



Tutorial on POLYRATE

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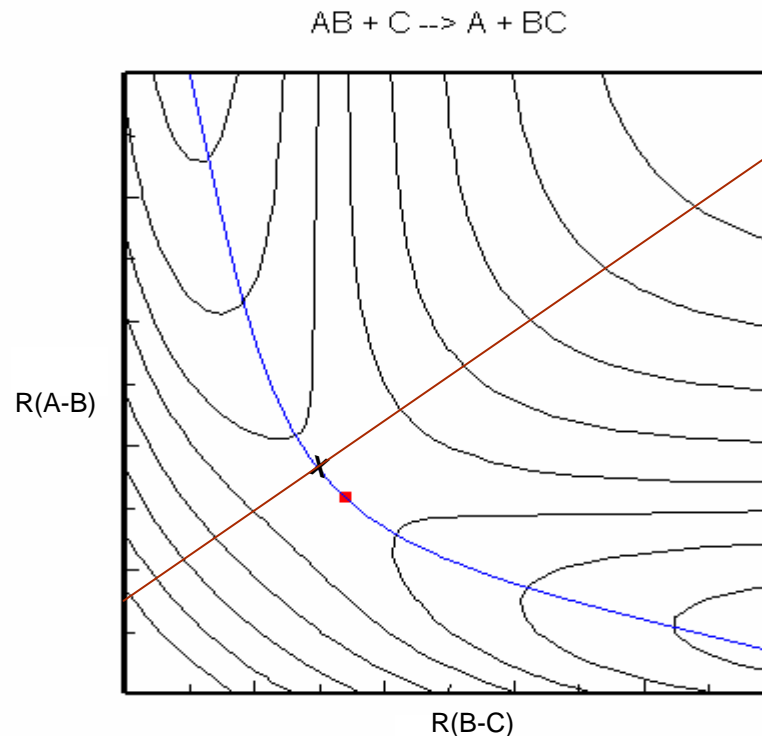


Outline

- Introduction
- Installation
- Input and output files
- How to run the program
- Advice on applications

Introduction to VTST

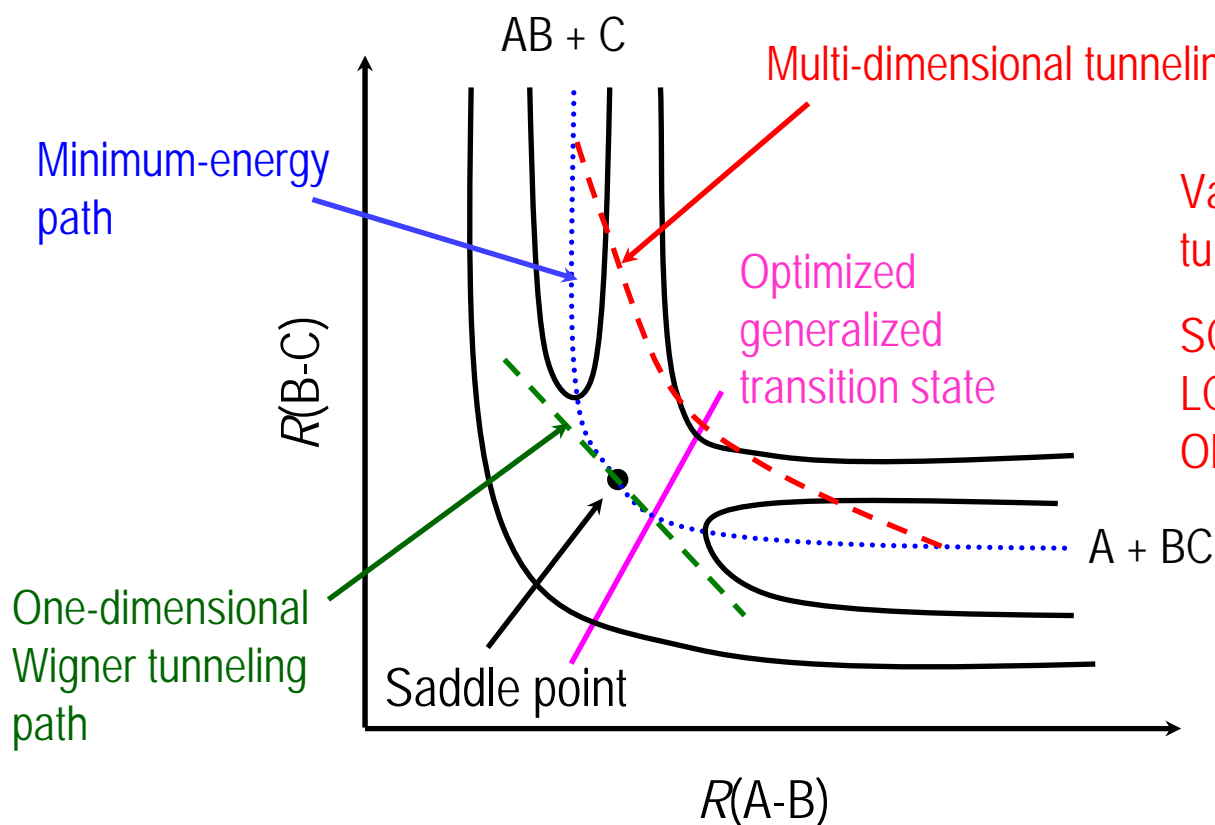
- Transition state theory (TST)
 - The transition state is a dividing surface that separates the reactant region from the product region in phase space.
 - **no-recrossing assumption**: TST assumes that all the trajectories that cross this dividing surface in the direction from reactants to products have originated in the reactant region and will proceed to products with ever recrossing the surface.
 - In a classical mechanical world with reactant states populated by a Boltzmann distribution, TST gives upper bound of the reaction rate.
- Variational transition state theory (VTST)
 - It optimizes the definition of the transition state to minimize the rate constant.
 - It provides a formalism in which quantum effects can readily be included.



