Manual
Gaussrate 17-B

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Abstract:

Gaussrate 17 is a set of Fortran subroutines and Unix scripts for interfacing the *Polyrate* and *Gaussian 16* and / or *09* computer programs to one another for the purpose of carrying out direct dynamics calculations of gas-phase, liquid-phase, and solid–gas-interface chemical reaction rates of polyatomic species (and also atoms and diatoms as special cases) using the electronic structure methods available in *Gaussian 16* and or *09* to calculate the potential energy surface and *Polyrate* for the dynamics. The interface is based on the *Polyrate* hooks protocol. The dynamical methods used are (i) variational transion state theory based on a reaction path (or conventional transition state theory) and multidimensional semiclassical approximations for tunneling and nonclassical reflection and (ii) variable-reaction-coordinate variational transion state theory with single-faceted or multifaceted dividing surfaces. For reaction-path calculations, multistructural and multi-path variational transition state theory can be carried out with the *MSTor* code. Also for reaction-path calculations, liquid-phase computations can be carried out by turning on implicit solvation model in Gaussian (for instance, via the keyword SCRF=SMD). Rate constants may be calculated by any of the methods available in the *Polyrate* program for both tight and loose transition states.

Reactions involving tight transition states are treated by reaction-path variational transition state theory (RP-VTST). The methods are canonical variational transition state theory, microcanonical variational state theory, or conventional transition state theory with multidimensional semiclassical approximations for tunneling and nonclassical

reflection. Bimolecular and unimolecular reactions are included. Both single-level and dual-level calculations may be carried out. In single-level mode, optimized geometries, potential energies, gradients, and Hessians can be calculated by any of the ab initio or semiempirical methods in the *Gaussian 16 / 09* package. In dual-level mode, the lower-level data is calculated by *Gaussian16 / 09,* and the higher-level data is read in from an external file.

Reactions involving loose transition states are treated using canonical or microcanonical ensembles or energy- and total-angular-momentum-resolved microcanonical ensembles. Multifaceted dividing surfaces based on a variable reaction coordinate may be used. For loose transition states, only bimolecular association reactions are included, and single-level calculations may be carried out.

Gaussrate 17 provides an interface between these two programs:

Polyrate–version 2017, by J. Zheng, J. L. Bao, R. Meana-Pañeda, S. Zhang, B. J. Lynch, J. C. Corchado, Y.-Y. Chuang, P. L. Fast, W.-P. Hu, Y.-P. Liu, G. C. Lynch, K. A. Nguyen, C. F. Jackels, A. Fernandez Ramos, B. A. Ellingson, V. S. Melissas, J. Villà, I. Rossi, E. L. Coitiño, J. Pu, T. V. Albu, A. Ratkiewicz, R. Steckler, B. C. Garrett, A. D. Isaacson, and D. G. Truhlar, POLYRATE17, University of Minnesota, Minneapolis, 2017.

and

Gaussian 16 / 09, by M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT.

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1.   USER AGREEMENT

Gaussrate 17 is a licensed program, and the use of this program implies acceptance of the terms of the license, which are repeated here for convenience:

A. No user or site will redistribute the source code or executable code to a third party in original or modified form without written permission of the principal investigator (Donald G. Truhlar). A license does not entitle the licensee to relicense the code or distribute it in original or modified form to parties not covered by the license. The licensee has no ownership rights in the *Gaussrate 17* software or in any copyrights for the *Gaussrate 17* software or documentation through this license. A user license covers the work of a single research group and the code may be shared and disseminated within a group without requiring permission. Site-license inquiries should be directed to the principal investigator (Donald G. Truhlar).

B. Publications resulting from using this package or the *Polyrate* or GAUSSIAN subsystems used by this package will cite the corresponding program. The required references are given in the documentation (see Section 2 of this manual for the required references for *Gaussrate 17*).

C. No guarantee is made that this program is bug-free or suitable for specific applications, and no liability is accepted for any limitations in the mathematical methods and algorithms used within the program.

D. No consulting or maintenance services are guaranteed or implied.

E. The *Polyrate17*, and *Gaussian 16 / 09* codes, which are both required to use *Gaussrate 17*, are covered by separate licenses.

2. REQUIRED REFERENCES

Publications based on results obtained with this computer code should include the following three references:

1. J. Zheng, J. L. Bao, S. Zhang, J. C. Corchado, R. Meana-Pañeda, Y.-Y. Chuang, E. L. Coitiño, B. A. Ellingson, and D. G. Truhlar, *Gaussrate 17*, University of Minnesota, Minneapolis, MN, 2017.

2. J. Zheng, J. L. Bao, R. Meana-Pañeda, S. Zhang, B. J. Lynch, J. C. Corchado, Y.-Y. Chuang, P. L. Fast, W.-P. Hu, Y.-P. Liu, G. C. Lynch, K. A. Nguyen, C. F. Jackels, A. Fernandez Ramos, B. A. Ellingson, V. S. Melissas, J. Villà, I. Rossi, E. L. Coitiño, J. Pu, T. V. Albu, A. Ratkiewicz, R. Steckler, B. C. Garrett, A. D. Isaacson, and D. G. Truhlar, POLYRATE17, University of Minnesota, Minneapolis, 2017.

3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 16 / 09* Gaussian, Inc., Wallingford CT.

Additional references are given in the documentation for *Polyrate* and GAUSSIAN.

3. INTRODUCTION

Gaussrate 17 is a program for the analysis of reactants, products, and transition states of chemical reactions and for direct dynamics calculations of variational transition state theory (VTST) rate constants and multi-dimensional semiclassical tunneling probabilities. One can use reaction-path variational transition state theory or variable-reaction-coordinate variational transition state theory, using the electronic structure methods in the *Gaussian 16 / 09* package to represent the potential energy of interaction and its first and second derivatives whenever they are needed. This version, *Gaussrate 17*, interfaces *Polyrate*–version 17, which is a program for dynamical rate calculations, with the electronic structure program *Gaussian 16 / 09*.

Using *Gaussrate 17* presupposes that the user has both *Polyrate17* and *Gaussian 16 / 09* on the same computer working properly before attempting to run *Gaussrate 17*. No part of *Polyrate17* or *Gaussian 16 / 09* is contained in *Gaussrate 17* or needs to be modified for running this program.

This *Gaussrate 17* manual covers only material that is not covered in the *Polyrate* and *Gaussian 16 / 09* manuals. The user of *Gaussrate 17* should read those manuals first.

The interface between *Polyrate* and *Gaussian 16 / 09* is made by a series of Fortran subroutines included in the files `hooks_gr.f` and `hooks_mdep.f`, which are specialized versions of the routines in the `hooks.f` file in *Polyrate* 2016 and by a C shell script for running *Gaussian 16 / 09*. This C shell script, named `shuttle`, is called from inside *Gaussrate 17,* and it has to be able to start running *Gaussian 16 / 09* using an input file named as the first argument given to `shuttle`. It produces an output file named as the second argument given to `shuttle`. For the user's convenience, a well documented `shuttle` script is provided, and in most cases the user will only need to change one or two line, in order to set the *gausspath* `variable` to the appropriate path where *Gaussian 16 / 09* is located and to set the executable to g09. In the provided script, the variable *scratchdir*, which indicates the directory where the temporary and scratch *Gaussian 16 / 09* files are going to be located, is set to the working directory; if desired, the user can change this. In some systems, the `g09.login` files have to be loaded previously to any *Gaussian 16 / 09* calculations. In such a case, the user should

uncomment the line in the `shuttle` script that loads it or contact the system manager in order to get instructions about how to load this file.

Note that running two *Gaussrate 17* calculations or a GAUSSIAN and a *Gaussrate 17* calculation in the same directory can cause problems due to overwriting of some of the temporary files.

Gaussrate 17 uses a subroutine usually included in libraries provided with Fortran compilers. This subroutine is called *system*. The prospective user of *Gaussrate 17* should be aware that this utility program is needed for running *Gaussrate 17*.

Gaussrate 17 (and older versions of GAUSSRATE dating back to version 2008) can perform both reaction-path VTST (RP-VTST) and variable-reaction-coordinate VTST (VRC-VTST) calculations. The RP-VTST method can be used for arbitrary kinds of reactions with tight transition states; VRC-VTST should be used for loose transition states of bimolecular association reactions. The RP-VTST and VRC-VTST calculations use different executables, i.e. `gaussrate.exe` for RP-VTST and `gaussrate-vrc.exe` for VRC-VTST.

4.   DISTRIBUTION

Gaussrate 17 is a set of subroutines for interfacing *Polyrate* and GAUSSIAN. The user needs to obtain four items of code:

– *Polyrate*   The *Polyrate* code is a licensed code available from the University of Minnesota. Currently the license fee is waived for all users. For further information see:
`http://comp.chem.umn.edu/`*Polyrate*

– GAUSSIAN   *Gaussian 16 / 09* is a licensed code available from Gaussian Inc. For further information see:
`http://www.gaussian.com`

– *Gaussrate 17*   The *Gaussrate 17* code is a licensed code available from the University of Minnesota. Currently the license fee is waived for all users. For further information see:
`http://comp.chem.umn.edu/gaussrate`

– *system*   This utility code is also required. It is available in standard Fortran libraries:

The prospective user of *Gaussrate 17* must obtain and install *Polyrate* and *Gaussian 16 / 09* before proceeding with *Gaussrate 17*.

The *Gaussrate 17* program is distributed as a compressed tar file named `gaussrate2017.tar.gz`. The distributed file should be uncompressed and untarred in the `polyrate17` directory. To uncompress, enter:

```
gunzip gaussrate2017.tar.gz
```

The uncompressed file will be named `gaussrate2017.tar.tar`. After extracting the files from the tar file, which can be done with the command:

```
tar -xvf gaussrate2017.tar
```

A new directory, `gaussrate,,` is created. This directory contains all the files included in the distribution package. If these instructions are followed correctly, the directory structure should be the following tree structure:

```
                        Gaussrate2017
                             |
 ----------------------------------------------------------------
 |     |      |          |       |        |       |       |       |      |
doc   exe  gaussrate   obj    poten   script    src   testo  testrun util
                |
        -----------------------------------------
        |          |        |                    |
      script    source    testo              testrun
                            |                    |
                           ---         -----------------------------
                            |          |      |     |      |      |  |
                           g16       ch4oh  ch5   oh3   nh3oh   h3 c2h6
```

The files will be distributed among the directories as follows:

gaussrate   the C shell script `shuttle` and five subdirectories:

script   1 files: `grcompile`

source   5 files comprising the source code for *Gaussrate 17*: `alloc_gr.f90`, `head_gr.F`, `hooks_gr.F`, `hooks_mdep.F`, and `module_gr.f90`.

testo   This directory contains the following subdirectories:
            -g16:   `ch4ohtr1.fu15, ch4ohtr2.fu15, ch4ohtr3.fu15,`
                        `ch4ohtr4.fu15, ch4ohtr5.fu15, ch4ohtr6.fu15,,`
                        `ch4ohtr7.fu15, ch5tr1.fu15, ch5tr2.fu15,`
                        `oh3tr1.fu15, oh3tr2.fu15, oh3tr3.fu15,`
                        `nh3ohtr1.fu15, h3tr1.fu15, h3tr2.fu15,`
                        `c2h6tr1.fu15, ohso2.fu15, c6h6ch3.fu15,`
                        `butanoltr1.fu15, butanoltr2.fu15,`
                        `butanoltr2.xlsx, c2f4.fu15, c6h4oh2.fu15,`
                        `sih4.fu15.`

            This subdirectory contains output files of the test runs.

testrun   4 files: `check09` and `run_all.jc`, and subdirectories: `c2h6, ch4oh, ch5, oh3, nh3oh, h3, ohso2, c6h6ch3, butanol, c2f4, c6h4oh2, and sih4` with the input files for the test calculations.

5.   INSTALLATION

First the user should obtain licensed copies and install the *Polyrate17* and *Gaussian 16 / 09* packages. Next the user should obtain a licensed copy of the *Gaussrate 2017* package. After downloading, uncompressing, and untarring the *gaussrate2017.tar* file, the *Gaussrate17* package should appear as a directory, as described in Section 4.

The installation of the *Gaussrate 17* program is carried out by running the Perl script `configure`. The script will copy `hooks_gr.wks` to the `hooks_mdep.f`, will compile the *Polyrate17* files substituting the `hooks.f` file of standard *Polyrate* by `hooks_gr.f` and `hooks_mdep.f`, and will create the executable file `gaussrate.exe` in the `exe` subdirectory in the *Polyrate17* directory. The executable `gaussrate.exe` will then be accessible for all the *Gaussrate 17* calculations.

The installation script `configure` will interactively ask if you want to choose the option that compiles the codes using variable reaction coordinate variational transition state theory with multifaceted dividing surfaces for barrierless association reactions (for context, see the last paragraph of Section 3). This option will generate a separate executable file (`gaussrate-vrc.exe`) that is only used for VRC-VTST calculations. This code is parallelized using MPI. This capability was introduced beginning with version 2008.

Before running *Gaussrate 17,* two lines of the C shell script `shuttle` should be changed as described in Section 8, in order to set the *gausspath* variable to the appropriate path where *Gaussian 16 / 09* is located and set the command *g16* or *g09* used to run *Gaussian 16 / 09* jobs.

6.   PROGRAM DESCRIPTION

The *Gaussrate 17* program follows the *Polyrate* hooks protocol. This means that if energy, gradient, and/or Hessian calculations are desired by *Polyrate* , the program calls the appropriate hooks subroutine that will return that information. (The user may read more about hooks in the *Polyrate* manual.)

