Abstract

MULTILEVELRATE is a set of FORTRAN subroutines and Unix scripts for interfacing the POLYRATE and MULTILEVEL computer programs. The interfaced programs can be used either to carry out direct dynamics calculations of gas-phase chemical reaction rates of polyatomic species (and also atoms and diatoms as special cases) using the electronic structure methods available in MULTILEVEL to calculate the potential energy surface and POLYRATE for the dynamics, or (ii) to carry out normal mode analysis using the multilevel methods of MULTILEVEL. The interface is based on the POLYRATE hooks protocol. The dynamical methods used are variational or conventional transition state theory and multidimensional semiclassical approximations for tunneling and nonclassical reflection. Rate constants may be calculated by any of the methods available in the POLYRATE-version 9.3 program for canonical or microcanonical ensembles or for specific vibrational states of selected modes with the translational, rotational, and other vibrational modes treated thermally. Bimolecular and unimolecular reactions are included. Both single-level and dual-level dynamics calculations may be carried out. In single-level mode, optimized geometries, potential energies, gradients, and Hessians can be calculated by any of the integrated molecular orbital (IMO) methods and linear combination (LC) methods provided by the MULTILEVEL package. In dual-level mode, the lower-level data is calculated by MULTILEVEL, and the higher-level data is read in from an external file.
Description

MULTILEVELRATE-version 9.4 provides an interface between two other programs:

POLYRATE-version 9.4.1
Department of Chemistry and Supercomputer Institute
University of Minnesota, Minneapolis, Minnesota

Rozeanne Steckler
San Diego Supercomputer Center, La Jolla, California

Bruce C. Garrett
Environmental Molecular Sciences Laboratory
Pacific Northwest Laboratory, Richland, Washington

Alan D. Isaacson
Department of Chemistry, Miami University, Oxford, Ohio

and Donald G. Truhlar
Department of Chemistry and Supercomputer Institute
University of Minnesota, Minneapolis, Minnesota

MULTILEVEL-version 4.2
Jocelyn M. Rodgers, Benjamin J. Lynch, Patton L. Fast,
Yan Zhao, Jingzhi Pu, Yao-Yuan Chuang, Benjamin A. Ellingson
and Donald G. Truhlar
Department of Chemistry and Supercomputer Institute
University of Minnesota, Minneapolis, Minnesota
User agreement

MULTILEVELRATE - version 9.4 is licensed under the Apache License, Version 2.0. The manual of MULTILEVELRATE - version 9.4 is licensed under CC-BY-4.0.

Publications of results obtained with the MULTILEVELRATE - version 9.4 software should cite the program and/or the article describing the program.

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

The use of the MULTILEVELRATE - version 9.4 implies acceptance of the terms of the licenses.
# Table of Contents

ABSTRACT .................................................................................................................. 1  
DESCRIPTION ............................................................................................................. 2  
USER AGREEMENT ..................................................................................................... 3  
TABLE OF CONTENTS ............................................................................................... 4  
1. INTRODUCTION ....................................................................................................... 5  
   1.1. Reference ........................................................................................................... 6  
   1.2. Versions ........................................................................................................... 6  
2. INSTALLATION ......................................................................................................... 8  
   2.1. Obtaining the codes ......................................................................................... 8  
   2.2. Installation ....................................................................................................... 9  
   2.3. Compiling ....................................................................................................... 10  
3. SUBROUTINES AND C SHELL SCRIPTS ............................................................. 10  
4. FILE USAGE ........................................................................................................... 15  
5. INPUT DESCRIPTION .............................................................................................. 17  
6. TESTING THE CODE .............................................................................................. 19  
7. TEST RUN ................................................................................................................ 20  
   7.1. CH$_5$ system test run ..................................................................................... 20  
   7.2. H$_2$SOH system test run ............................................................................... 21  
   7.3. Al$_2$ frequencies ......................................................................................... 21  
   7.4. CH$_3^+$ frequencies .................................................................................... 21  
8. BIBLIOGRAPHY ...................................................................................................... 22  
9. REVISION HISTORY ............................................................................................... 23
Chapter One

