to represent a 1-D torsional potential:

$$V = \sum_{j=0}^{j_{\max}} b_j \cos(j\phi) \qquad (43)$$

where $j_{\max}$ is the maximum order to be used, b_j is a coefficient, and ϕ is torsional coordinate. The user needs to input a reduced moment of inertia and a number of potential energy values

along the torsional coordinate; these values are used to fit the coefficients of the Fourier cosine series. The Hamiltonian with this fitted potential is represented in a basis of the form $(1/\sqrt{2\pi})\exp(ik\phi)$ and diagonalized. The resulting eigenvalues are then used to calculate a partition function for a one-dimensional separable torsion with a constant reduced moment of inertia. This algorithm is not used anywhere in a MS-T calculation; it is simply provided in case a user wishes to calculate comparison results.

The input file for the *tes.exe* is illustrated by the following example.

Example:

```
2
0.7456101 ! moment of inertia (in amu*Å2)
200       ! number of eigenvalues to be calculated
1.00      ! frequency scaling factor
10        ! number of terms in a Fourier cosine series to be used in potential fitting
41        ! number of input data (angles in degree and energy in kcal/mol)
59.65955        0      ! value of the angle in degree and energy in kcal/mol
68.65955        0.053651993
77.65955        0.206199357
              :                       :
3             ! number of temperatures
200           ! temperatures in K
800
2000
```

7. 8. Input files for the *vorm.exe* executable

The executable *vorm.exe* calculates M_j values using Voronoi tessellation, and it can only handle 2-D and 3-D cases; for higher-dimensional systems the Monte Carlo based mcvorm.exe code may be used. This program calls *hull.exe* to perform the Voronoi tessellation calculations, and then reads the output of *hull.exe*.

The input file for the *vorm.exe* is illustrated by the following example.

Example:

```
2         ! number of torsions
5         ! number of structures
2  1      ! symmetry number for each torsion
-152.3         65.1  ! values of the dihedral angles for the first structure
 159.7        178.8
  84.3       -180.0
 152.3        -65.1
```

-159.7 -178.8

Explanation of the example: The first line is the number of torsions; the second line gives the number of structures; the third line gives the symmetry number of each torsion; starting from the fourth line, each line has the dihedral angles of the torsions for each structure.

In the *mstor/utili/vorm-test/* directory, five examples of using *vorm.exe* for calculating M_j values are provided, and their output files are located in the *mstor/utili/vorm-test/* directory.

7. 9 Input files for *DLMSTor.exe* executable

The generation of inputs for carrying out dual-level MS-T calculations is done by the following steps.

(1) Do a conformational search with a lower-level electronic structure theory, and pick out distinguishable conformers; we name this set of conformers as set L.

(2) Pick the first *N* lowest-energy conformers from set L (the value of *N* is based on users' choice); we name these picked conformers as set P. Re-optimize the conformers in set P with higher-level electronic structure theory, and pick out distinguishable conformers; we name this set of conformers as set H.

(3) Remove the conformers, which are in the difference set P\H, from set L (here, the notation P\H is the standard set-theory notation, which means $P \setminus H = \{x \in P, x \notin H\}$). This step removes the conformers that are distinguishable at the low level, but actually are redundant or not the correct structures at the higher level.

(4) Carry out frequency calculations for conformers in set L with lower-level theory (The title line of the *Gaussian* input must be the same as the name of the file, i.e., sXXXXXX, which is the automatically generated title for conformer XXXXXX in the conformational search step); create an empty file named *LAll.fchk* and put all the *sXXXXXX.fchk* files of the frequency calculations into *LAll.fchk*.

(5) Carry out frequency calculations for conformers in set H with higher-level theory (The title line of the *Gaussian* input must be the same as the name of the file, i.e., sXXXXXX); create an empty file name *Hpart.fchk* and put all these frequency *.fchk* files into *Hpart.fchk*.

(6) Execute *DLMSTor.exe* (i.e., *./DLMSTor.exe*), and the program will ask you to input the scale factor for the higher-level theory and for the lower-level theory, and to choose the option for reference (please input "0"); a new file named *HAll.fchk* is automatically generated.