6.1.   Description of *Gaussrate 17* subprograms

This is a brief description of *Gaussrate 17* subprograms. In most of the cases, a more detailed description is given in the comment cards at the beginning of the Fortran code for each subprogram.

ehook   Equivalent to the *ehook* subroutine in the *Polyrate* hooks. For a given set of coordinates, it calculates the energy using *Gaussian 16 / 09*.

enatin   Calculates the energy for atomic systems.

escener   Carries out GAUSSIAN energy calculations.

escfirst   Carries our gaussian energy and first derivative calculations.

escsec   Carries out GAUSSIAN Hessian calculations.

geoin   Carries out GAUSSIAN geometry optimizations.

ghook   Equivalent to the *ghook* subroutine in the *Polyrate* hooks. For a given geometry, calculates the energy and first derivatives.

ginpene   Creates the GAUSSIAN input file for energy calculations.

ginpfrs   Creates the GAUSSIAN input file for gradient calculations.

ginpsec   Creates the GAUSSIAN input file for Hessian calculations.

goutsec   Reads the formatted checkpoint file `Test.FChk` generated by GAUSSIAN and extracts the geometry, energy, and first and second derivatives of the energy with respect to atomic coordinates.

grest   Reads and writes the information in the restart files of a *Gaussrate 17* restart calculation.

headr   Prints out the program header.

hhook   Equivalent to the *hhook* subroutine in the *Polyrate* hooks. For a given geometry, calculates the Hessian matrix using whether GAUSSIAN or *Polyrate* methods.

ohook   Equivalent to the *ohook* subroutine in the *Polyrate* hooks. Optimizes a given initial geometry, using either *Polyrate* or GAUSSIAN methods.

prep   Prepares the calculation and, depending on the selected options, carries out certain geometry optimizations and Hessian calculations.

prepj   Initialize variables dependent on each stationary point.

rchmul   Reads the charge and multiplicity of a system from the GAUSSIAN formatted checkpoint file.

rcodgr   Reads the input option for the GAUSSIAN runs from file `esp.fu70`.

redinf   Reads the information about reactants, products and saddle point calculated in the *prep* subroutine.

renergr   Reads the input options for GAUSSIAN energy calculations.

rfirstgr   Reads the input options for GAUSSIAN gradient calculations.

rgenbas   Reads the basis set for GAUSSIAN calculations when a nonstandard basis set is used.

rgengr   Reads the options in the general section of the `esp.fu70` input file.

rinpgr   Reads the `esp.fu70` *Gaussrate 17* input file.

rlincer   Reads the `Link0` options for GAUSSIAN calculations.

rlingr   Utility program for reading in a line of the `esp.fu70` input file and parsing off comments and extra spaces.

rsecgr   Reads the input options for GAUSSIAN Hessian calculations.

rstatgr   Reads the input options given in the `esp.fu70` input file for the stationary points.

secin   Carries out GAUSSIAN Hessian calculations for stationary points.

setup   Initializes some variables and calls the subroutines for reading in the `esp.fu70` input file.

store   Stores some information that could be useful in future calculations in order to avoid duplicate GAUSSIAN calls.

Note that *Gaussrate 17* does not use any of the utility routines (routines starting with *y*) of the generic hooks package of *Polyrate*.

6.2.   Restarting a calculation

The *Gaussrate 17* restart option should not be confused with the *Polyrate* restart options (see Section 7.C of the *Polyrate* manual). The *Polyrate* restart options can be used with *Gaussrate 17,* but *Gaussrate 17* also has its own, unique restart capability. The rest of this section concerns this *Gaussrate 17* restart capability.

The *Gaussrate 17* restart option is controlled by the GRRESTART keyword in the GRGENERAL section of the unit `esp.fu70` input file. The *Gaussrate 17* restart option is designed to take advantage of any previous calculations that may have been made on

the same system, so that the number of *Gaussian 16 / 09* calls is minimized. As long as the information on the stationary points from previous calculations is still applicable, a restart calculation can be made (if there is a change in any stationary point input or option, the program will not read this information, and the results of trying a restart calculation are unpredictable). This restart option allows the user to change any parameter related to the reaction path calculations using as much information as possible from previous calculations.

Two restart files are used in this kind of restart calculation: `esp.fu83`, which stores the information to be read, as originated in a previous *Gaussrate 17* calculation, and `esp.fu84`, where the useful information read from `esp.fu83` is stored along with the information calculated for the first time in the present *Gaussrate 17* run (`esp.fu84` is the file to be used for future restart runs). The `esp.fu84` file has to be created by *Gaussrate 17,* so if the program finds that this file exists, it will stop, to prevent overwriting a restart file.

One important practical point related to this restart option is that, if one finds that the range of the reaction path calculated in a *Gaussrate 17* run is not large enough to describe some effect (for example, tunneling), one can extend the calculated reaction path without repeating the calculation of the points included in the previous *Gaussrate 17* run. Also, one must check whether or not there is any imaginary frequency along the whole reaction path; and if there is, one should firstly try to eliminate all the imaginary frequencies by using an appropriate definition of internal coordinates (via "CURV2" or "CURV3" options). Along the reaction path, there should be no imaginary frequencies after projecting out the reaction coordinate degree of freedom. Unphysical / unreliable VTST results could be obtained if one ignores our advice about eliminating imaginary frequencies and using internal coordinates for the generalized normal mode analysis along the reaction path (Cartesian coordinates for generalized normal mode analysis along the reaction path are a bad choice in VTST calculations, and the user should not use it). One should rename the `esp.fu84` file provided by the first run as `esp.fu83` and then run again with GRRESTART on. In a similar way, if one finds problems in the SCF convergence at some points along the reaction path, one can repeat the calculation including some of the options for improving SCF convergence available in *Gaussian 16 / 09* without recalculating the well converged points. Another possibility is computing one side of the reaction path with one computer (or one processor of a multiprocessor computer) and the other side with a different computer (or different processor); a new

restart file combining the information from both calculations can be constructed by just appending one restart file to the end of the other restart file, allowing a calculation using the whole reaction path with no duplication of effort, at least in principle; in practice, due to the different precision of two different machines and round-off errors, some recalculation might be needed. One should be aware, though, that if a calculation is made using a step-size that is too large, giving a non-converged reaction path, a restart calculation using a different step-size would probably be unsuccessful, since the points along the two reaction paths would be different.

There is only one parameter related to the path that should not be changed between an original calculation and a restart calculation, namely the value of SCALEMASS. Changing this parameter will cause a miscalculation of the frequencies. It is important to note that its default value is 1.0 amu, and this is the value assumed if no reaction path calculation is desired. Therefore, if a restart calculation including the reaction path is based on a restart file written by a TST-only calculation, SCALEMASS must be set to 1 amu in order to get the right frequencies. In general, we recommend always using a value of 1.0 amu for SCALEMASS in *Gaussrate 17*.

A *Gaussrate 17* restart run requires that all the information about all the stationary points be present on file `esp.fu83`, and this data cannot be updated in this kind of restart run. However, the use of the STATUS keyword in the REACT1, REACT2, PROD1, PROD2, WELLR, WELLP, and START sections of the *Polyrate* `fu5` input file can alleviate this inconvenience. Thus, the user can calculate reactants and products separately and include the information obtained in the `fu5` input file. See the ch4oh test runs in the *Gaussrate 17* and Section 16.B of the *Polyrate* manual.

The *Gaussrate 17* restart option works in the following way: when *Polyrate* needs an energy, gradient, and/or Hessian for a given geometry, it first check if the geometry is stored in `esp.fu83`, and then it checks if the required information is stored in this same file. If one of these conditions is not fulfilled, a GAUSSIAN calculation is run to obtain the desired information. If both conditions are fulfilled, the information is read from `esp.fu83`, and no GAUSSIAN job is spawned. The geometry check is performed by comparing each of the Cartesian coordinates of the desired geometry with the Cartesian coordinates in `esp.fu83`. If the values differ by more than a criterion given by RSTTOL, the geometries are considered to be different. It is important to have an appropriate value for RSTTOL: if the criterion is too tight, the check might fail due to the numerical round-

off and to the fact that the precision of the written information is limited, and redundant calculations could be carried out, increasing unnecessarily the cpu time of the calculation. However, if this criterion is too loose, the check could be passed for two geometries that are only slightly different, but different enough to matter, and the restart option can be giving to *Gaussrate 17* inaccurate information. The later case can be especially true when performing reaction-path calculations with very small step-sizes, numerical differentiations, or accurate geometry optimizations. Therefore, the user must be very careful about changing this parameter. The default value is `1.D-8`, which is very conservative, but it is safe. For very expensive calculations, one might want to use a higher value, but a value that is too high can give unphysical results. If the user increases this parameter, he or she has to be very aware of the risk it posses in the calculation, and all the results must be carefully checked. Therefore, only experienced users are advised to change this parameter.

Note that the number of processors should not be changed when restarting a parallel calculation using variable reaction coordinate transition state theory for loose transition states.

6.3.   Parallel capabilities

The VRC-VTST code in the *Polyrate* program is highly parallelized using MPI. This portion of the program uses variable reaction coordinates and multifaceted dividing surfaces for association reactions with loose transition states. The most time-consuming part of the calculation is an integral on an eight-dimensional multifaceted hypersurface in the coordinate space of the interacting reactants. This integral is evaluated by the Monte Carlo method. The Monte Carlo integration requires thousands of samples of the energy to achieve a reasonably accurate result, and each sample requires a full electronic structure calculation by the GAUSSIAN program. Each core independently performs GAUSSIAN calculations for the Monte Carlo samples generated in that core. When the Monte Carlo sampling is finished on all cores, one core (rank 0 in MPI) is used to collect the data calculated on all the cores and to perform the rest of the calculations to get reaction rate constants.

GAUSSIAN has two parallel versions. One is an OpenMP or symmetric multiprocessing (SMP) version that is used in a shared memory system, and the other one is a Linda version that can be used in a distributed memory system. There are some technical

difficulties to use the Linda implementation of the GAUSSIAN program together with the MPI *Polyrate* code together. Therefore only the SMP version of GAUSSIAN is tested for *Gaussrate 2017.*

To run a parallel VRC-VTST calculation, the number of the cores to be used should be specified as a flag of the *mpirun* command in the *.jc* file (job control file). The same number of the cores should also be specified in the queue submission script. For example, if *n* cores are required for a parallel calculation, one should use the command "mpirun –np *n* gaussrate-vrc.exe" in a *.jc* file. Note that if the keyword "%nprocs=1" is set or omitted in the esp.70 file (see Section 7.4), each GAUSSIAN calculation is performed by one core, and *n* Monte Carlo samples are calculated simultaneously.

If desired, one can use two kinds of parallelism together in a VRC-VTST calculation. In particular, one can use multiple cores for each SMP GAUSSIAN calculation and also multiple cores for the MPI VRC-VTST code. Here is an example to show how to use this double parallel strategy at script level. Assume that *n* cores on each computer node are used in each SMP GAUSSIAN calculation and *m* computer nodes are used for the MPI VRC-VTST calculation.

- In the esp.70 file, one should add the "%nprocs=n" keyword that is used for each GAUSSIAN job.
- In the *.jc* file, one should use the command "mpirun –np *m* **–bynode** gaussrate-vrc.exe".
- In the *.pbs* submission file, one should specify the number of cores and nodes as "nodes=*m*: ppn=*n*".

In this setting, there are totally $n \times m$ cores are used in the whole VRC-VTST direct dynamics calculation. In this calculation, each GAUSSIAN calculation is performed by *n* cores, and *m* Monte Carlo samples are calculated simultaneously This hybrid parallel strategy is only recommended when a large number of cores are available, and of course it can only be used when each node has multiple cores.

The RP-VTST code in the *Polyrate* program only performs direct dynamics sequentially. However, RP-VTST calculations can be performed using multiple cores for direct dynamics by using them in each SMP GAUSSIAN calculation. For example, if *n* cores are available for an SMP GAUSSIAN calculation, the user can specify the number of cores by the "%nprocs=n" keyword in the esp.fu70 file (see Section 7.4) and require *n* cores in the queue submission script for RP-VTST calculations. Therefore, the whole dynamics

calculation is performed by the serial RP-VTST code sequentially, while each electronic structure calculation required for direct dynamics is performed in parallel.

7. DESCRIPTION OF INPUT FILES

We will assume that the user knows how to use *Polyrate* 2016 and *Gaussian 16 / 09* and is familiar with all their keywords. Therefore, when talking about the common input files, we will only discuss the differences between running *Polyrate* 2016 and running *Gaussrate 17.*

7.1. File usage

In addition to the *Polyrate* 2016 and *Gaussian 16 / 09* input files, *Gaussrate 17* uses several files of its own for input data, for storing restart information, and for output. All these files have the name `esp.fu#`, where # denotes an integer.

`esp.fu70`   General *Gaussrate 17* input data.

`esp.fu71`   *Gaussian 16 / 09* input file for geometry optimization of reactant 1, if such optimization is going to be carried out.

`esp.fu72`   *Gaussian 16 / 09* input file for geometry optimization of reactant 2, if the reaction studied is bimolecular and if such optimization is going to be carried out by means of the *Gaussian 16 / 09* program.

`esp.fu73`   *Gaussian 16 / 09* input file for geometry optimization of product 1, if such optimization is going to be carried out.

`esp.fu74`   *Gaussian 16 / 09* input file for geometry optimization of product 2, if the reaction studied has two products and if such optimization is going to be carried out by means of the *Gaussian 16 / 09* program.

`esp.fu75`   *Gaussian 16 / 09* input file for geometry optimization of the saddle point or constrained optimization of a reaction path starting geometry, if such optimization is desired.

`esp.fu76`   reserved

esp.fu77   *Gaussian 16 / 09* input file for geometry optimization of a well on the reactant side of the reaction path, if it exists and its optimization is going to be carried out by means of the methods in *Gaussian 16 / 09.*

esp.fu78   *Gaussian 16 / 09* input file for geometry optimization of a well on the product side of the reaction path, if it exists and its optimization is going to be carried out by means of the methods in *Gaussian 16 / 09.*

esp.fu81   *Gaussian 16 / 09* temporary input file, generated by *Gaussrate 17.*

esp.fu82   *Gaussian 16 / 09* temporary output file, generated by GAUSSIAN. If the *Gaussian 16 / 09* calculation fails, it can be examined in order to find out why the failure occurred.

esp.fu83   Restart file to be read during a restart calculation (see Section 6.1).

esp.fu84   Restart file to be written during a restart calculation (see Section 6.1).

esp.fu85   *Gaussrate 17* uses the formatted checkpoint file generated by *Gaussian 16 / 09. Gaussian 16 / 09* calls this file `Test.FChk`, and *Gaussrate 17* does not delete it. *Gaussrate 17* reads this file from Fortran unit 85. This file will not be removed after finishing a calculation, so if the *Gaussian 16 / 09* calculation fails, it can be examined in order to find the cause of the failure.

Note that this file usage is consistent with Section 17 of the *Polyrate* manual. Note also that `esp` stands for electronic structure package, and `fu` stands for Fortran unit. Finally note that `esp.fu76` is reserved for future use, but it is not used in this version.