1. Introduction

MULTILEVELRATE is a program for the analysis of reactants, products, and transition states of chemical reactions and for direct dynamics calculation of variational transition state theory (VTST) rate constants and multi-dimensional semiclassical tunneling probabilities using the dual-level or multi-level electronic structure methods in MULTILEVEL package to represent the potential energy of interaction and its first and second derivatives whenever they are needed. This version 9.4/P9.4.1-M4.2 interfaces POLYRATE-version 9.4.1, which is a program for dynamical rate calculations, with the electronic structure program MULTILEVEL-version 4.2.

MULTILEVEL is a program for calculating optimized geometries, single point energies, single point gradients, and/or single-point Hessians using dual-level and multi-level methods, in which GAUSSIAN03 (or 98 or 94) is used as an external program for the components calculation.

MULTILEVELRATE requires that the user has both POLYRATE-version 9.4.1 and MULTILEVEL-version 4.2 on the same computer working properly before attempting to run MULTILEVELRATE.

No part of POLYRATE-version 9.4.1 or MULTILEVEL-version 4.2 is contained in MULTILEVELRATE or needs to be modified for running this program.

This MULTILEVELRATE manual covers only material that is not covered in the POLYRATE and MULTILEVEL manuals. The user of MULTILEVELRATE should read those manuals first.
The interface between POLYRATE and MULTILEVEL is made by a series of FORTRAN subroutines included in the files hooks_mr.f and hooks_mdep.f, which are specialized versions of the routines in the hooks.f file in POLYRATE-version 9.3 and by a C shell script shuttle_mr for running MULTILEVEL. This C shell script shuttle_mr takes the name of a MULTILEVEL input file and a MULTILEVEL output file as its first and second argument respectively.

After call to MULTILEVEL, the MULTILEVELRATE program generates formatted summary file that contains necessary information, such as geometries, energies, gradients, and Hessians. This formatted summary file will be read by MULTILEVELRATE, which passes all the requested information to the dynamics subroutines of POLYRATE.

1.1. Reference

Publications based on MULTILEVELRATE should give the following references:


1.2. Versions

The version number of MULTILEVELRATE has three parts, e.g., MULTILEVELRATE-version y/Pz-Mx, where y denotes the version of POLYRATE, z denotes the version of MULTILEVEL, and x denotes the version of MULTILEVELRATE. If y or z changes, or if anything except the manual changes in the interface package (which is
MULTILEVELRATE proper), then $x$ will always change. Thus $x$ is a unique identifier, and one can say version $x$ instead of version $x/Py-Mz$ except when one wants to emphasize the versions of the underlying codes.
Chapter Two

2

2. Installation

2.1. Obtaining the codes

The user needs to obtain three items of code:

POLYRATE:
The POLYRATE code is available from the University of Minnesota. For further information see:

http://comp.chem.umn.edu/polyrate

MULTILEVEL:
The MULTILEVEL code is also available from the University of Minnesota. For further information see:

http://comp.chem.umn.edu/multilevel

MULTILEVELRATE:
The MULTILEVELRATE code is also available from the University of Minnesota. For further information see:

http://comp.chem.umn.edu/multilevelrate

The prospective user of MULTILEVELRATE must obtain and install POLYRATE and MULTILEVEL before proceeding with MULTILEVELRATE.
2.2. Installation

Before installing MULTILEVELRATE, the user should first successfully install POLYRATE and MULTILEVEL. MULTILEVELRATE is distributed in tar format. The tar file needs to be untarred in the POLYRATE-version 9.4.1 directory. The command is `tar -xvf multilevelrate9.4.tar`. This command will create a directory called multirate. The C shell shuttle_mr and the directories script, source, doc, testo, and testrun are located in this MULTILEVELRATE parent directory. If instructions are followed correctly, the directory structure should be the following:

```
polyrate9.4.1
    ├── doc
    │    ├── exe
    │    │    └── multirate
    │    ├── obj
    │    │    └── poten
    │    ├── script
    │    │    └── src
    │    └── testo
    └── testrun
```