(7) In *HAll.fchk*, add and input the total number of coupled torsions in the first line (excluding -XH_3 group (X = C, Si etc.)); and then define these torsions at each following lines. For instance, the beginning of *HAll.fchk* should be like (if you have 3 coupled torsions):

```
3
18  17  15  16
17  15  16  5
1   5   6   9
```

(8) Proceed to compute *M* values, i.e., first executing *mvinput.exe* (*./mvinput.exe*), then *mcvorm.exe* (*mcvorm.exe < mvorm.inp > mvorm.out*), and generate *mstor.inp* (*msinput.exe < HAll.fchk*), **with HAll.fchk**. After you generated *mstor.inp*, in the same directory, please execute *DLMSTor.exe* again, and this time the program will modify the *mstor.inp* file. The modified *mstor.inp* file contains "raiseL 100", which means the frequency of the *lower-level theory*

conformers will be replaced by floor frequency 100 cm^{-1}, if lower-level computed frequency is smaller than the floor frequency. User can use other value of cutoff frequency; and we recommend the user to optimize this floor frequency especially at lower temperatures to minimize the effect of significant differences between the vibrational partition functions that are computed at higher-level and lower-level theory. A formula for optimization of the floor frequency is proposed in J. L. Bao, L. Xing, and D. G Truhlar, Journal of Chemical Theory and Computation 13 (6), 2511–2522.

(9) Make sure that in the new *mstor.inp* file, the frequency scale factor inputted is for the lower-level theory.

(10) Finally, one is ready to execute *mstor.exe*, and the results in *mstor.out* are then dual level MS-T results.

8. Test suites

The test suites have been designed to provide examples of input and output files for the *MSTor* program and its utility programs. The test suites include examples of radicals and transition structures as well as closed-shell molecules. The test suite is located in the *mstor/testrun/* directory, and the output files are in the *mstor/testo*/ directory. There are ten directories under *mstor/testrun/* as shown below:

Directory name	For program:
ConfGen-test	*ConfGen.exe*
kpmoments-test	*kpmoments.exe*
mcvorm-test	*mcvorm.exe*
msinput-test	*msinput.exe*
mstor-test	*mstor.exe*
mvinput-test	*mvinput.exe*
tes-test	*tes.exe*
vorm-test	*vorm.exe*
DLMSTor-test	*DLMSTor.exe*
C5H12	Independent C_5H_{12} test case for *ConfGen.exe*, *mvinput.exe*, *mcvorm.exe*, and *msinput.exe*

8.1. Test runs for *ConfGen.exe*

One input file, *2hexyl.inp*, for *ConfGen.exe* is given in the *mstor/testrun/ConfGen-test/* directory. This test run generates conformational structures for 2-hexyl radical. The initial structure is the all-trans structure. The *ConfGen.exe* program will generate 27 structures (including the initial one) by rotating three C–C bonds.

8.2. Test runs for *kpmoments.exe*

Two input files, *kp_butanol.inp* and *kp_butanol.inp*, are given in the *mstor/testrun/kpmoments-test/* directory. The two input files use the same molecule/geometry, but they label the frames differently.

8.3. Test runs for *mcvorm.exe*

Seven input files for the *mcvorm.exe* are given in the *mstor/testrun/mcvorm-test/* directory. They cover cases from 2D to 6D Monte Carlo sampling of the Voronoi volumes. All test runs set the target Monte Carlo standard error for *M* values to 0.005. These test runs are outlined below.

Dimensions	Input files	Description
2D	pentyl-2d-set1.dat	5 structures of 1-pentyl radical using a scheme with NS:SC = 2:2
	pentyl-2d-set2.dat	5 structures of 1-pentyl radical using NS:SC = 2:2.
3D	butanol.dat	29 structures of 1-butanol
	pentyl_3d.dat	15 structures of 1-pentyl radical
4D	test-4d.dat	16 evenly distributed points in 4D torsional space with each torsional coordinate going from 0 to 360 degrees.
5D	test-5d.dat	32 evenly distributed points in 5D torsional space with each torsional coordinate going from 0 to 360 degrees.
6D	test-6d.dat	64 evenly distributed points in 6D torsional space with each torsional coordinate going from 0 to 360 degrees.