7.2.   Description of `fu5` unit

A *Gaussrate 17* calculation requires some input from input units for *Polyrate.* At the very least, an `fu5` input file is required for indicating several options such as electronic degeneracies, temperatures for the rate constant calculations, etc. Therefore, an `fu5` file must be written, exactly as if we were using an analytical potential energy surface. If the

calculation requires some additional input files, the user must provide them, following the instructions in the *Polyrate* 2016 manual. It is important to clarify some points about preparing the input file for unit `fu5`:

RESTART

If a *Polyrate* restart run is selected (option *readfu1* or *readfu1&2* for the RESTART keyword in the GENERAL section), the program will not modify any characteristic of the calculated reaction path. We therefore advise the user to use only the restart option in *Gaussrate 17,* controlled by the GRRESTART keyword in GRGENERAL section of the `esp.fu70` input file, until the reaction path calculation is completely converged and all the desired tunneling options are calculated. When no more electronic structure calculations are required, the *Polyrate* restart is recommended, since it is faster than the *Gaussrate 17* restart.

ATOMS

The ordering in the ATOMS keyword list of the GENERAL section of the input file for unit `fu5` must be consistent with the ordering in unit `fu75`, if this unit is used in the calculation.

NOSUPERMOL

Because of the way the interface is constructed, the NOSUPERMOL keyword is required (note that SUPERMOL is the default option). Therefore, only size-consistent methods should be used in *Gaussrate 17*.

EZERO

Because of the way the interface is constructed, the user must choose the *calculate* option for the EZERO keyword of the ENERGETICS section, which is the default option.

POTENTIAL

The *hooks* option is required.

OPTTS and **OPTMIN**

In *Gaussrate 17* there are two ways to optimize the geometries: by means of *Gaussian 16 / 09* methods or by means of *Polyrate* methods. The choice between the two methods is done in the OPTIMIZATION section of the `fu5` input file. Choosing the option *BFGS*, *NR*, or *EF*, for the OPTMIN or OPTTS keywords in the OPTIMIZATION section, will cause *Gaussrate 17* to use the methods native to *Polyrate* , using as starting geometries those in the `fu5` input file and controlling the optimization procedure by means of the keywords selected in the OPTIMIZATION section of the `fu5` input file. In these cases, the input files `fu71` through `fu75` will not be required. The INITGEO keyword needs to take the option *GEOM* in the REACT1, REACT2, PROD1, PROD2, WELLR, WELLP, and START sections of the `fu5` input file.

If the option *OHOOK* is chosen for both the OPTTS and OPTMIN keywords in the OPTIMIZATION section of the `fu5` input file, *Gaussrate 17* will optimize the geometries of the stationary points using the *Gaussian 16 / 09* program according to the options selected in the `fu70` input file and the `fu71-fu78` input files. The initial geometries for the optimization will be those indicated in the `fu71-fu78` input files and the options selected in the OPTIMIZATION section in the `fu5` input file will be ignored. INITGEO should take the value *HOOKS* in the REACT1, REACT2, PROD1, PROD2, WELLR, WELLP, and START sections of the `fu5` input file.

If the user wishes to optimize the stationary points, we recommend the use of *Gaussian 16 / 09* methods; in particular this is accomplished by using the *OHOOK* option for both the OPTMIN and the OPTTS keyword in the OPTIMIZATION section of the `fu5` input file, using initial geometries given in the `fu71` through `fu75` input files, and setting INITGEO equal to *HOOKS*. A further explanation of these keywords will be provided below.

SECOND

The calculation of the Hessian matrices can be done by numerical differentiation of the gradients, by means of the *Polyrate* methods, or by the *Gaussian 16 / 09* methods, with the latter option strongly recommended. The choice is made by means of the *GHOOK* or *HHOOK* options in the HESSCAL keyword in the SECOND section of the `fu5` input file. If *HHOOK* is selected, the remaining keywords of the SECOND section are ignored and

the Hessian calculations will be controlled by the options selected in the `fu70` input file. If *GHOOK* is selected, the Hessian calculation will be carried out following the options indicated in the SECOND section, ignoring the options for the Hessian calculation selected in the `fu70` input file.

Although *Gaussian 16 / 09* can perform Hessian calculations using any of the electronic structure methods available in GAUSSIAN, the option of performing the Hessian calculation using *Polyrate* methods is implemented for completeness. However the user is advised for efficiency reasons against using *Polyrate* for the Hessian calculations.

GEOM

The ordering of the atoms in the GEOM keyword in sections REACT1, REACT2, PROD1, PROD2, and START must be consistent with the ordering in units `fu71`, `fu72`, `fu73`, `fu74`, and `fu75`, when they are used; and also the ordering in `fu75` must be consistent with the one in ATOMS in the GENERAL section.

CONSTANT

If the user selects *Gaussian 16 / 09* for optimizing the geometries (this is accomplishing with the *OHOOK* option for the OPTMIN and OPTTS keywords in the OPTIMIZATION section of the *Polyrate* `fu5` input), the CONSTANT keyword in the REACT1, REACT2, PROD1, PROD2, WELLR, WELLP and START sections of the `fu5` input file is meaningless. The frozen parameters must be indicated in units `fu71-fu78`, according to the instructions explained in the *Gaussian 16 / 09* manual. If a user selects *Polyrate* for optimizing the geometries, this keyword has the same function as in any other *Polyrate* calculation, fixing the value of the selected coordinates and avoiding their optimization, as explained in Section 11.A.6 of the *Polyrate* 2016 manual.

INITGEO and **STATUS**

There are two options for reading the initial geometries of reactants, products, wells, and saddle point: the first one is by means of units `fu71` through `fu78`, if a *Gaussian 16 / 09* optimization is desired (*OHOOK* option for the OPTMIN and OPTTS keywords in the OPTIMIZATION section). In this case, the INITGEO keyword has to be set to *HOOKS*, and the files `fu71-fu78` should be the appropriate input files for a *Gaussian 16 / 09*

optimization. The second one is by means of the GEOM keyword, if a *Polyrate* optimization (`BFGS`, `NR`, or `EF` options in the OPTMIN or OPTTS keyword in the OPTIMIZATION section) or no optimization is going to be carried out. Then, the INITGEO keyword needs to be set to `GEOM`. Therefore, the initial geometry for the optimization of those systems that are going to be optimized using *Gaussian 16 / 09* methods should be given in units `fu71-fu78` and the INITGEO keyword in the respective section has to be set to `HOOKS`, while the initial geometry for those systems which are to be set to `HOOKS`, while the initial geometry for those systems which are going to be optimized using *Polyrate* methods or the optimized geometry of the systems which are not going to be further optimized should be given in unit `fu5` and the INITIGEO keyword in the respective sections has to be set to `GEOM`.

The combination of the keywords INITGEO, STATUS and OPTTS and OPTMIN, therefore, will indicate the procedure of the initial and/or optimized geometries for the stationary points. The combinations are:

– For optimizing the geometries using the methods in GAUSSIAN: OPTTS and OPTMIN in the OPIMIZATION section have to be set to `OHOOKS`, INITGEO has to be set to `HOOKS` and STATUS set to `0` in the corresponding REACT1, REACT2, PROD1, PROD2, WELLR, WELLP, and/or START sections. The initial geometry should be given in the files `fu71` through `fu78`.

– If the geometry optimization of one of the stationary points is not desired, the INITGEO keyword has to be set to `GEOM`, and the STATUS keyword should be set to an allowed value greater than zero in the corresponding REACT1, REACT2, PROD1, PROD2, WELLR, WELLP, and START sections of the `fu5` input file. The optimized geometry will be read from the `fu5` input file.

– For optimizing the geometries using the methods in *Polyrate* (not recommended): OPTTS and OPTMIN in the OPTIMIZATION section have to be set to `BFGS`, `NR` and/or `EF`, and INITGEO has to be set to `GEOM` and STATUS set to `0` in the corresponding REACT1, REACT2, PROD1, PROD2, WELLR, WELLP, and/or START sections of the `fu5` input file. The initial geometry will be given in the appropriate section of the `fu5` input file. If the geometry of one of the stationary points is already optimized, the only parameter that has to be changed is the value of the STATUS keyword in the corresponding section of the `fu5` input file.

A value greater than *0* for the STATUS keyword in any of the REACT1, REACT2, PROD1, PROD2 and/or START sections involves no optimization of the geometry input in the `fu5` file and, if a value greater than *2* is selected, no Hessian calculation. If STATUS is set to *4* in the START section of the `fu5` input file, the Hessian matrix as it appears in a *Gaussian 16 / 09* formatted checkpoint file can be input, according to the instructions in the *Polyrate* manual.

ANHARMONICITY

Although anharmonic calculations can be carried out, the user must keep in mind the extremely high cost of numerical third or fourth derivatives of the energy when using ab initio methods. With the anharmonicity options available in *Polyrate* 2016, this extra cost is not usually warranted. We therefore recommend not using anharmonic options in the REACT1, REACT2, PROD1, PROD2, WELLR, WELLP, and START sections when they require derivatives of order higher than two, at least until some later version of *Polyrate* with better anharmonicity options becomes available. The only anharmonicity option that do not require derivatives higher than second are Morse I and hindered rotator.

In addition, when calculating second or higher order derivatives using the numerical methods of *Polyrate* 2016, *Gaussian 16 / 09* is unable to successfully calculate some slightly distorted structures of linear molecules, such as the hydrogen molecule, stopping in the SYMM subroutine. Therefore, we recommend that Hessians be calculated with GAUSSIAN rather than with the methods native to *Polyrate*.

SCALEMASS

If restart calculations are desired, the value of the SCALEMASS variable keyword must be the same for the whole series of calculations. Note that SCALEMASS is the reduced mass to which all isoinertial coordinates are scaled. See also the discussion of SCALEMASS in Section 6.2.

7.3.   Description of `esp.fu71` through `esp.fu78` input files

The data files `esp.fu71` through `esp.fu78` are GAUSSIAN-type data files. They are used only as input files for GAUSSIAN optimization on reactants 1 and 2 (`esp.fu71` and `esp.fu72`, respectively), products 1 and 2 (`esp.fu73` and `esp.fu74`), of the well on the reactant side (`esp.fu77`), of the well on the product side (`esp.fu78`), and of the saddle point or other starting geometry (`esp.fu75`). If no optimization using GAUSSIAN is desired, these files are not needed.

For constructing these files, the user must check the GAUSSIAN manual. With only one restriction, any option available for GAUSSIAN can be used; the restriction is that GAUSSIAN must generate a formatted checkpoint file at the end of the optimization. The GAUSSIAN keyword FCHK (or any of its equivalent keywords, FORMCHECK or FCHECK) must therefore be specified, and options in GAUSSIAN that do not generate such a file (for example, a non-standard route) cannot be used.

As mentioned above, when creating these files, the order of the atoms in unit `fu75` must be consistent with the order of the atoms input in the ATOMS keyword in the GENERAL section of the *Polyrate* `fu5` input file, and the order of the atoms in units `fu71`-`fu78` must be consistent with the index specifications in the GEOM keyword in the REACT1, REACT2, PROD1, PROD2, WELLR, WELLP, and START sections of the `fu5` input file.

For the sake of consistency, the method chosen for the electronic structure calculations for a given reaction must be the same in all the `esp.fu71` through `esp.fu78` files representing the species for that reaction. Only if one of the species is the hydrogen atom and electronic correlation is included can the quantum methods be different (since no correlation energy can be calculated for the hydrogen atom). The electronic structure method must also be consistent with the options related to energy and first and second derivatives chosen in the `fu70` input file.

When studying a reaction with no saddle point, the user must insure that the optimization procedures chosen for the starting point will not lead the system to reactants or products. This can be accomplished by freezing the appropriate geometrical parameters. If no geometrical parameter is kept fixed, the optimization will lead to a point where the gradients are zero and the procedure for following the reaction path will not work successfully.

7.4. Description of `esp.fu70` input file

Along with the input `fu5` file, which controls the *Polyrate* options, the `fu70` input file will control all of the *Gaussrate 17* options and some of the GAUSSIAN input options. The `fu70` input file is divided into sections which, like the `fu5` sections, are denoted by a header preceded by an asterisk (*). There are eight sections, each starting with GR in order to avoid confusion with similar sections in the `fu5` input file. These sections are GRGENERAL, GRCOMMON, GRREACT1, GRREACT2, GRPROD1, GRPROD2, GRWELLR, GRWELLP, GRSTART and GRPATH. In these sections, the appropriate keywords have to be specified.

Section name	Description
GRGENERAL	Restart options
GRCOMMON	GAUSSIAN options common to all the stationary points
GRREACT1	GAUSSIAN options specific to the first reactant
GRREACT2	GAUSSIAN options specific to the second reactant, if any
GRPROD1	GAUSSIAN options specific to the first product
GRPROD2	GAUSSIAN options specific to the second product, if any
GRWELLR	GAUSSIAN options specific to the reactant well, if any
GRWELLP	GAUSSIAN options specific to the product well, if any
GRSTART	GAUSSIAN options specific to the starting (or saddle) point
GRPATH	GAUSSIAN options common to all the nonstationary points along the reaction path

There are three type of keywords: switch (which does not have any argument), variable (which requires one argument following the keyword), and list (which requires a list of options, with an END line). See the *Polyrate* manual for a more thorough discussion of the three types of keywords.

7.4.1. The GRGENERAL section

The GRGENERAL section controls *Gaussrate 17* 's own options. There are only three keywords allowed in this section, GRRESTART and NOGRRESTART, with GRRESTART being the default, and RSTTOL.

GRRESTART (NOGRRESTART)

This is a switch keyword that tells the program to check the restart file `esp.fu83` and search for information about the point to be calculated. If it finds the required information about that point, the program writes it in the `esp.fu84` file and uses the stored information instead of calculating it. If the information needed is not present in the `fu83` file, *Gaussrate 17* runs GAUSSIAN and writes the GAUSSIAN output information to unit `fu84`. If NOGRRESTART is selected, neither reading file `fu83` nor writing file `fu84` will be performed.

RSTTOL

RSTTOL is a variable keyword that must be followed by a real number, which is the value of the tolerance in the comparison of geometries between the geometry currently used by *Gaussrate 17* and the geometry found in a restart file `esp.fu83`. The meaning of this keyword is explained in detail in Section 6.2. The inexperienced user is not advise to change this value from its default value, *1.E-8*.