The files will be distributed among the directories as follow:

- **multirate**: configure, and five subdirectories
- **doc**: empty
- **script**: mrcompile, shuttle_mr
- **source**: hooks_mr.f, hooks_mr.wks, head_mr.f, multirate.inc
- **testo**: al2sac.fu6, al2mcg3.fu6, al2-mcg3.fu6, al2+mcg3.fu6, ch5hf.fu6, ch5sac.fu6, ch5mcomp2_gp.fu6, ch5mcomp2_srp.fu6, h2soh_sac.fu6, meth+mqcisd.fu6
- **testrun**: al2/, ch5/, h2soh/, meth+/,
2.3. Compiling

The configure script will make use of Makefile in the polyrate9.4.1/src directory to compile MULTILEVELRATE. The configure script will create a section in that Makefile and then call the script mrcompile, which will compile the source code. The multirate.exe executable will be placed in the polyrate9.4.1/exe directory.

Chapter Three

3

3. Subroutines and C Shell Scripts

Below is a brief description of MULTILEVELRATE subprograms and scripts utilized in MULTILEVELRATE. The final name on the first line is the name of the file in which the routine is found. Detailed caller and callee information can be found as comments in the source code.

**EHOOK** Subroutine hooks_mr.f
Calculates the energy using MULTILEVEL for a given set of coordinates.

**ENATIN** Subroutine hooks_mdep.f
Calculates a MULTILEVEL energy for atomic systems.

**ESCENER** Subroutine hooks_mdep.f
Carries out a MULTILEVEL single-point energy calculation.

**ESCFIRST** Subroutine hooks_mdep.f
Carries out a MULTILEVEL energy and gradient calculation.

**ESCSEC** Subroutine hooks_mdep.f
Carries out a MULTILEVEL Hessian calculation.
GEOIN Subroutine hooks_mdep.f

Carries out a MULTILEVEL geometry optimization.

GHOOK Subroutine hooks_mr.f

Calculates the energy and its first derivatives for a given geometry.

HEADR Subroutine head_mr.f

Writes the program header in the file fu6.

HHOOK Subroutine hooks_mr.f

Calculates the Hessian matrix for a given geometry using either MULTILEVEL or one of the methods in POLYRATE.

MINPENE Subroutine hooks_mr.f

Writes a standard MULTILEVEL input file for single-point energy calculation.

MINPFRS Subroutine hooks_mr.f

Writes a standard MULTILEVEL input file for a first derivative calculation.

MINPGE0 Subroutine hooks_mr.f

Writes the new geometry to the MULTILEVEL input file.

MINPSEC Subroutine hooks_mr.f

Writes a standard MULTILEVEL input file used to perform a second derivative calculation.

MOPTOFF Subroutine hooks_mr.f

Removes MULTILEVEL optimization options to generate a MULTILEVEL input file for a single-point calculation.

MOUTSEC Subroutine hooks_mr.f
Extracts electronic structure information from the MULTILEVEL format summary file `ml.sum`.

**MREST** Subroutine `hooks_mr.f`

Reads and writes the information in the restart files for a MULTILEVELRATE restart calculation.

**MTASK** Subroutine `hooks_mr.f`

Rewrites charge, multiplicity, number of atoms, and calculation task options of a MULTILEVEL input file.

**OHOOK** Subroutine `hooks_mr.f`

Optionally accepts an initial guess to the Cartesian coordinates of the full system and carries out a geometry optimization using either MULTILEVEL or a method in POLYRATE.

**PREP** Subroutine `hooks_mr.f`

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

**PREPJ** Subroutine `hooks_mr.f`

Initializes variables dependent on each stationary point.

**RCHMUL** Subroutine `hooks_mr.f`

Reads the charge and multiplicity from the MULTILEVEL formatted summary file `ml.sum`.

**RCODMR** Subroutine `hooks_mr.f`

Reads MULTILEVELRATE general option in file `fu70`.

**REDINF** Subroutine `hooks_mr.f`

Reads the information about reactants, products and saddle point calculated in
PREP subroutine.