8.4. Test runs for *msinput.exe*

One input file (*ethanol-all.fchk*) is in the *mstor/testrun/msinput-test/* directory. This input file contains two formatted checkpoint files of ethanol (two conformational structures) from *Gaussian 09* calculations. The msinput.exe program will generate two output files, *mstor.inp* and *hess.dat* from this run.

8.5. Test runs for *mvinput.exe*

One input file (*1-pentyl-all.fchk*) is in the *mstor/testrun/mvinput-test/* directory. This input file contains eight formatted checkpoint files of 1-pentyl radical (eight conformational structures) from *Gaussian 09* calculations. The *mvinput.exe* program will generate one output file,

mvorm.inp from this run. This *mvorm.inp* file can be used as a template of the input file for *vorm.exe/mcvorm.exe* calculation.

8.6. Test runs for *mstor.exe*

All test cases except the test calculations of the density of states include three *mstor.inp* files; one uses a default redundant internal coordinates scheme named ***.dat, the second uses a nonredundant internal coordinates scheme named ***_NonRed.dat, and the third uses the user-defined redundant internal coordinates named ***_Red_RICs.dat. Examples: ethanol.dat, ethanol_NonRed.dat, and ethanol_Red_RICs.dat.

8.6.1. Ethanol

Input files for ethanol are given in the *mstor/testrun/mstor-test/ethanol/* directory.

8.6.2. 1-Butanol

Input files for 1-butanol are given in the *mstor/testrun/mstor-test/butanol*/ directory.

8.6.3. 1-Pentyl radical

Input files for 1-pentyl are given in the *mstor/testrun/mstor-test/pentyl*/ directory. Three test runs using different NS:SC schemes for $M_{j,\tau}$ values are given in this directory. They all share the same *hess.dat* file for Hessians.

Test run main input	Description
1-pentyl-intM.dat	Integer $M_{j,\tau}$ values (4:0 scheme)
1-pentyl-2dvor.dat	$M_{j,\tau}$ values obtained by NS:SC = 2:2
1-pentyl-3dvor.dat	$M_{j,\tau}$ values obtained by NS:SC = 1:3.

8.6.4. 1,4-Hydrogen shift saddle point of pentyl radical

Input files for 1, 4-hydrogen shift saddle point of pentyl radical are given in the *mstor/testrun/mstor-test/pentyl-ts14*/ directory. There are two pairs of mirror images for the saddle point in the input file, but only the terminal methyl group torsion is treated by torsional corrections because these four structures cannot be interconverted through internal rotations.

8.6.5. *n*-propylbenzene

Input files for *n*-propylbenzene are given in the *mstor/testrun/mstor-test/n-propyl/* directory.

8.6.6. 2-hexyl

Input files for 2-hexyl are given in the *mstor/testrun/mstor-test/2-hexyl/* directory.

8.6.7. $C_6H_9O_6$ radical (5-hydroperoxy-6-oxohexanoylperoxy radical)

Input files for $C_6H_9O_6$ radical are given in the *mstor/testrun/mstor-test/C6H9O6/* directory.

8.6.8. Hydrogen abstraction saddle point of cyclopentane + ethyl group

Input files for saddle point of hydrogen abstraction reaction of cyclopentane by ethyl radical are given in the *mstor/testrun/mstor-test/cyclopentane_ts/* directory.

8.6.9. Test case for calculating the density of states of *n*-propylbenzene

Input files for calculating the density of states for *n*-propylbenzene are given in the *mstor/testrun/mstor-test/dos_test_n-propyl/* directory. This test will take ~15 minutes.

8.7. Test runs for *tes.exe*

One input file, *ethanol-OH.inp*, is given in the *mstor/testrun/tes-test/* directory. This input file contains a potential of the internal rotation of the hydroxyl group in ethanol.