> *Example:*
>   RSTTOL   0.00000001

7.4.2. The GRCOMMON section

The GRCOMMON section reads the information common to all the GAUSSIAN calculations for the stationary points and points along the reaction path, excepting the *Gaussian 16 / 09* geometry optimizations, which are totally controlled by the `fu71` through `fu78` input file. The options selected in this section will be applied to all the GAUSSIAN calculations unless a different keyword is specified in the section corresponding to a specific point. This section needs to precede the specific sections GRREACT1, GRREACT2, GRPROD1, GRPROD2, GRSTART, GRWELLR, GRWELLP, and GRPATH. The following keywords are allowed in the GRCOMMON section:

GRENER

This is a list type keyword and therefore it must include an END line to indicate the end of the list (see the *Polyrate* manual for a description of list keywords). GRENER includes the keywords that GAUSSIAN will use for carrying out an energy calculation. The default for this keyword is *#HF/STO-3G UNITS=AU FCHK NOSYMM*. In order to get the desired results, two particular keywords must always be supplied for this kind of calculation: *UNITS=AU* and *FCHK* (or their equivalent GAUSSIAN keywords; see the GAUSSIAN manual for a discussion of alternative forms of GAUSSIAN keywords). No blank lines can appear in this list, since GAUSSIAN would take those blank lines as the end of keyword inputs. Just as in GAUSSIAN inputs, the pound symbol (#) must precede the complete set of keywords.

> *Example:*
> ```
> GRENER
> #HF/6-31G SCF=QC UNITS=AU FCHK
> END
> ```

GRFIRST

This accomplishes a similar purpose as the GRENER keyword, but it indicates the keywords to be used in gradient calculations. Again, *UNITS=AU* and *FCHK* are required. The default is *#HF/STO-3G UNITS=AU FCHK NOSYMM FORCE*.

GRSEC

This keyword is only used when the *HHOOK* option is specified in the HESSCAL keyword of the SECOND section of the `fu5` input file. It accomplishes a purpose similar to the GRENER and GRFIRST keywords, but indicating the options for a Hessian calculation. *UNITS=AU* and *FCHK* are required, and the *NORAMAN* option is recommended (since it saves computer time). The default is *#HF/STO-3G UNITS=AU FCHK NOSYMM FREQ=NORAMAN*.

GRLINK0

GRLINK0 is a list keyword for indicating the link0 options for GAUSSIAN calculations (note that the last character is zero). This keyword controls the options for renaming scratch files, creating checkpoint files, determining memory size, etc. If it is not indicated, no link0 options are assumed, since they are not needed for the calculations. If indicated,

they are assumed to be the same for all the GAUSSIAN calculations, no matter which species or type of calculation is involved, the only exception being the *Gaussian 16 / 09* optimizations which are fully controlled by the `fu70` through `fu78` input files. No blank lines are allowed in this keyword.

GRBASIS

When running GAUSSIAN, if a non-standard basis set is desired, the keyword GEN must be indicated, and the general basis set must follow the geometry specification in the GAUSSIAN input. If a non-standard basis set is desired in a *Gaussrate 17* calculation, it must be indicated in GRBASIS, and it must be the same for all the calculations on all the systems. Again, no blank lines are allowed, and (because of dimension limitations) a maximum of 100 lines are allowed for indicating the basis set. If a larger space is required, the basis set can be specified by an external file, using the symbol '@' (see the *Gaussian 16 / 09* manual for further details of this option). For example, for selecting a modified STO-3G basis set, located in the `msto3g.gbs` file in the directory `/usr/g16/basis,` one should write:

> *Example:*
> ```
> GRBASIS
> @/usr/g16/basis/msto3g.gbs
> END
> ```

Also, please remember to specify the /gen keyword in order to use the user-specified basis set in Gaussian. If you are also using .71 - .75 files, please also specify /gen keyword and specify `@/usr/g16/basis/msto3g.gbs` in these files (DO NOT leave any blank space in front of the `@` sign); for example, in the .71 file:

```
#HF/gen FCHK OPT

CH3

0 2
C
H 1 a
H 1 a 2 b
H 1 a 2 b 3 c

a 1.08
b 118.2647
c 153.9868

@/usr/g16/basis/msto3g.gbs
```

Although the above example illustrates what will probably be the most common use for this keyword, actually any information that needs to be located in a GAUSSIAN input file after the geometry specification can be included by means of the GRBASIS keyword. For example, electronic excited states require input information indicating the orbitals involved in the electronic excitation; this information can be entered by this keyword with two limitations: the information will be included in all the GAUSSIAN inputs (except the optimizations, which are read directly from units `fu71-fu78`), and no blank lines are allowed in this keyword. The later limitation can be overcome by using the external file option mentioned in the previous paragraph.

It should be noted that the isotope input, which must be contained in this section of the *Gaussian 16 / 09* input file if nonstandard isotopes are desired, should never be included in a *Gaussrate 17* run. The choice of the isotopic masses has to be done in the `fu5` input file of *Polyrate.*

7.4.3.   The GRREACT1, GRREACT2, GRPROD1, GRPROD2, GRWELLR, GRWELLP, GRSTART, and GRPATH sections

Since in some cases, the options selected in the GRCOMMON section might not be the most useful for all the points to be calculated, these eight sections allow us to select different keywords for the energy, gradients, and Hessian calculations by means of the GRENER, GRFIRST, and GRSEC list keywords. The options for the first reactant should be specified in the GRREACT1 section; in the GRREACT2 the options for the second reactant, if it exists; in GRPROD1 and GRPROD2 the options for the first product and, if it exists, the second one; in GRWELLR the options for a well on the reactant side of the reaction path, if it exists; in GRWELLP the options for a well on the product side, if it exists; section GRSTART will indicate the options for the saddle point or starting geometry, and GRPATH will indicate the options for GAUSSIAN calculations on the non-stationary points along the reaction path. If no changes from the options selected in the GRCOMMON section are wanted, these sections can be skipped.

These sections can include one or more of the GRENER, GRFIRST, and GRSEC keywords explained above for the GRCOMMON section, with the same syntax that we explained in the previous section, and requiring the keywords *UNITS=AU* and *FCHK* in all the inputs.

In order to avoid problems related to the reorientation of the systems that *Gaussian 16 / 09* performs, in addition to *UNITS=AU* and *FCHK*, the keyword *NOSYMM* is strongly recommended for its use in the GRPATH section; otherwise, the results could be wrong even though they would seem reasonable and no error would be detected without a careful study of the directions of the gradients (see the *Polyrate* manual for a more thorough discussion of reorientation problems and GAUSSIAN reorientation).

The *NOSYMM* keyword is also recommended when third or fourth derivatives of the energy are needed (i.e., for anharmonic calculations or when using the cubic algorithm for starting the reaction path) and when the *GHOOK* option is selected for the HESSCAL keyword in the SECOND section of the fu5 input file is on, since for the numerical differentiation of the derivatives computed using GAUSSIAN it is necessary to have them oriented in a consistent way.

The options entered by means of GRBASIS and GRLINK0 keywords in the GRCOMMON section are used in all the GAUSSIAN calculations for which input is constructed by *Gaussrate 17* (all the calculations but geometry optimizations, for which the input is written by the user in units fu71-fu78); therefore, the GRBASIS and GRLINK0 keywords are only allowed in the GRCOMMON section and not in the .GRREACT1, GRREACT2, GRPROD1, GRPROD2, GRWELLR, GRWELLP, GRSTART, and GRPATH sections.

Besides using the GRENER, GRFIRST, and GRSEC keywords, some additional issues need to be clarified, and two new keywords need to be introduced:

CHARGE and **MULTIPLICITY**

If GAUSSIAN optimization is required, *Gaussrate 17* will read the charge and multiplicity of each species from the GAUSSIAN optimization output. Nevertheless, if no optimization is selected or if *Polyrate* 2016 is selected for carrying out the optimizations, *Gaussrate 17* will need to know the charge and multiplicity of the system before making any GAUSSIAN calculation. The way to input these characteristics is by means of the CHARGE and MULTIPLICITY keywords. These keywords are not allowed in the GRCOMMON section since they are dependent on the species and are only required for the systems which will not be optimized using *Gaussian 16 / 09,* being ignored if they are specified for a species that is going to be optimized using *Gaussian 16 / 09*. For the points along

the reaction path, the charge and multiplicity are assumed to be the same as the values for the saddle point or starting geometry, and if they are specified in the GRPATH section they will also be ignored.

CHARGE is a variable keyword that must be followed by an integer, which is the value of the charge of the system. The default value for CHARGE is *0*. MULTIPLICITY is also a variable keyword followed by an integer indicating the multiplicity of the species. The default value for MULTIPLICITY is *1*, which corresponds to a singlet. Values of *2* and *3* correspond to doublets and triplets.

Example:
```
CHARGE          -1
MULTIPLICITY     2
```

8.   SPEED UP OF DIRECT DYNAMICS CALCULATIONS

The direct dynamics calculations can be speeded up by decreasing the time required to reach the SCF convergence threshold in the electronic structure calculations (i.e., when the energies, gradients, and Hessians are computed) of the non-stationary points along the minimum energy path (MEP). To accomplish this, the molecular orbitals guess generated in the previous electronic structure calculation must be used as the initial guess in the current calculation, instead of computing it from *ab initio*. In this way, problems with the SCF convergence along the MEP should be avoided. A couple of examples given in test run directory are provided to demonstrate this strategy. Below it is explained how to perform such calculations.

Because the Gaussian formatted checkpoint file (`Test.FChk`) is written for all electronic structure calculations, it can be used to generate its corresponding binary checkpoint file using the *unfchk Gaussian 16 / 09* utility.

Example of shuttle:
```
# We will remove the existent files
# with the same names than the
# required GAUSSIAN 94/98/03/09/16 output files
#
/bin/rm $argv[2]
/bin/rm Test.FChk
#
```

For Gaussian 09, one must include the followings:
```
# Start running GAUSSIAN 94/98/03/09
$gausspath/g09 < $argv[1] > $argv[2]
```

However, for Gaussian 16, one must include the following two lines (this is the key part in the shuttle in order to let Gaussrate work with Gaussian 16) in the shuttle file (the shuttle file should also be copied to Polyrate/exe/ directory):
```
# Start running GAUSSIAN 94/98/03/09/16
#for Gaussian 16, the following TWO lines are needed!
$gausspath/g16 –fchk=Test < $argv[1] > $argv[2] #for G16
/bin/mv Test.fck  Test.FChk                      #for G16
```

That checkpoint file must be read by the following *Gaussian 16 / 09* calculation, i.e. the keyword *%chk=guess.chk* and *guess=read* in the route section of Gaussian must be added in all the items of the GRPATH section of the `esp.fu70` file.

Example of `esp.fu70` file:

```
*GRPATH
 GRENER
    %chk=guess.chk
    #HF/STO-3G FCHK UNITS=AU NOSYMM guess=read
  END


  GRFIRST
    %chk=guess.chk
    #HF/STO-3G FORCE FCHK UNITS=AU NOSYMM guess=read
  END


  GRSEC
    %chk=guess.chk
    #HF/STO-3G FREQ=NORAMAN FCHK UNITS=AU NOSYMM guess=read
  END
```

The first non-stationary point computed along the MEP uses the guess of the transition structure (TS) as its initial guess, and it must be generated in a previous step. There are two possible ways to do that.

In the first way *Gaussrate 17* computes the guess of the TS and writes it in a checkpoint file, i.e. the keyword *%chk=guess.chk* must be added to the `esp.fu75` file. (Note that this way is valid only if the value of the STATUS keyword of the *START section in the `polyrate.dat` input file is equal to 0 or 2).

Example of `esp.fu75`:

```
%chk=guess.chk
# HF/6-31G OPT=(TS,NOEIGENTEST,CALCFC) FCHK
```

In the second way, the *Gaussian 16 / 09* checkpoint file (*filename.chk*) that contains the initial guess of the TS must be computed in a previous step to run *Gaussrate 17,* and then copied to *Gaussrate 17* work directory (i.e., *$actdir/* in .jc file) by including the sentence *cp $actdir/$filename.chk guess.chk* in the `.jc` file. It should be noted that this method is designed for when the energy and the Hessian or the frequencies of the TS are provided by the user in the `polyrate.dat` input file using the STATUS keyword equal 4 or, 6 and the use of STATUS 6 for reactants and products is mandatory.

Example of `.jc` *file:*

```
cp $actdir/guess.chk guess.chk
#
# Write system message to .time file
#
(time $exe) >& $actdir/$name.time
echo " " >> $actdir/$name.time
```

9.   TESTING *Gaussrate 17*

9.1.   Tests performed

We tested *Gaussrate 17* using versions 2016 and 17 of *Polyrate* and revision D01 of *Gaussian 16 / 09* on an HP Linux cluster with Intel Xeon X5560 "Nehalem EP" processors and an HP c7000 Linux Cluster with Intel Haswell E5-2680v3 processors (CentOS Linux).

Important note
Gaussian 09 version E01 does not work with *Gaussrate 17* due to a bug in the *Gaussian 09* code that writes the formatted checkpoint file.

9.2.   Test suite

The purpose of the test suite is to provide some examples of the way *Gaussrate 17* works, not to check all *Gaussian 16 / 09* or *Polyrate17* options. The test suite has 24 test runs, and the tests illustrate only the most important capabilities of *Gaussrate 17.* The level of calculation, size of the systems, and computational requirements of the test runs have been chosen in such a way that running the whole suite does not consume an inordinate amount of computing time.

The test suite is located in the `testrun` directory that contains several subdirectories. Each subdirectory contains one or more tests based on the same reaction. The summary output files for these test runs that are distributed in the current version of the program are located in the `testo` directory. The Korn shell script `check09` in the `testrun` directory allows an easy comparison between the `poly.fu15` output files obtains after running all the test runs using *Gaussian 16 / 09* and the equivalent `poly.fu15` files in the `testo` directory.