RENERMR Subroutine hooks_mr.f
Reads the input options in file fu70 for MULTILEVEL energy calculation.

RFIRSTMR Subroutine hooks_mr.f
Reads the input option for MULTILEVEL gradient calculation.

RGENMR Subroutine hooks_mr.f
Reads the general option in file fu70.

RINPMR Subroutine hooks_mr.f
Reads MULTILEVELRATE options from file fu70.

RLINMR Subroutine hooks_mr.f
Reads a line and parses out the comments and extra spaces.

RSECMR Subroutine hooks_mr.f
Reads the input option for a MULTILEVEL Hessian calculation.

RSTATMR Subroutine hooks_mr.f
Reads input options for stationary points.

SETUP Subroutine hooks_mr.f
Initializes some variables and calls the subroutines for reading in input file fu70.

SET_VERSION Perl script set_version
Interactively sets the POLYRATE and MULTILEVEL versions.

SHUTTLE_MR C Shell Script shuttle.mr
Runs a MULTILEVEL calculation and creates the summary file.
STORE Subroutine hooks_mr.f

Stores information that may be useful for future calculations to avoid duplicated MULTILEVEL calls.

SECIN Subroutine hooks_mr.f

Carries out the MULTILEVEL Hessian calculation for stationary points.
Chapter Four

4

4. File usage

<table>
<thead>
<tr>
<th>File</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>esp.fu70</td>
<td>General option for MULTILEVELRATE</td>
</tr>
<tr>
<td>esp.fu71</td>
<td>MULTILEVEL input file for geometry optimization, energy, and</td>
</tr>
<tr>
<td></td>
<td>gradient calculation for reactant 1.</td>
</tr>
<tr>
<td>esp.fu72</td>
<td>MULTILEVEL input file for geometry optimization, energy, and</td>
</tr>
<tr>
<td></td>
<td>gradient calculation for reactant 2.</td>
</tr>
<tr>
<td>esp.fu73</td>
<td>MULTILEVEL input file for geometry optimization, energy, and</td>
</tr>
<tr>
<td></td>
<td>gradient calculation for product 1.</td>
</tr>
<tr>
<td>esp.fu74</td>
<td>MULTILEVEL input file for geometry optimization, energy, and</td>
</tr>
<tr>
<td></td>
<td>gradient calculation for product 2.</td>
</tr>
<tr>
<td>esp.fu75</td>
<td>MULTILEVEL input file for geometry optimization, energy, and</td>
</tr>
<tr>
<td></td>
<td>gradient calculation for saddle point.</td>
</tr>
<tr>
<td>esp.fu77</td>
<td>MULTILEVEL input file for geometry optimization, energy, and</td>
</tr>
<tr>
<td></td>
<td>gradient calculation for the well on the product side.</td>
</tr>
<tr>
<td>esp.fu78</td>
<td>MULTILEVEL input file for geometry optimization, energy, and</td>
</tr>
<tr>
<td></td>
<td>gradient calculation for the well on the reactant side.</td>
</tr>
<tr>
<td>esp.fu81</td>
<td>MULTILEVEL temporary input file, generated by MULTILEVELRATE.</td>
</tr>
<tr>
<td>esp.fu82</td>
<td>MULTILEVEL temporary output file, generated by MULTILEVELRATE.</td>
</tr>
<tr>
<td>esp.fu83</td>
<td>Restart file to be read during a restart calculation.</td>
</tr>
<tr>
<td>esp.fu84</td>
<td>Restart file to be written during a restart calculation.</td>
</tr>
</tbody>
</table>
esp.fu86  A temporary MULTILEVEL input file template for all the
generalized transition state points along the reaction path.

ml.sum  A formatted MULTILEVEL output summary generated by
MULTILEVEL. It uses the fu85 unit.