8.8. Test runs for *vorm.exe*

Five input files are given in the *mstor/testrun/vorm-test/* directory for the *vorm.exe* program. These test runs are described below.

Dimensions	Input files	Description
2D	pentyl-2d-set1.dat	5 structures of 1-pentyl radical using NS:SC = 2:2
	pentyl-2d-set2.dat	5 structures of 1-pentyl radical using NS:SC = 2:2
	pentyl-2d-set3.dat	5 structures of 1-pentyl radical using NS:SC = 2:2
3D	butanol.dat	29 structures of 1-butanol
	pentyl_3d.dat	15 structures of 1-pentyl radical using NS:SC = 1:3

9. Computers, operating systems, and compilers on which the code has been tested

9.1. Version 2011

Computer	OS	Compiler[1]
Itasca[2]	SuSE Linux Enterprise Server 11 SP1	ifort/11.1 and icc/11.1 gfortran/4.4 and gcc 4.4
Calhoun[3]	SuSE Linux Enterprise Server 10 SP3	ifort/11.1 and icc/11.1 gfortran/4.4 and gcc 4.4
Koronis[4]	SuSE Linux Enterprise Server 11 SP1	ifort/11.1 and icc/11.1 gfortran/4.4.3 and gcc/4.4.3
Elmo[5]	SuSE Linux Enterprise Server 10 SP3	ifort/11.1 and icc/11.1 gfortran/4.4.3 and gcc/4.4.3
Mac (Intel Xeon)	Mac OS X 10.5.8	gfortran/4.4 and gcc 4.4

1. On most computers, two sets of compilers were tested.
2. Itasca is a Linux cluster of HP Proliant BL280c G6 Blade servers.
3. Calhoun is an SGI Altix XE 1300 cluster.
4. Koronis is a constellation of SGI systems.
5. Elmo is a Sun Fire X4600 Linux cluster.

9.2. Version 2011-2

Computer	OS	Compiler[1]
Itasca[2]	SuSE Linux Enterprise Server 11 SP1	ifort/11.1 and icc/11.1 gfortran/4.4 and gcc 4.4
Calhoun[3]	SuSE Linux Enterprise Server 10 SP3	ifort/11.1 and icc/11.1 gfortran/4.4 and gcc 4.4
Koronis[4]	SuSE Linux Enterprise Server 11 SP1	ifort/11.1 and icc/11.1 gfortran/4.4.3 and gcc/4.4.3
Elmo[5]	SuSE Linux Enterprise Server 10 SP3	ifort/11.1 and icc/11.1 gfortran/4.4.3 and gcc/4.4.3
Mac (Intel Xeon)	Mac OS X 10.5.8	gfortran/4.4 and gcc 4.4

1. On most computers, two sets of compilers were tested.
2. Itasca is a Linux cluster of HP Proliant BL280c G6 Blade servers.
3. Calhoun is an SGI Altix XE 1300 cluster.
4. Koronis is a constellation of SGI systems.

5. Elmo is a Sun Fire X4600 Linux cluster.

9.3. Version 2011-3

Computer	OS	Compiler[1]
Itasca[2]	SuSE Linux Enterprise Server 11 SP1	ifort/11.1 and icc/11.1 gfortran/4.4 and gcc 4.4
Calhoun[3]	SuSE Linux Enterprise Server 10 SP3	ifort/11.1 and icc/11.1 gfortran/4.4 and gcc 4.4
Koronis[4]	SuSE Linux Enterprise Server 11 SP1	ifort/11.1 and icc/11.1 gfortran/4.4.3 and gcc/4.4.3
Elmo[5]	SuSE Linux Enterprise Server 10 SP3	ifort/11.1 and icc/11.1 gfortran/4.4.3 and gcc/4.4.3
Mac (Intel Xeon)	Mac OS X 10.5.8	gfortran/4.4 and gcc 4.4

1. On most computers, two sets of compilers were tested.
2. Itasca is a Linux cluster of HP Proliant BL280c G6 Blade servers.
3. Calhoun is an SGI Altix XE 1300 cluster.
4. Koronis is a constellation of SGI systems.
5. Elmo is a Sun Fire X4600 Linux cluster.