Each directory in `testrun` includes one or more test runss based on one of the following reactions:

Reaction	Directory	Test names
$CH_3 + H_2 \rightarrow CH_4 + H$	`ch5`	`ch5tr1, ch5tr2`
$OH + H_2 \rightarrow H_2O + H$	`oh3`	`oh3tr1, oh3tr2, oh3tr3.`
$CH_4 + OH \rightarrow CH_3 + H_2O$	`ch4oh`	`ch4ohtr1, ch4ohtr2, ch4ohtr3,`
		`ch4ohtr4, ch4ohtr5, ch4ohtr6.`
$NH_3 + OH \rightarrow NH_2 + H_2O$	`nh3oh`	`nh3ohtr1`
$CH_3 + CH_3 \rightarrow C_2H_6$	`c2h6`	`c2h6`
$CF_2 + CF_2 \rightarrow C_2F_4$	`c2f4`	`c2f4`
$C_6H_6CH_3 \rightarrow C_6H_5CH_3+H$	`c6h6ch3`	`c6h6ch3`
Liquid-phase p-$C_6H_4(OH)_2$		
$+ HO_2 \rightarrow C_6H_5(OH)O + H_2O_2$	`c6h4oh2`	`c6h4oh2`
tert-butanol $+ HO_2$		
$\rightarrow (CH_3)_2C(OH)CH_2 + H_2O_2$	`butanol`	`butanol`
$(SiH_3)_2SiH^- + SiH_4$		
$\rightarrow (SiH_3)_2SiH_2 + SiH_3^-$	`sih4`	`sih4`
$OH + SO_2 \rightarrow HSO_3$	`ohso2`	`ohso2`

The test runs are run in a subdirectory created for each run. This way, one avoids problems that could be caused when running other *Gaussian 16 / 09* or *Gaussrate 17* calculations in the same directory that *Gaussrate 17* is using. After a test run is completed, the directory is removed, and the temporary files created are moved to the GRTEMPFILES directory.

All test runs are for gas-phase reactions except the h3tr2 and c6h4oh2 test runs, which are run in aqueous solution. One can run reactions in water or any organic solvent or ionic liquid by using the SMD solvation model. The theory for liquid-phase variational transition state theory is presented in the following references:

"Interface of Electronic Structure and Dynamics for Reactions in Solution," Y.-Y. Chuang, C. J. Cramer, and D. G. Truhlar, International Journal of Quantum Chemistry **70**, 887-896 (1998). (Sanibel issue)

and

"Free Energy Surfaces for Liquid-Phase Reactions and Their Use to Study the Border Between Concerted and Nonconcerted α,β-Elimination Reactions of Esters and Thioesters," Y. Kim, J. R. Mohrig, and D. G. Truhlar, Journal of the American Chemical Society **132**, 11071-11082 (2010). dx.doi.org/10.1021/ja101104q.

9.2.1. Test run ch5tr1

Tunneling:	SCT
Number of levels:	single level
Hindered rotation:	none

This sample run for the reaction $CH_3 + H_2 \rightarrow CH_4 + H$ gives the same results as the test run ch5fu30tr5 included in the *Polyrate* 2016 test suite. It performs calculations of the TST, CVT and ICVT rate constants at the UHF/STO-3G level, and it is based on following the reaction path using the Euler steepest descents method (also called Euler single-step method). For all the stationary points symmetry is employed in all the *Gaussian 16 / 09* calculations (which is the default for *Gaussian 16 / 09* calculations); nevertheless, this option is turned off when calculating points along the reaction coordinate in order to avoid possible problems due to the reorientation of the system. A restart file is created (GRRESTART keyword), and all the input of the geometries is done by means of files fu71 through fu75, in order to allow *Gaussian 16 / 09* to optimize the

stationary points (*ohook* option in OPTTS and *optmin* in the OPTIMIZATION section of the `fu5` input file, and INITGEO set to *hooks* in the REACT1, REACT2, PROD1, PROD2, and START sections in the input file `fu5`).

Gaussrate 17 I/O files	*Gaussrate 17* file names	
`ch5tr1.70`	`esp.fu70`	Input data for *Gaussrate 17*
`ch5tr1.71`	`esp.fu71`	Input data for reactant 1
`ch5tr1.72`	`esp.fu72`	Input data for reactant 2
`ch5tr1.73`	`esp.fu73`	Input data for product 1
`ch5tr1.74`	`esp.fu74`	Input data for product 2
`ch5tr1.75`	`esp.fu75`	Input data for the saddle point
`ch5tr1.dat`	`poly.fu5`	Input data for *Polyrate*
`ch5tr1.61`	`esp.fu61`	*Polyrate* output file containing information about the stationary points
`ch5tr1.fu6`	`poly.fu6`	Long output file
`ch5tr1.fu15`	`poly.fu15`	Summary output file
`ch5tr1.rst`	`esp.fu84`	*Gaussrate 17* restart file generated by *Gaussrate 17* in this run

9.2.2. Test run `ch5tr2`

Tunneling:	SCT
Number of levels:	single level
Hindered rotation:	none

This test run uses the restart file created by the previous run and performs a calculation using the ISPE technique by using ten MP2/6-31G** energies input in the `esp.fu51` input file. Of these ten energies, two are for products and the saddle point, and eight are for nonstationary points. Since the ISPE technique does not modify the reaction path, the calculation can be restarted successfully. The user must run the `ch5tr1` test run before running `ch5tr2`, in order to create the restart file to be read, `ch5tr2.rst`, which will be a copy of the `ch5tr1.rst` file generated by the previous run and located in the same directory.

Gaussrate 17 I/O files	*Gaussrate 17* file names

`ch5tr2.51`	`poly.fu51`	Input data for ISPE information
`ch5tr2.70`	`esp.fu70`	Input data for *Gaussrate 17*
`ch5tr2.71`	`esp.fu71`	Input data for reactant 1
`ch5tr2.72`	`esp.fu72`	Input data for reactant 2
`ch5tr2.73`	`esp.fu73`	Input data for product 1
`ch5tr2.74`	`esp.fu74`	Input data for product 2
`ch5tr2.75`	`esp.fu75`	Input data for the saddle point
`ch5tr2.dat`	`poly.fu5`	Input data for *Polyrate*
`ch5tr2.61`	`esp.fu61`	*Polyrate* output file containing information about the stationary points
`ch5tr2.fu6`	`poly.fu6`	Long output file
`ch5tr2.fu15`	`poly.fu15`	Summary output file
`ch5tr2.rst.old`	`esp.fu83`	*Gaussrate 17* restart file read by *Gaussrate 17* in this run
`ch5tr2.rst`	`esp.fu84`	*Gaussrate 17* restart file generated by *Gaussrate 17* in this run

9.2.3. Test run `oh3tr1`

Tunneling: none
Number of levels: single level
Hindered rotation: none

This is a test run for a conventional TST calculation for the reaction $OH + H_2 \rightarrow H_2O + H$. The geometries for the reactants and products are given (it is assumed that they already are fully optimized) in the `fu5` input file (INITGEO is set to *geom*, and STATUS set to *2* in the REACT1, REACT2, PROD1 and PROD2 sections of the `fu5` input file), while the saddle point optimization is carried out by means of *Gaussian 16 / 09,* requiring, therefore, the `esp.fu75` input file, and STATUS set to *0* and the option *hooks* for the INITGEO keyword in the START section of the input file `fu5`. The *Gaussrate 17* restart file `esp.fu84` is written. The level of electronic structure calculation used for this test run is MP2, using Dunning's aug-cc-pVDZ basis set, which is entered by means of the GRBASIS keyword. The unformatted checkpoint file generated for *Gaussian 16 / 09* is renamed `oh3tr1.chk` by means of the GRLINK0 keyword.

Gaussrate 17 I/O files	*Gaussrate 17* file names	
oh3tr1.70	esp.fu70	Input data for *Gaussrate 17*
oh3tr1.75	esp.fu75	Input data for the saddle point
oh3tr1.dat	poly.fu5	Input data for *Polyrate*
oh3tr1.61	esp.fu61	*Polyrate* output file containing information about the stationary points
oh3tr1.fu6	poly.fu6	Long output file
oh3tr1.fu15	poly.fu15	Summary output file
oh3tr1.rst	esp.fu84	*Gaussrate 17* restart file generated by *Gaussrate 17* in this run

9.2.4. Test run `oh3tr2`

Tunneling: none
Number of levels: single level
Hindered rotation: none

This is a test run that, by making use of the `oh3tr1.rst` file previously written by the `oh3tr1` test run, restarts the calculation performed by the previous test run and makes a canonical variational theory (CVT) calculation, without tunneling, by following the reaction path using the variational reaction path algorithm based on the Euler method (*VRPE* option of RPM keyword) with a step size of 0.025 bohr. The reaction path is calculated between –0.3 bohr and +0.3 bohr. Nonredundant internal coordinates are used for describing the vibrations. The user must run the `oh3tr1` test run before running `oh3tr2`, since the restart file to be read, `oh3tr2.rst`, will be a copy of the `oh3tr1.rst` file generated by the previous run and located in the same directory. Otherwise, the `oh3tr2.rst` file will not exist, and the program will calculate the frequencies for all the stationary points and the optimum geometry for the saddle point instead of reading them from the restart file. It should be noted that the `fu75` file is required, and it is used by *Gaussrate 17* although not by *Gaussian 16 / 09*. At the end of the calculation, a new restart file, including the information calculated for the first time in the present run, will take the name of `oh3tr2.rst`, while the old restart file will be renamed as `oh3tr2.rst.old` (and this will be unchanged from what was in file `oh3tr1.rst` at the start of the present run).

Gaussrate 17 I/O files	*Gaussrate 17* file names	
`oh3tr2.70`	`esp.fu70`	Input data for *Gaussrate 17*
`oh3tr2.75`	`esp.fu75`	Input data for the saddle point
`oh3tr2.dat`	`poly.fu5`	Input data for *Polyrate*
`oh3tr2.61`	`esp.fu61`	*Polyrate* output file containing information about the stationary points
`oh3tr2.fu6`	`poly.fu6`	Long output file
`oh3tr2.fu15`	`poly.fu15`	Summary output file
`oh3tr2.rst.old`	`esp.fu83`	*Gaussrate 17* restart file read by *Gaussrate 17* in this run
`oh3tr2.rst`	`esp.fu84`	*Gaussrate 17* restart file generated by *Gaussrate 17* in this run

9.2.5. Test run `oh3tr3`

Tunneling: none
Number of levels: single level
Hindered rotation: none

This test run uses the `oh3tr2.rst` file written by the `oh3tr2` test run, copying it as `oh3tr3.rst`, and it performs the same calculation as the `oh3tr1` test. Since more information than is required for the calculation is stored in the `oh3tr2.rst` file, the restart file created by this test run, `oh3tr3.rst`, will be smaller than the file `oh3tr2.rst`. This is the reason why it is convenient to keep the file from which a restart calculation reads the information (in the executable scripts of these test runs, such files are renamed with the extension `old`). No *Gaussian 16 / 09* calculations are needed for this test run, so it is the fastest test run of the suite.

Gaussrate 17 I/O files	*Gaussrate 17* file names	
`oh3tr3.70`	`esp.fu70`	Input data for *Gaussrate 17*
`oh3tr3.75`	`esp.fu75`	Input data for the saddle point
`oh3tr3.dat`	`poly.fu5`	Input data for *Polyrate*
`oh3tr3.61`	`esp.fu61`	*Polyrate* output file containing information about the stationary points
`oh3tr3.fu6`	`poly.fu6`	Long output file
`oh3tr3.fu15`	`poly.fu15`	Summary output file
`oh3tr3.rst.old`	`esp.fu83`	*Gaussrate 17* restart file read by *Gaussrate 17* in this run
`oh3tr3.rst`	`esp.fu84`	*Gaussrate 17* restart file generated by *Gaussrate 17* in this run

9.2.6. Test run `ch4ohtr1`

Tunneling: none
Number of levels: single level
Hindered rotation: none

This is the first of a series of tests that try to show how *Gaussrate 17* would usually be used. We study the $CH_4 + OH \rightarrow CH_3 + H_2O$ reaction. The sequence actually has five stages. The first four stages may be thought of a complete single-level calculation or as runs 1-4 of a five-run dual-level calculation. The first step we will take is the calculation of the first reactant, CH_4. In the `fu5` input file we only include the REACT1 section, and only the additional input files `fu70` and `fu71` are required. The *Gaussrate 17* restart option is *off*, since the restart is only available when all the information about the stationary points is read from the restart file or written in it.

The output file `esp.fu61` will contain the information calculated for this reactant, and this information will be included in the `fu5` input file for the following runs.

Gaussrate 17 I/O files	*Gaussrate 17* file names	
`ch4ohtr1.70`	`esp.fu70`	Input data for *Gaussrate 17*
`ch4ohtr1.71`	`esp.fu71`	Input data for reactant 1
`ch4ohtr1.dat`	`poly.fu5`	Input data for *Polyrate*
`ch4ohtr1.61`	`esp.fu61`	*Polyrate* output file containing information about reactant 1
`ch4ohtr1.fu6`	`poly.fu6`	Long output file

9.2.7. Test run `ch4ohtr2`

Tunneling: none

Number of levels: single level

Hindered rotation: none

This is the second run in the four-stage single-level calculation for the CH_4 + OH $\rightarrow$ CH_3 + H_2O reaction. The information included in the `fu61` output file from the previous run is cut and pasted to the `fu5` input file for the present run. The properties of the other reactant, OH, and the products, CH_3 and H_2O, are calculated here. Therefore, the `fu5` input file will not contain the START section, and the input files `fu70`, `fu72`, `fu73`, and `fu74` are required. Once again, the *Gaussrate 17* restart option is *off*.

Usually, the user would calculate the stationary points one by one, instead of calculating three in a row. Thus, if some problem is encountered in any stationary point calculation, the user can check the error in that particular point, instead of repeating several optimizations.

The `fu61` input file will contain all the information about the reactants and products needed for the next run. This includes both the information calculated in test run `ch4ohtr1` and the information calculated in the present test run.

Gaussrate 17 I/O files	*Gaussrate 17* file names	
ch4ohtr2.70	esp.fu70	Input data for *Gaussrate 17*
ch4ohtr2.72	esp.fu72	Input data for reactant 2
ch4ohtr2.73	esp.fu73	Input data for product 1
ch4ohtr2.74	esp.fu74	Input data for product 2
ch4ohtr2.dat	poly.fu5	Input data for *Polyrate*
ch4ohtr2.61	esp.fu61	*Polyrate* output file containing information about the stationary points
ch4ohtr2.fu6	poly.fu6	Long output file

9.2.8. Test run `ch4ohtr3`

Tunneling: none

Number of levels: single level

Hindered rotation: none

This is the third run in the four-stage single-level calculation for the $CH_4 + OH \rightarrow CH_3 + H_2O$ reaction. In this test run, we calculate the saddle point properties and evaluate the conventional TST rate constant, including all the information on reactants and products in the `fu5` input file, as they appeared in the `fu61` output file from the previous run.