.dat(fu5)  Input file for POLYRATE option

.fu6(fu6)  MULTILEVELRATE output file

If the execution script .mr (see Chapter 7) is used for running MULTILEVELRATE,
files generated by MULTILEVEL including MULTILEVEL output files, GAUSSIAN
input/output files, GAUSSIAN checkpoint files, and non-standard basis sets files, will be all
transferred to a new directory named MRTEMPFILES in the working directory at the end of
each calculation. One can check for those MULTILEVEL files if a task crashes.
Chapter Five

5

5. Input Description

MULTILEVELRATE is written in a way that puts no limitation on MULTILEVEL and POLYRATE options. In other words, all valid options for MULTILEVEL and POLYRATE are usable in the MULTILEVELRATE input file. The MULTILEVELRATE program simply acts as an interface without interfering with the dynamics and electronic structure parts.

The following files are MULTILEVELRATE input files:

<table>
<thead>
<tr>
<th>Fortran Unit</th>
<th>Extension</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>fu70</td>
<td>.70</td>
<td>MULTILEVELRATE general options</td>
</tr>
</tbody>
</table>

Comment:

The input option format follows the POLYRATE input convention. The section containing general options is "*MRGENERAL". Currently, only one keyword called "MRRESTART" is available in this section. The switch "MRRESTART" is used to specify that a restart calculation if restart information exists or to write a restart file if a restart file does not exist. The remaining input sections are regarding to stationary points: *MRREACT1, *MRREACT2, *MRPROD1, *MRPROD2, *MRSTART, *MRWELLR, and *MRWELLP, corresponding to reactants, products, the saddle point, the reactant well, and the product well. One can specify the charge of each species under these sections by variable keywords "CHARGE n", where n is the
charge of the species (see the revision history of MULTILEVELRATE-v9.3 for more detailed information).

2) fu71-fu78 .71-.78 MULTILEVEL input
Comment:
The usage of these files has been discussed in Chapter 4. They are MULTILEVEL input files for stationary points, the saddle point, and the reactant or the product well. Please check the MULTILEVEL manual for details of options, lists, and switches keywords.

The order of the atoms should be consistent with the order used in the POLYRATE input file .dat(fu5) specified. "GRADIENT" switch is supposed to be turned on for all the stationary points except for an atomic species in those MULTILEVEL input files. The switch keyword "PRSUM" MUST be turned on to specify a summary file named "ml.sum" is printed by MULTILEVEL. For atomic species, the "MULTIOPT" section should not be present due to the meaninglessness of geometry optimization on an atom.

3) fu5 .dat POLYRATE input
Comment:
The format and options follow the POLYRATE input file fu5. Check the POLYRATE manual for further details.
Chapter Six

6. Testing the code

MULTILEVELRATE-version 9.4 was tested on the following computers and operating systems:

<table>
<thead>
<tr>
<th>Platform</th>
<th>Operating System</th>
<th>Compilers</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBM Regatta, Power4 procs</td>
<td>AIX 5.2</td>
<td>XL Fortran version 8.1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>g77 from gcc version 3.4.1</td>
</tr>
<tr>
<td>IBM Netfinity, Dual Pentium III procs</td>
<td>Redhat Enterprise Linux 3</td>
<td>Portland group fortran compiler version 5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>g77 from gcc version 3.3.3</td>
</tr>
<tr>
<td>SGI Altix, Itanium 2 procs</td>
<td>SuSE Linux</td>
<td>Intel ifort version 9.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>g77 from gcc version 3.2.3</td>
</tr>
</tbody>
</table>
Chapter Seven

7. Test run

To run test runs, well commented scripts ending with .mr are provided in this package. For example, type ch5hf.mr to run the first CH₅ test run. The output file inherits the root name of the test run, for example, in this case the output file is ch5hf.fu6.

7.1. CH₅ system test run

Reaction:  \( \text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H} \)

Test run ch5hf

Dynamics:  TST and CVT reaction rates, with ZCT and SCT tunneling.

Electronic Structure:  HF/STO-3G

Test run ch5mcomp2_gp

GP (general parameters)

Dynamics:  TST and CVT reaction rates, with ZCT and SCT tunneling. ESD/RODS algorithm is used to follow the reaction path.