9.4. Version 2013

Computer	OS	Compiler[1]
Itasca[2]	CentOS 6.2	ifort/11.1 and icc/11.1 gfortran/4.4 and gcc 4.4
Calhoun[3]	CentOS 6.2	ifort/11.1 and icc/11.1 gfortran/4.4 and gcc 4.4
Koronis[4]	SuSE Linux Enterprise Server 11 SP1	ifort/11.1 and icc/11.1 gfortran/4.4.3 and gcc/4.4.3 gfortran/4.4.3 and gcc/4.4.3
Mac (Intel Xeon)	Mac OS X 10.8.2	gfortran/4.4 and gcc 4.4

1. On most computers, two sets of compilers were tested.
2. Itasca is a Linux cluster of HP Proliant BL280c G6 Blade servers.
3. Calhoun is an SGI Altix XE 1300 cluster.
4. Koronis is a constellation of SGI systems.

9.5. Version 2017-A and 2017-B

Computer	OS	Compilers
Mesabi[1]	CentOS 6.9	ifort/13.1.3.192 and icc/13.1.3.192

[1] Mesabi is an HP Linux cluster using Intel Haswell E5-2680v3 processors.

9.6. Version 2023

Computer	OS	Compilers
HP Linux cluter[1]	CentOS 7.3	ifort/18.0.5 and icc/18.0.5 gfortran/9.3.0 and gcc/9.3.0
HP workstations[2]	Opensuse tumbleweed Linux kernel 6.0	gfortran/12.2.1 and gcc/12.2.1 NVidia HPC Fortran compiler pgfortran (version 21.3)

[1] This cluster uses Intel Xeon E5-2603v3 processors.
[2] These machines use Intel i9-9900 and Intel i7-11700 processors.

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11. Revision history

Version 2011 (October 6, 2011)

Authors: J. Zheng, S. L. Mielke, K. L. Clarkson, and D. G. Truhlar

This is the first distributed version.

Version 2011-2 (November 2, 2011)

Authors: J. Zheng, S. L. Mielke, K. L. Clarkson, and D. G. Truhlar

This revision added the capability to calculate the heat capacity at constant pressure by using a four-point central finite difference scheme.

In addition, more comments were added to the source code.

Version 2011-3 (February 15, 2011)

Authors: J. Zheng, S. L. Mielke, K. L. Clarkson, and D. G. Truhlar

This is the first version distributed by *CPC*.

This revision added one more utility program, in particular a program to calculate 1-D torsional partition functions using the torsional eigenvalue summation (TES) method.

Version 2011-3-A (December 19, 2012)

Authors: J. Zheng, S. L. Mielke, K. L. Clarkson, and D. G. Truhlar
Contributors to this revision: J. Zheng and D. G. Truhlar

This revision has a bug fixed in the *vib.f90* file. Line 33 is uncommented to initialize the array of center-of-mass coordinates as zero.

Version 2013 (January 31, 2013)

Authors: J. Zheng, S. L. Mielke, K. L. Clarkson, R. Meana-Pañeda, and D. G. Truhlar
Contributors to new revision: J. Zheng, R. Meana-Pañeda, and D. G. Truhlar

This revision was submitted to *Computer Physics Communication* in February 2013 by means of a new version announcement. This announcement has now been published (see page 8 of this manual).

New features and bug fixes:

- The MS-T method based on a coupled torsional potential is added, which is called MS-T(C), where C denotes coupled. The original method that is based on an uncoupled potential is called MS-T(U).
- The capability of treating linear bending motions is added.
- The sections $framechain and $framedef are no longer needed in the input file, which simplifies the input file. (Note that these sections were reintroduced into the code as optional, but strongly recommended, sections in version 2017.)
- The code for evaluating of the point group symmetry of a structure from Serguei Patchkovskii is included.
- The *mvinput.exe* utility program is added to generate the input file for the *vorm.exe* and/or *mcvorm.exe* codes. The *msinput.exe* utility code has been modified to write the *M* values taken from the *mvorm.out* file. Both *mvinput.exe* and *msinput.exe* use the *symmetry.exe* program to determine the point group of each structure.
- The *ConfGen.exe* has been completely written in Fortran 90 and reads news fields corresponding to the *Gaussian* input keywords.
- A bug in the generation of different structures that affects *ConfGen.exe*, *vorm.exe* and *mcvorm.exe* utility codes has been fixed