Gaussrate 17 I/O files	*Gaussrate 17* file names	
`ch4ohtr3.70`	`esp.fu70`	Input data for *Gaussrate 17*
`ch4ohtr3.75`	`esp.fu75`	Input data for the saddle point
`ch4ohtr3.dat`	`poly.fu5`	Input data for *Polyrate*
`ch4ohtr3.61`	`esp.fu61`	*Polyrate* output file containing information about the stationary points
`ch4ohtr3.fu6`	`poly.fu6`	Long output file

9.2.9. Test run `ch4ohtr4`

Tunneling: SCT
Number of levels: single level
Hindered rotation: mode 14

This is the fourth and final run in the four-stage calculation for the $CH_4 + OH \rightarrow CH_3 + H_2O$ reaction. Actually this fourth stage may be considered either as stage 4 of a complete four-stage single-level calculation or as the fourth stage in five-stage dual-level calculation. In this test run we use the information about the stationary points appearing in the `fu61` output file from the `ch4ohtr3` test run and evaluate the reaction path, CVT, CVT/ZCT and CVT/SCT rate constants using Euler method.

We assumed the hindered rotor approximation for treating the lower vibrational mode along the reaction path, and we calculated the vibrational frequencies by using redundant internal coordinates.

The *Gaussrate 17* restart option was selected in the `fu70` input file, writing the information for future calculations in the `fu84` file. It is interesting to note that, since no *Gaussian 16 / 09* calculation is carried out for the saddle point in this particular run, the charge and multiplicity for the nonstationary points along the reaction path must be provided in the START section of the `fu70` file (since the program assumes that these nonstationary points have the same charge and multiplicity as the saddle point).

The Hessians along the reaction path are calculated using the keywords (specified in GRSEC list keyword in the GRPATH section of the `fu70` input file):

```
#PM3 OPT=(NOEIGENTEST,CALCFC) UNITS=AU FCHK NOSYMM OPTCYC=1
```

The reason for using these keywords, rather than FREQ as in the other test runs, is that when using the FREQ keyword for calculating the frequencies, some calculations of points along the reaction path performed with revision B.1 of GAUSSIAN 94 stop when the program reaches the *matcor* subroutine. The keywords given above make GAUSSIAN follow a different route, avoiding the *matcor* subroutine, ending successfully, and providing *Gaussrate 17* with the required information.

Gaussrate 17 I/O files *Gaussrate 17* file names

`ch4ohtr4.70`	`esp.fu70`	Input data for *Gaussrate 17*
`ch4ohtr4.dat`	`poly.fu5`	Input data for *Polyrate*
`ch4ohtr4.61`	`esp.fu61`	*Polyrate* output file containing information about the stationary points
`ch4ohtr4.fu6`	`poly.fu6`	Long output file
`ch4ohtr4.fu15`	`poly.fu15`	Summary output file
`ch4ohtr4.rst`	`esp.fu84`	*Gaussrate 17* restart file generated by *Gaussrate 17* in this run

9.2.10. Test run `ch4ohtr5`

Tunneling: LCT
Number of levels: dual level
Hindered rotation: mode 14

This test run completes an IOC dual-level calculation of the $CH_4 + OH \rightarrow CH_3 + H_2O$ reaction. The lower-level information is read from the restart file from the previous run. The higher-level data is included by means of the `fu50` file. Tunneling is calculated by the microcanonical optimized multidimensional tunneling method (µOMT), requiring therefore some calculation in the reaction-swath region that are not present in the restart file, since the tunneling for the previous run was calculated using the SCT approach. The frequencies are calculated using Cartesian coordinates, instead of the set of redundant curvilinear coordinates from the `ch4ohtr4` run. Since the different choice of coordinates does not affect the reaction path calculation, the restart option does not prevent us from changing the coordinate system from one run to another. The hindered rotor approximation is used for computing the partition function of the lowest vibrational mode. The lowest four frequencies are interpolated directly by the IVTST–0 interpolation algorithm.

The restart file to be read is copied from the ch4ohtr4.rst file, generated by the previous run, `ch4ohtr4`. The user should, therefore, run the previous run (`ch4ohtr4`) in this set of tests before running this one. A new restart file, which includes all the previous information plus the additional calculations needed for estimating the LCT tunneling, is generated by this test run.

Since *Gaussrate 17* tries to minimize the number of calculations spooled to *Gaussian 16 / 09,* any calculation involves several checking steps, which can actually slow the *Gaussrate 17* calculation when the *Gaussian 16 / 09* jobs are as fast as in this set of test runs. This fact, added to the large requirements of input-output data transfer, make this calculation (and, in general, any calculation based on semiempirical methods) much slower when using *Gaussrate 17* than when using MORATE.

Gaussrate 17 I/O files	*Gaussrate 17* file names	
`ch4ohtr5.70`	`esp.fu70`	Input data for *Gaussrate 17*
`ch4ohtr4.rst`	`esp.fu83`	Restart file read by *Gaussrate 17*
`ch4ohtr5.dat`	`poly.fu5`	Input data for *Polyrate*
`ch4ohtr5.50`	`poly.fu50`	Additional input data for the *Polyrate* VTST-IC calculation
`ch4ohtr5.61`	`esp.fu61`	*Polyrate* output file containing information about the stationary points
`ch4ohtr5.fu6`	`poly.fu6`	Long output file
`ch4ohtr5.fu15`	`poly.fu15`	Summary output file
`ch4ohtr5.rst`	`esp.fu84`	*Gaussrate 17* restart file generated by *Gaussrate 17* in this run

9.2.11. Test run `ch4ohtr6`

Tunneling: LCT
Number of levels: dual level
Hindered rotation: mode 14

This test run completes a IOC dual-level calculation of the $CH_4 + OH \rightarrow CH_3 + H_2O$ reaction. The lower-level information is read from the restart file from the `ch4ohtr4` run. The higher-level data is included by means of the `fu50` file. Tunneling is calculated by the microcanonical optimized multidimensional tunneling method (muOMT), with LCT method being calculated using the LCG4 approach. The frequencies are calculated using Cartesian coordinates, instead of the set of redundant curvilinear coordinates from the `ch4ohtr4` run. Since the different choice of coordinates does not affect the reaction path calculation, the restart option does not prevent us from changing the coordinate system from one run to another. The hindered rotor approximation is used for computing the partition function of the lowest vibrational mode. The lowest four frequencies are interpolated directly by the IVTST-0 interpolation algorithm.

The restart file to be read is copied from the `ch4ohtr4.rst` file, generated by the previous run, `ch4ohtr4`. The user should, therefore, run the previous run (`ch4ohtr4`) in this set of tests before running this one. A new restart file, which includes all the previous information plus the additional calculations needed for estimating the LCT tunneling, is generated by this test run.

Gaussrate 17 I/O files	*Gaussrate 17* file names	
`ch4ohtr6.70`	`esp.fu70`	Input data for *Gaussrate 17*
`ch4ohtr4.rst`	`esp.fu83`	Restart file read by *Gaussrate 17*
`ch4ohtr6.dat`	`poly.fu5`	Input data for *Polyrate*
`ch4ohtr6.50`	`poly.fu50`	Additional input data for the *Polyrate* VTST-IC calculation
`ch4ohtr6.61`	`esp.fu61`	*Polyrate* output file containing information about the stationary points
`ch4ohtr6.fu6`	`poly.fu6`	Long output file
`ch4ohtr6.fu15`	`poly.fu15`	Summary output file
`ch4ohtr6.rst`	`esp.fu84`	*Gaussrate 17* restart file generated by *Gaussrate 17* in this run

9.2.12. Test run `ch4ohtr7`

Tunneling: SCT
Number of levels: single level
Hindered rotation: none

This test run is for the $CH_4 + OH \rightarrow CH_3 + H_2O$ reaction where the electronic structure calculations used the M06-2X/6-31+G(d,p) model chemistry. The optimized geometries of reactants, transition state and products are given in the ch4oh.fu71-fu75 *Gaussrate 17* input files. Tunneling is calculated by small curvature tunneling method (SCT) and the frequencies along the minimum energy path are calculated using non-redundant internal coordinate.

Gaussrate 17 I/O files	*Gaussrate 17* file names	
ch4ohtr7.70	esp.fu70	Input data for *Gaussrate 17*
ch4ohtr7.71	esp.fu70	Input data for *Gaussrate 17* (reactant 1)
ch4ohtr7.72	esp.fu70	Input data for *Gaussrate 17* (reactant 2)
ch4ohtr7.73	esp.fu70	Input data for *Gaussrate 17* (product 1)
ch4ohtr7.74	esp.fu70	Input data for *Gaussrate 17* (product 2)
ch4ohtr7.75	esp.fu70	Input data for *Gaussrate 17* (Transition structure)
ch4ohtr7.dat	poly.fu5	Input data for *Polyrate*
ch4ohtr7.61	esp.fu61	*Polyrate* output file containing information about the stationary points
ch4ohtr7.fu6	poly.fu6	Long output file
ch4ohtr7.fu15	poly.fu15	Summary output file
ch4ohtr7.rst	esp.fu84	*Gaussrate 17* restart file generated by *Gaussrate 17* in this run

9.2.13. Test run `nh3ohtr1`

Tunneling: none
Number of levels: single level
Hindered rotation: none

This is a test run for the $NH_3 + OH \rightarrow NH_2 + H_2O$ reaction including a well on the reactant side and a well on the product side. The geometries are optimized by means of *Gaussian 16 / 09* methods. Therefore, the initial geometries and keywords for the optimization are given in the input files `esp.fu71-75`, `esp.fu77`, and `esp.fu78`, and INITGEO is set to *hooks* and STATUS to *0* in the REACT1, REACT2, PROD1, PROD2, WELLR, WELLP, and START sections of the `fu5` input file. The Hessian matrices are also calculated, as recommended, using the methods in *Gaussian 16 / 09.* With the information for the stationary points obtained in this way, a conventional TST rate constant without tunneling is calculated.

Gaussrate 17 I/O files	*Gaussrate 17* file names	
nh3ohtr1.70	esp.fu70	Input data for *Gaussrate 17*
nh3ohtr1.71	esp.fu71	Input data for reactant 1
nh3ohtr1.72	esp.fu72	Input data for reactant 2
nh3ohtr1.73	esp.fu73	Input data for product 1
nh3ohtr1.74	esp.fu74	Input data for product 2
nh3ohtr1.75	esp.fu75	Input data for the saddle point
nh3ohtr1.77	esp.fu77	Input data for the reactant well
nh3ohtr1.78	esp.fu78	Input data for the product well
nh3ohtr1.dat	poly.fu5	Input data for *Polyrate*
nh3ohtr1.61	esp.fu61	*Polyrate* output file containing information about the stationary points
nh3ohtr1.fu6	poly.fu6	Long output file
nh3ohtr1.fu15	poly.fu15	Summary output file

9.2.14. Test run `nh3ohtr2`

Tunneling: ZCT, SCT

Number of levels: single level

Hindered rotation: none

This is a test run for the $NH_3 + OH \rightarrow NH_2 + H_2O$ reaction including a well on the reactant side and a well on the product side using IVTST-M method. The geometries are read from `fu5` file with INITGEO set to *geom* and STATUS to *0* in the REACT1, REACT2, PROD1, PROD2, WELLR, WELLP, and START sections of the `fu5` input file. The potential energy surface is provided by `fu31` file. Rate constants are calculated using conventional TST, CVT, CVT/ZCT, and CVT/SCT methods.

Gaussrate 17 I/O files	*Gaussrate 17* file names	
`nh3ohtr1.70`	`esp.fu70`	Input data for *Gaussrate 17*
`nh3ohtr1.dat`	`poly.fu5`	Input data for *Polyrate*
`nh3ohtr1.fu31`	`poly.fu31`	Input data (potential energy surface) for *Polyrate*
`nh3ohtr1.61`	`esp.fu61`	*Polyrate* output file containing information about the stationary points
`nh3ohtr1.fu6`	`poly.fu6`	Long output file
`nh3ohtr1.fu15`	`poly.fu15`	Summary output file

9.2.15. Test run `h3tr1`

Tunneling: none

Number of levels: single level

Hindered rotation: none

This is a test run for the $H_2 + H \rightarrow H + H_2$ reaction. The geometries are optimized by means of *Gaussian 16 / 09* methods. Therefore, the initial geometries and keywords for the optimization are given in the input files `esp.fu71-75`, and INITGEO is set to *hooks* and STATUS to *0* in the REACT1, REACT2, PROD1, PROD2, and START sections of the `fu5` input file. The Hessian matrices are also calculated, as recommended, using the methods in *Gaussian 16 / 09*. With the information for the stationary points obtained in this way, a conventional TST rate constant without tunneling is calculated. This test run demonstrates that a linear system may be calculated using *Gaussrate 17*

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Gaussrate 17 I/O files	*Gaussrate 17* file names	
h3tr1.70	esp.fu70	Input data for *Gaussrate 17*
h3tr1.71	esp.fu71	Input data for reactant 1
h3tr1.72	esp.fu72	Input data for reactant 2
h3tr1.73	esp.fu73	Input data for product 1
h3tr1.74	esp.fu74	Input data for product 2
h3tr1.75	esp.fu75	Input data for the saddle point
h3tr1.dat	poly.fu5	Input data for *Polyrate*
h3tr1.61	esp.fu61	*Polyrate* output file containing information about the stationary points
h3tr1.fu6	poly.fu6	Long output file
h3tr1.fu15	poly.fu15	Summary output file

9.2.16. Test run `h3tr2`

Tunneling:	none
Number of levels:	single level
Hindered rotation:	none
Solvation model:	PCM

This is a test run for the $H_2 + H \rightarrow H + H_2$ reaction using the PCM solvation model. The geometries are optimized by means of *Gaussian 16 / 09* methods. Therefore, the initial geometries and keywords for the optimization are given in the input files `esp.fu71-75`, and INITGEO is set to *hooks* and STATUS to *0* in the REACT1, REACT2, PROD1, PROD2, and START sections of the `fu5` input file. The Hessian matrices are also calculated, as recommended, using the methods in *Gaussian 16 / 09*. With the information for the stationary points obtained in this way, a conventional TST rate constant without tunneling is calculated. This test run demonstrates that a linear system may be calculated using the PCM model found in *Gaussrate 17;* however, we recommend SMD for liquid-phase reactions.