Multilevel Method:  MCCM-CO-MP2/MG3;6-31G(d), using the version v2m parameters.

Test run ch5mcomp2_srp
SRP (specific reaction parameters)

Dynamics: TST and CVT reaction rates, with ZCT and SCT tunneling. ESD/RODS algorithm is used to follow the reaction path.

Multilevel Method: MCCM-CO-MP2/MG3;6-31G(d) using the reaction specific parameters.

Test run ch5sac

Dynamics: TST and CVT reaction rates, with ZCT and SCT tunneling. ESD/RODS algorithm is used to follow the reaction path.

Multilevel Method: SAC with the version v2m parameters

7.2. H$_2$SOH system test run

Reaction: $\text{H}_2\text{S} + \text{OH} \rightarrow \text{SH} + \text{H}_2\text{O}$

Test run h2soh_sac

Dynamics: TST reaction rates

Multilevel Method: SAC with v3s parameters

Test runs 7.3 and 7.4 show how to use MULTILEVELRATE to carry out multilevel frequency calculations for stationary points, in which the POLYRATE normal mode analyzer takes Hessians computed by MULTILEVEL as input.

7.3. Al$_2$ frequencies

Test run a12sac Al$_2$ frequency, SAC with v3s parameters

Test run a12mcg3 Al$_2$ frequency, MCG3 with v3s parameters

Test run a12-mcg3 Al$_2^-$ frequency, MCG3 with v3s parameters

Test run a12+mcg3 Al$_2^+$ frequency, MCG3 with v3s parameters

7.4. CH$_3^+$ frequencies

Test run meth+mcqcisd CH$_3^+$ frequencies, MC-QCISD with v3s parameters
Chapter Eight

8

8. Bibliography


Chapter Nine

9

9. Revision History

MULTILEVELRATE - version 8.7/P8.6-M2.3 (May 2001)

- The first version


- The scripts (*.mr) for running MULTILEVELRATE jobs are modified. The script automatically make a scratch directory so that all intermediate files created by MULTILEVELRATE will be put into this scratch directory which is separate from the input files. At the end of the calculations, the MULTILEVELRATE output files are copied from the scratch directory to the directory containing the input files. The MULTILEVEL input and output files are moved to a directory called MRTEMPFILES for any possible debug. Then the temporary scratch directory containing unnecessary intermediate files is deleted. It makes the end user much easier to manage the major input and output files by running MULTILEVELRATE jobs through this modified script.

- Input sections *MRREACT1, *MRREACT2, *MRPROD1, *MRPROD2, *MRSTART, *MRWELLR, and *MRWELLP are added to the fu70 file in order to specify charges for each corresponding species by the keyword CHARGE. For a MULTILEVELRATE calculation in which the stationary points are optimized through hooks, above information are ignored, regardless whether the species is neutral or not. When one defines the initial geometry as an optimized structure in POLYRATE (STATUS=2) for a charged species, this additional input of charges in fu70 is required. This corrects a bug for charged species in the previous version.
• A bug has been fixed in subroutine RSTATMR (hooks_mr.f), where a comma was missed in a print format statement. For some compilers, this bug could generate an error.

• The input keywords "SGLV" and "MTLV" (in section *MRGENERAL of fu70) are removed. By utilizing the summary file (ml.sum) printed out by MULTILEVEL, the special treatment required for a single level calculation does not exist any longer.

• Test runs for H$_2$SOH, Al$_2$, and CH$_3^+$ are added. The latter two cases are to show how to compute multilevel frequencies by using MULTILEVELRATE. The original CH$_5$ test runs have been reorganized.

MULTILEVELRATE - version 9.4/P9.4-M4.2 (July 2006)

• Installation is now accomplished by using the Makefile in the polyrate/src directory. The numerous installation scripts for various platforms have been replaced by the single configure script.

• All system calls now include “./”, which makes the code portable to environments that do not include the current working directory in the path.

• The scripts have been updated to the more generic naming system using .poly_path and .multi_path, which allows for easier updating.

• The testruns have been updated to use the g03 rather than g98 as the default.