Version 2017 (June 23, 2017)

Authors: J. Zheng, S. L. Mielke, J. L. Bao, R. Meana-Pañeda, K. L. Clarkson, and D. G. Truhlar
Contributors to new revision: J. L. Bao, S. L. Mielke, and D. G. Truhlar

New features and bug fixes:

- A new utility code, *DLMSTor.exe*, was provided to allow dual level calculations.
- The $framechain and $framedef sections were reintroduced to the code as optional sections. If these sections are used, the **D** matrix is calculated using the scheme of Kilpatrick and Pitzer and one should always get correct values for the KP moments of inertia. If the user omits these sections, the **D** matrix is calculated from the inverse of the G_{tor} matrix, but one must choose the torsional coordinates carefully to ensure that this produces correct results. Use of the $framechain and $framedef sections is recommended. This option is explained in sections 7.1.C and 7.1.D of the manual.

- Various utility codes were modified to help ensure that structures that are equivalent under rotation to other structures (and thus indistinguishable when considering overall rotation and torsion) are still properly included in the Voronoi tessellation step (which does not fully exploit overall rotational symmetry).
- The *mcvorm.exe* utility code was modified to correctly calculate uncertainties and to take advantage of rotational symmetries (at least for linear chain molecules) and mirror-image symmetries, if present, in the calculation of the uncertainty estimates.
- The following sections of the manual were greatly improved:
  - 5.5. Treatment of rotational symmetry and mirror images
  - 5.6. Voronoi tessellation scheme for *M* values

Version 2017-A (Aug. 2, 2017)

We fixed the problem of minor bugs in the *input.f90* file affecting the counting of the number of degrees of freedoms for linear bending modes.

Version 2017-B (Nov. 20, 2017)

A minor improvement was made for mvinput.f90.

Version 2023 (Mar. 14, 2023)

Authors: J. Zheng, W. Chen, S. L. Mielke, J. L. Bao, K. L. Clarkson, R. Meana-Pañeda, X. Xu, and D. G. Truhlar
Contributors to new revision: W. Chen, J. Zheng, D. G. Truhlar, and X. Xu

New features:

- The MS-T(CD) method is added. This is a newly developed torsional identification approach using redundant internal coordinates based on Baker et al.'s delocalized redundant internal coordinates and on Zheng and Truhlar's torsional projection method. The new method circumvents the need in the previous MS-T(C) and MS-T(U) methods to define nonredundant internal coordinates, and it can straightforwardly separate any number of coupled torsions from the primitive Hessian.
- The code for automatic generation of redundant internal coordinates is included. By using the automatic generation procedure for internal coordinates, the MS-T(CD) method greatly simplifies the user input for MS-T calculations by automating the identification and separation of the coupled torsions, and it helps users obtain robust and consistent results.
- *MSTor* now sets the redundant internal coordinate scheme as default method.
- The *mstor.exe* code has been cleaned up by modifying the output format and information and by removing unused variables and arrays.
- A bug in the calculation of density of states has been fixed.
- A new keyword, MTUMME, has been added to the $GENERAL section of the input file of

mstor.exe. This keyword provides an option to write a density-of-state file for TUMME 2023 and later.

- *MSTor* now provides default values for the ESTEP and EMAX keywords.
- The *mvinput.exe* code has been modified.
- New test runs for *n*-propyl, 2-hexyl, $C_6H_9O_6$, cyclopentane_ts, and dos_test_n-propyl (runs 8.6.5–8.6.9) are added, and the MS-T(CD) calculations also are tested for the ethanol, 1-butanol, 1-pentyl radical, and the 1,4-hydrogen-shift saddle point of pentyl radical in the corresponding test runs (8.6.1-8.6.4).
- The manual has been correspondingly updated and improved.