Gaussrate 17 I/O files	*Gaussrate 17* file names	
`h3tr2.70`	`esp.fu70`	Input data for *Gaussrate 17*
`h3tr2.71`	`esp.fu71`	Input data for reactant 1
`h3tr2.72`	`esp.fu72`	Input data for reactant 2
`h3tr2.73`	`esp.fu73`	Input data for product 1
`h3tr2.74`	`esp.fu74`	Input data for product 2
`h3tr2.75`	`esp.fu75`	Input data for the saddle point
`h3tr2.dat`	`poly.fu5`	Input data for *Polyrate*
`h3tr2.61`	`esp.fu61`	*Polyrate* output file containing information about the stationary points
`h3tr2.fu6`	`poly.fu6`	Long output file
`h3tr2.fu15`	`poly.fu15`	Summary output file

9.2.17. Test run `c2h6`

Tunneling: none

Number of levels: single level

Hindered rotation: VRC-VTST for transitional modes

This is a test run for the $CH_3 + CH_3 \rightarrow C_2H_6$ reaction. This reaction occurs without a potential energy barrier. The calculation of rate constants for this reaction is carried out by using variable reaction coordinate variational transition state theory with multifaceted dividing surfaces. The rate constants are calculated by canonical variational theory, microcanonical variational theory, and total energy and angular momentum resolved microcanonical variational theory. Tunneling is not included. The test run is identical to a calculation in the following reference

> Density Functional Study of Methyl Radical Association Kinetics,
> Jingjing Zheng, Shuxia Zhang and Donald G. Truhlar, J. Phys. Chem. A,
> 2008, 112 (46), pp 11509–11513. DOI: 10.1021/jp806617m

9.2.18. Test run `c2f4`

Tunneling: None
Number of levels: single level
Hindered rotation: VRC-VTST for transitional modes

This sample run is for the reaction $CF_2 + CF_2 \rightarrow C_2F_4$. It computes the high-pressure-limit rate constants; pressure-dependent rate constants can then be computed by the SS-QRRK utilty program of *Polyrate* (please see the SS-QRRK manual in the *Polyrate* distribution) Test run `c2f4` performs calculations of the VRC-VTST rate constants at the unrestricted M08-HX/MG3S level. The calculation of rate constants for this reaction is carried out by using variable reaction coordinate variational transition state theory with multifaceted dividing surfaces. The rate constants are calculated by canonical variational theory, microcanonical variational theory, and total energy and angular momentum resolved microcanonical variational theory. Tunneling is not included. This run is identical to one of runs in

> "Barrierless Association of CF_2 and Dissociation of C_2F_4 by Variational Transition State Theory and System-Specific Quantum RRK Theory," J. L. Bao, X. Zhang, and D. G. Truhlar, Proceedings of the National Academy of Sciences, U.S.A. **113**, 13606-13611 (2016). dx.doi.org/10.1073/pnas.1616208113

9.2.19. Test run `c6h6ch3`

Tunneling: SCT
Number of levels: single level
Hindered rotation: none in *Polyrate* input

This sample run is for the reaction $C_6H_6CH_3 \rightarrow C_6H_5CH_3 + H$, where $C_6H_6CH_3$ is methylcyclohexadienyl radical (the adduct of H and toluene). A scale factor 0.956 is used in the computation. It computes the high-pressure-limit rate constants; pressure-dependent rate constant can then be computed by the SS-QRRK utilty program of *Polyrate* (please see the SS-QRRK manual in the *Polyrate* distribution) Test run `c6h6ch3` performs calculations of the CVT/SCT rate constants at the MPW1K/MG3S level. This run is identical to one of runs in

> "Kinetics of Hydrogen Radical Reactions with Toluene by Chemical Activation Theory Employing System-Specific Quantum RRK Theory

Calibrated by Variational Transition State Theory," J. L. Bao, J. Zheng, and D. G. Truhlar, Journal of the American Chemical Society **138**, 2690-2704 (2016) dx.doi.org/10.1021/jacs.5b11938

9.2.20. Test run `c6h4oh2`

Tunneling:	SCT
Number of levels:	single level
Hindered rotation:	none in *Polyrate* input
Solvation model:	SMD in aqueous solution

This sample run is for the reaction $p\text{-}C_6H_4(OH)_2 + HO_2 \rightarrow C_6H_5(OH)O + H_2O_2$. It performs calculations of the CVT/SCT rate constants at the M05-2X/MG3S level in water by using the SMD implicit solvation model. A scale factor 0.962 is used in the computation. This run is similar to one of the runs in

"Hydrogen Abstraction Reactions from Phenolic Compounds by Peroxyl Radicals: Multireference Character and Density Functional Theory Rate Constants," A. Galano, L. Muñoz-Rugeles, J. R. Alvarez-Idaboy, J. L. Bao, and D. G. Truhlar, Journal of Physical Chemistry A **120**, 4634-4642 (2016). dx.doi.org/10.1021/acs.jpca.5b07662

9.2.21. Test run `butanoltr1`

Tunneling:	SCT
Number of levels:	single level
Hindered rotation:	none in *Polyrate* input

This sample run is for the reaction $(CH_3)_3COH + HO_2 \rightarrow (CH_3)_2C(OH)CH_2 + H_2O_2$. It is an example of calculating MS-CVT/SCT rate constants at the M08-HX/MG3S level. For MS-VTST, the user only needs to calculate the lowest-energy path (which is the one we have included in the test run). A scale factor 0.973 is used in the computation. Note that, as shown in this example, when one adds torsional anharmonicity by the MS-T method with the *MSTor* program, one does not employ the hindered-rotator options of *Polyrate*. The MS-CVT/SCT rate constant is the product of the multistructural and torsional anharmonicity *F* factor for reaction with the CVT/SCT rate constant. The CVT.SCT rate constant is obtained with *Polyrate*. The *F* factor is obtained by the *MSTor* code, and it is equal to:

$$F = \frac{Q^{\ddagger}_{MS\text{-}T} / Q^{\ddagger}_{SS\text{-}T}}{(Q^{R1}_{MS\text{-}T} / Q^{R1}_{SS\text{-}T})(Q^{R2}_{MS\text{-}T} / Q^{R2}_{SS\text{-}T})}$$

where $Q^{X}_{MS\text{-}T}$ is the MS-T partition function for X (X = transition structure or reactant structure), and $Q^{X}_{SS\text{-}T}$ is the single-structural rovibrational partition function for X.

This test run is identical to the run that calculates the lowest-energy reaction path for the $(CH_3)_3COH + HO_2 \rightarrow (CH_3)_2C(OH)CH_2 + H_2O_2$ reaction in

> "Path-Dependent Variational Effects and Multidimensional Tunneling in Multi-Path Variational Transition State Theory: Rate Constants Calculated for the Reactions of HO2 with tert-Butanol by Including all 46 Paths for Abstraction at C and All Six Paths for Abstraction at O," J. L. Bao, P. Sripa, and D. G Truhlar, Physical Chemistry Chemical Physics **18**, 1032-1041 (2016) dx.doi.org/10.1039/c5cp05780a

9.2.22. Test run `butanoltr2`

Tunneling:	SCT
Number of levels:	single level
Hindered rotation:	none in *Polyrate* input

This sample run is for the reaction $(CH_3)_3COH + HO_2 \rightarrow (CH_3)_2C(OH)CH_2 + H_2O_2$. It is an example of calculating a second reaction path so that one can do a two-path MP-VTST rate constant for the same reaction as considered in the previous test run. In particular we calculate the second-lowest energy path. Notice that the inputs have the same format as for the lowest-energy path. Then the user only needs to use a program like Microsoft Excel to combine the results of the individual path runs to calculate MP-VTST rate constants; the formulas that one should input in Excel are documented in the *Polyrate* manual in Section 10.O, equations (13) and (14). Briefly, the MP-CVT/SCT rate constant is the product of $\langle \gamma \rangle$, the *F* factor, and the lowest-energy-path conventional TST rate constant. If we only consider two-path MP-VTST, then

$$\langle \gamma \rangle_2 = \frac{\kappa_{path1}\Gamma_{path1}Q^{\ddagger}_{path1} + \kappa_{path2}\Gamma_{path2}Q^{\ddagger}_{path2}}{Q^{\ddagger}_{path1} + Q^{\ddagger}_{path2}}$$

where κ_p is the SCT tunneling transmission coefficient for path *p*, Γ_p is the variational transmission coefficient for path *p*, and $Q^{\ddagger}$ is a single structure SS-T partition function.

The *Gaussrate 17* distribution contains a spreadsheet file (called butanoltr2.xls) that combines the relevant output of test runs butanoltr1 and butanoltr2 to calculate two-path MP-VTST rate constants for this test case.

9.2.23. Test run `sih4`

Tunneling: SCT
Number of levels: single level
Hindered rotation: none in *Polyrate* input

This sample run is for the reaction $(SiH_3)_2SiH^- + SiH_4 \rightarrow (SiH_3)_2SiH_2 + SiH_3^-$. It performs calculations of the CVT/SCT rate constants at the M06-2X/MG3S level. A scale factor 0.970 is used in the computation. This run is identical to one of the runs in
   "Silane-Initiated Nucleation in Chemically Active Plasmas: Validation
   of Density Functionals, Mechanisms, and Pressure-Dependent
   Variational Transition State Calculations," J. L. Bao and D. G. Truhlar,
   Physical Chemistry Chemical Physics **18**, 10097-10108 (2016)
   dx.doi.org/10.1039/c6cp00816j

9.2.24. Test run `ohso2`

Tunneling: SCT
Number of levels: single level
Hindered rotation: none in *Polyrate* input

This sample run is for the reaction $OH + SO_2 \rightarrow OHSO_2$. It performs calculations of the CVT/SCT rate constants at the M08-HX/MG3S level. A scale factor 0.973 is used in the computation. This run is identical to one of the runs in
   "Reaction of SO_2 with OH in the Atmosphere," B. Long, J. L. Bao, and
   D. G. Truhlar, Physical Chemistry Chemical Physics **19**, 8091-8100
   (2017) dx.doi.org/10.1039/c7cp00497d.

10. DETAILS OF CODE TESTING

This section details the computers, operating systems, and *Gaussian* versions on which the code has been DEVELOPED and tested. In each case we give the *Gaussrate* version number, then the computers and operating system on which *Gaussrate* was tested. For each computer and operating system we also specify the *Gaussian* version that was used for testing.

| *Gaussrate* version | GAUSSIAN Version | | | |
Machine (Operating system)	98	03	09	16
7.1/P7.1.1-G94				
IBM RS/6000 model 550 (AIX 4.1)	B.1			
Cray C90 (UNICOS 8.0.3)	D.3			
Silicon Graphics IRIS-Power Challenge L R8000 (IRIX 6.2)	B.1			
7.2/P7.2-G94				
IBM RS/6000 model 550 (AIX 4.1)	B.1			
Cray C90 (UNICOS 8.0.3)	D.3			
Silicon Graphics IRIS-Power Challenge L R8000 (IRIX 6.2)	B.1			
7.3/P7.3-G94				
IBM RS/6000 model 550 (AIX 4.2)	B.1			
Cray C90 (UNICOS 8.0.3)	D.4			
Silicon Graphics IRIS-Power Challenge L R8000 (IRIX 6.2)	B.1			
7.4/P7.4-G94 – 7.4.1/P7.4.1-G94				
IBM RS/6000 model 550 (AIX 4.2)	B.1			
Cray C90 (UNICOS 8.0.3)	D.4,E.1			
Silicon Graphics IRIS-Power Challenge L R8000 (IRIX 6.2)	B.1			
7.8/P7.8-G94 – 7.9.1/P7.9.1-G94				
IBM RS/6000 model 550 (AIX 4.2)	B.1			
Cray C90 (UNICOS 8.0.3)	E.1			
Silicon Graphics IRIS-Power Challenge L R8000 (IRIX 6.2)	D.4			

Gaussrate version	GAUSSIAN Version			
Machine (Operating system)	**98**	**03**	**09**	**16**
8.0/P8.0-G94				
IBM RS/6000 model 550 (AIX 4.2)	B.1			
IBM RS/6000 43P model 240 (AIX 4.3)	D.2			
Silicon Graphics IRIS-Power Challenge L R10000 (IRIX 6.2)	D.4			
8.1.1/P8.1-G94G98 – 8.2/P8.2-G94G98				
IBM SP with 604e processor (AIX 4.3.1)	D.2	A.7		
SGI-Origin 2000 with R10000 processor (IRIX 6.5)	D.4	A.7		
8.6/P8.5.1-G94G98				
SGI-Origin 2000 with R10000 processor (IRIX 6.5)	D.4			
8.7/P8.7-G94G98				
IBM SP with Power3 processor (AIX 4.3.4.0)		A.11		
SGI Origin 2000 with R12000 processor (IRIX 6.5.12f)		A.11		
8.9/P8.9-G94G98 – 9.0/P9.0-G94G98				
IBM SP with Power3 processor (AIX 4.3.4.0)		A.11		
SGI-Origin 2000 with R12000 processor (IRIX 6.5.12f)	E.2	A.11		
9.1/P9.1-G03G98G94				
IBM SP with Power3 processor (AIX 4.3.4.0)			A.11	B.01
SGI-Origin 2000 with R12000 processor (IRIX 6.5.12f)	E.2		A.11	B.01
Netfinity Linux Cluster with Pentium III (RedHat Linux 7.2)			A.11.3	B.01
SunBlade 2000 with UltraSparcIII processor (Solaris 8)			A.11	B.01
9.5/P9.5-G03G98G94				
IBM Regatta with Power4 processor (AIX 5.2)			A.11	D.01
SGI Altix with Itanium 2 processor (SuSE Linux)			A.11	D.01
IBM Netfinity with Pentium III (RedHat Enterprise Linux 3)			A.11.3	D.01
9.7/P9.7-G03G98G94				
IBM Regatta with Power4 processor (AIX 5.3)			A.11	D.01

Gaussrate version		GAUSSIAN Version		
Machine (Operating system)	**98**	**03**	**09**	**16**

SGI Altix with Itanium 2 processor (SuSE Linux)   A.11 D.01
IBM Netfinity with Pentium III (RedHat Enterprise Linux 3)   A.11.3 D.01
IBM BladeCenter with AMD Opteron processor (SuSE Linux)   D.01

2008/P2008-G03G98G94

SGI Altix with Itanium 2 processor (SuSE Linux)   A.11 E.01
IBM BladeCenter with AMD Opteron processor (SuSE Linux)   E.01
SGI Altix XE 1300 with 2.66 GHz Intel Xeon processor (SuSE Linux)   E.01

2009/P2008-G09G03G98G94

SGI Altix with Itanium 2 processor (SuSE Linux)   E.01 A.02
IBM BladeCenter with AMD Opteron processor (SuSE Linux)   E.01 A.02
SGI Altix XE 1300 with 2.66 GHz Intel Xeon processor (SuSE Linux)   E.01 A.02

2009-A/P2008-G09G03G98G94

SGI Altix with Itanium 2 processor (SuSE Linux)   E.01 A.02
IBM BladeCenter with AMD Opteron processor (SuSE Linux)   E.01 A.02
SGI Altix XE 1300 with 2.66 GHz Intel Xeon processor (SuSE Linux)   E.01 A.02

2016/P2016-G09

HP c7000 Linux Cluster (CentOS) with Intel Haswell E5-2680v3 processors (CentOS
Linux)   E.01
HP Haswell Linux Cluster (CentOS).HP Linux cluster with Intel Xeon X5560
"Nehalem EP" processors (CentOS Linux)   E.01

*Gaussrate 17 / 17-***B**

HP c7000 Linux Cluster (CentOS) with Intel Haswell E5-2680v3 processors (CentOS
Linux)   E.01
HP Haswell Linux Cluster (CentOS).HP Linux cluster with Intel Xeon X5560
"Nehalem EP" processors (CentOS Linux)   E.01

11.   *Gaussrate* REVISION HISTORY

Prior to *Gaussrate 17*, the GAUSSRATE version numbers have the general form v/Pv'-Gv"
where v is the overall version number, v' is the number of the version of *Polyrate* on
which it is based, and v" is the version of GAUSSIAN on which it is based. The part before
the solidus, i.e., v, is unique, that is, it changes if the interface changes, or if the *Polyrate*
version changes, or if the GAUSSIAN version changes. Thus, the part after the solidus is
redundant information, and it may be omitted when brevity is desirable. However, with
Gaussrate 17 we use a simpler naming scheme.

Note: We sometimes update one or more of the manuals without updating the version
number. The manual version is determined by the date of its most recent change and is
given on its first page. Any changes other than the manual(s) always involve a change in
version number of the code.

This section contains the revision history subsequent to version 7.1 (March 1997), which
was the first distributed version of the code.

Version 7.1.1/P7.1.1-G94 (March 1997)

1. A bug that caused the energy of the products (and therefore of the reverse rate
    constants) to be miscalculated for reactions with one product when the *Polyrate* 7.1.1
    methods were selected for the Hessian calculation optimization, and the GAUSSIAN 94
    methods were selected for geometry optimizations has been fixed.

2. A bug that caused some restart calculations to abort when an atomic species is
    involved has been fixed.

Version 7.2/P7.2-G94 (April 1997)

1. The test runs have been modified to take account of changes in the new version of
    Polyrate. This will lead to incompatibilities between the `fu5` input files for *Gaussrate*
    7.1 and the `fu5` files for *Gaussrate* 7.2 if certain options are used. The user is advised
    to check Section 23.E of the *Polyrate* 7.2 manual in order to modify the `fu5` input file

from previous calculations. No incompatibilities are present in the `fu31` through `fu35` input files. The interface has not changed.

2. The compiling scripts have been modified in order to make the compilation cleaner and safer.

Version 7.3/P7.3-G94 (July 1997)

1. This version is based on a new version of *Polyrate.* The test runs have been changed in order to use the new set of keywords and options. This will lead to incompatibilities between the `fu5` input files for previous versions of the program and the `fu5` files for *Gaussrate* 7.3 if certain options are used. The user is advised to check the Section 23.E of the *Polyrate* 7.3 manual in order to modify the `fu5` input file from previous calculations.

2. The *Gaussrate* files have been renamed from `gr.#` to `esp.#`, for the sake of consistency with the *Polyrate* and MORATE programs. Moreover, the numbering of these Fortran units was updated according to the new conventions established by *Polyrate* 7.3; in particular, the files are assigned to Fortran units 71-76 instead of 31-36.

3. The input file `fu70` is now a case sensitive file. Hence, when typing Unix path names, a capital letter in the path name must be entered as a capital letter, and a lower case letter must be entered as lower case.

Version 7.4/P7.4-G94 (August 1997)

1. This version is based on a new version of *Polyrate*. The test runs have been modified in order to interface with *Polyrate* 7.4, using the new keywords and options. These changes in *Polyrate* will lead to incompatibilities between the `fu5` input files for previous versions of the *Gaussrate* program and the `fu5` files for *Gaussrate* 7.4 if certain options are used. The user is advised to check Section 23.E of the *Polyrate* 7.4 manual in order to see whether it is necessary to modify the `fu5` input file from previous calculations.

2. Four new test runs for the CH$_4$OH system were added in order to illustrate the use of the STATUS keyword. In addition, some test runs were modified in order to apply the new *Polyrate* capability for calculating vibrational frequencies by using redundant internal coordinates.

3. The code has been changed in order to interface with version E.1 of GAUSSIAN 94. Minor changes in the formatted checkpoint file written by GAUSSIAN make previous versions of *Gaussrate* incompatible with the E.1 revision of GAUSSIAN 94.

Version 7.4.1/P7.4.1-G94 (September 1997)

1. This version is based on a new version of *Polyrate.* The interface between *Polyrate* and GAUSSIAN has not changed. Please review the *Polyrate* 7.4.1 revision history for details.

Version 7.8/P7.8-G94 (December 1997)

1. This version is based on a new version of *Polyrate.* The user is advised to review section 23.D of the *Polyrate* 7.8 manual to determine the possible incompatibilities in `fu5` input files from previous *Polyrate* versions.

2. This update also involves the possibility of including wells along the reaction path. With this aim, files `esp.fu77` and `esp.fu78` have been included in the program.

3. The keywords GROPT and NOGROPT have been removed. The code now determines the optimization options automatically from the information in the `fu5` input file. This leads to incompatibilities with `esp.fu70` input files from older versions of the program.

4. A new test, `nh3ohtr1`, has been added to illustrate the use of the files `esp.fu77` and `esp.fu78` for calculating wells on the reaction path. Moreover, the test run `oh3tr2` has been modified in order to provide an example of the use of the RODS method.

5. Several minor modifications in the test runs have been introduced to reduce the timings.

Version 7.8.1/P7.8.1-G94 (February 1998)

1. This version is based on a new version of *Polyrate.* The interface between *Polyrate* and GAUSSIAN has not changed. Please review the *Polyrate* 7.8.1 revision history for details.

Version 7.9/P7.9-G94 (March 1998)

1. This version is based on a new version of *Polyrate.* The interface between *Polyrate* and GAUSSIAN has not changed. The user is advised to review section 23.D of the *Polyrate* 7.9 manual to determine the possible incompatibilities in `fu5` input files from previous *Polyrate* versions.

Version 7.9.1/P7.9.1-G94 (April 1998)

1. This version is based on a new version of *Polyrate.* The interface between *Polyrate* and GAUSSIAN has not changed. Please review the *Polyrate* 7.9.1 revision history for details.

Version 7.9.2/P7.9.2-G94 (June 1998)

1. A bug in the print out of the gradients of some stationary points after their optimization using GAUSSIAN 94 methods has been fixed. This bug fix involved changes in the *ohook* subroutine.

Version 8.0/P8.0-G94 (September 1998)

1. This version is based on a new version of *Polyrate.* The Fortran source for the interface routines has not changed. Please review the *Polyrate* 8.0 revision history for details. The test run input files have been updated to interface with *Polyrate* 8.0. A new test run, `ch5tr2,` has been added to test the new ISPE method; and test run `oh3tr2` has been modified in order to use the new VRPE option for following the reaction path, allowing a larger step size.

2. A Korn shell script, `check`, has been included in the `testrun` directory to automatically compare the `fu15` output files obtained after running the test suite with those in the `testo` directory.

3. The structure of the distribution files and the compiling scripts have been modified in an attempt to make the compilation more straightforward. In addition, a compiling script for IBM computers with the 604e processor has been added.

Version 8.1.1/P8.1.1-G94G98 (July 1999)

1. This version is based on a new version of *Polyrate.*

2. Modifications in the subroutine *goutsec* are added to make the interface work with a new version of GAUSSIAN (in particular, for GAUSSIAN 98 Rev. A.7). In this case, the user only needs to indicate the directory of the GAUSSIAN 98 executable in the script `shuttle`.

3. The compilation script was modified to O3 with 64 bits for the IBM SP 604e processor.

Version 8.1.2/P8.1.2-G94G98 (August 1999)

1. This version is based on a new version of *Polyrate.*

Version 8.2/P8.2-G94G98 (August 1999)

1. This version is based on a new version of *Polyrate.*

Version 8.3/P8.3-G94G98 (December 1999)

1. This version is based on a new version of *Polyrate.*

Version 8.4/P8.4-G94G98 (August 2000)

1. This version is based on a new version of *Polyrate.*

2. A new keyword, RSTTOL, in the GENERAL section of input file `poly.fu70` has been added.

3. Modifications in the test suite were added in order to make all the test runs to run in a subdirectory of each test directory, so that the calculations are performed in a more clear fashion and the possibility of interfering with other GAUSSIAN or *Gaussrate* runs were minimized.

4. A new test run, `ch4ohtr6`, is added to test the LCG4 method for LCT tunneling.

Version 8.5/P8.5-G94G98 (October 2000)

1. This version is based on a new version of *Polyrate.*

Version 8.6/P8.5.1-G94G98 (November 2000)

1. This version is based on a new version of *Polyrate.*

Version 8.7/P8.7-G94G98 (October 2001)

1. This version is based on a new version of *Polyrate.*

Version 8.9/P8.9-G94G98 (May 2002)

1. This version is based on a new version of *Polyrate.*

2. The Korn shell script, `check`, has been renamed to `check94`. A new Korn shell script, `check98`, has been added to compare the `fu15` output files obtained after running the test suite with those in the `testo/g98` directory.

3. The SGI compilation script was modified to turn off some warnings during compilation.

Version 9.0/P9.0-G94G98 (May 2002)

1. This version is based on a new version of *Polyrate.*

Version 9.1/P9.1-G03G98G94 (July 2003)

1. This version is based on a new version of *Polyrate.*

2. This version allows interfacing *Polyrate* with the GAUSSIAN 03 as well as GAUSSIAN 98 and GAUSSIAN 94. This new feature required modifications in the `shuttle` script and upgrading the *headr* subroutine. The distributed output files obtained by running *Gaussrate* with GAUSSIAN 03 are located in the new directory `testo/g03`. A new Korn shell script, `check03`, has been added to compare the `fu15` output files obtained after running the test suite with those in the `testo/g03` directory.

3. Test runs `ch4ohtr4`, `ch4ohtr5`, and `ch4ohtr6` were updated to include the new SPECSTOP keyword of *Polyrate.*

4. The *Gaussrate* manual is now distributed as Word and pdf files instead of a txt file.

5. A few old variables that were not used anymore have been removed from the code.

6. The Cray platform is no longer supported. The `hooks_gr.cray` and `gaussrate.cray` files were removed.

7. The Sun and Linux platforms were added to the supported platforms. The `gaussrate.linux` and `gaussrate.sun` compiling scripts have been added in the `script` directory.

Version 9.4/P9.4-G03G98G94 (June 2006)

1. This version is based on a new version of *Polyrate.* The code has been modified to accept the MPI processor number from *Polyrate* , however, it does not yet take advantage of this information.

2. This version edits the *Polyrate* Makefile for easy installation.

3. The code has been modified to work on systems that do not have '.' in $PATH.

Version 9.5/P9.5-G03G98G94 (January 2007)

1. The H3 test runs have been added to demonstrate compatibility of linear systems and with the PCM solvation model.

Version 9.7/P9.7-G03G98G94 (June 2007)

1. This version is based on a new version of *Polyrate.* The code has been modified to be compatible with the new keywords INPUNIT and OUTUNIT in *Polyrate* version 9.7.

2. Most input files of test runs are modified by adding "INPUNIT AU" keyword to be compatible with *Polyrate* version 9.7. Two test runs do not use this keyword, and these test runs use angstroms for input.

Version 2008/P2008-G03G98G94 (May 2009)

1. This version is based on a new version of *Polyrate.* The code has been modified to be compatible with the *Polyrate* 2008. This allows one, for example, to now carry out VRC-VTST calculations in parallel using MPI. To illustrate the new capability, we added a test run for methyl radical association.

Version 2009/P2008-G09G03G98G94 (December 2009)

1. The subroutine *goutsec* is modified so that it can read the Test.fchk file generated by either G03 or G09. This modification make the subroutine *goutsec* read the geometry, energy, gradient, and Hessian independent of their order stored in the Test.fchk file.

Version 2009-A/P2008-G09G03G98G94 (March 2010)

1. A bug that causes WELLR geometry is overwritten by WELLP geometry is fixed in *prep* subroutine in hooks_gr.F file.

Version 2016/P2016-G09 (August 2016)

1. The common blocks are replaced by modules in order to be compatible with *Polyrate* version 2016.
2. A new test run, `ch4ohtr7`, is added.

***Gaussrate 17* (April 2017)**

1. The common blocks were replaced by modules in order to be compatible with *Polyrate* version 17. This program works with version D01 of *Gaussian 09*.

2.   Seven new test runs have been added.

Gaussrate 17-B (Aug 2017; Revision made by J. L. Bao and D. G. Truhlar)

1.   The current program works with either Gaussian 16 or Gaussian 09.

2.   A bug that affects reading the basis set from the external basis-set file via "@/usr/basis_set_directroy/basis.gbs" has been fixed.

12. ACKNOWLEDGMENTS