Potential energy surface for a system in which atom B is transferred from group A to group C

The blue curve is the minimum energy path (MEP). The red dot denotes the saddle point. The red line that crosses the MEP at an X is a possible dividing surface.

Variational transition state theory with multi-dimensional tunneling



Various approximations for the tunneling paths may be considered:

SCT \equiv small-curvature tunneling
LCT \equiv Large-curvature tunneling
OMT \equiv optimized multidimensional tunneling
 $\equiv \max \begin{cases} \text{SCT} \\ \text{LCT} \end{cases}$

For more discussion and details, see reviews:

Truhlar, Garrett, and Klippenstein *J. Phys. Chem.* **1996**, *100*, 12771.

Fernandez-Ramos, Ellingson, Garrett, and Truhlar, *Rev. Comp. Chem.* **2007**, *23*, 125.

Introduction to POLYRATE

- POLYRATE is a computer program for calculations of **chemical reaction rates** of polyatomic species (and also atoms and diatoms as special cases).
- Theory:
 - Variational or conventional transition state theory (VTST or TST)
 - Multidimensional semiclassical approximations for tunneling and nonclassical reflection (ZCT, SCT, LCT, and μ OMT)
- Bimolecular and unimolecular reactions and **gas-phase, solid-state, and gas-solid-interface** reactions are all included.
- Rate constants may be calculated for **canonical or microcanonical** ensembles. (VTST may be also be applied to reactions with specific vibrational states of selected modes with translational, rotational, and other vibrational modes treated thermally, but this requires additional assumptions that make it less accurate than for un-state-selected cases.)

Options for the Potential Energy Surface (PES)

- Analytic PES: (**old fashioned**)
 - An analytic function to be compiled and linked with the program. (User is responsible for providing corresponding Fortran subroutines.)
- Implicit PES: (**direct dynamics**)
 - Defined by input files containing energies, gradients, and Hessians at selected points on a reaction path.
 - Defined by energies, gradients, and Hessians calculated by an electronic structure program “on the fly”.

Options for the Potential Energy Surface (PES)

For direct dynamics, POLYRATE is interfaced to an electronic structure software package. Several possible electronic structure codes are available:

Electronic structure package	Interfaced program
GAUSSIAN	GAUSSRATE
JAGUAR	JAGUARATE
GAMESSPLUS	GAMESSPLUSRATE
MOPAC	MORATE
MULTILEVEL	MULTILEVELRATE
NWCHEM	NWCHEMRATE
MC-TINKER	MC-TINKERATE
CHARMM	CRATE

<http://comp.chem.umn.edu/truhlar/index.htm#software>

Options for the Potential Energy Surface (cont.)

As an example of how the direct dynamics rate programs work, this is how GAUSSRATE works:

- Every time that POLYRATE needs an energy, gradient, or Hessian, it writes a GAUSSIAN input file, runs GAUSSIAN, and reads the GAUSSIAN formatted checkpoint file to get the needed values.
- Optimizations can be done with either POLYRATE or GAUSSIAN optimizers.
- Any electronic structure method in GAUSSIAN may be used. If analytic gradients or Hessians are available in GAUSSIAN, they can be used; if not, numerical derivatives can be used. Usually we recommend that calculations be done only for methods with analytic gradients, but this is not a requirement.

The other interfaced programs work in the same way.

Installation

- GAUSSRATE is taken as an example to illustrate how to install these interfaced programs.
- GAUSSRATE is an interface program between POLYRATE and *Gaussian 03*. *Gaussian 03* is a separate commercial product that must be installed first.
- POLYRATE and GAUSSRATE can be acquired from the Truhlar group web page <http://comp.chem.umn.edu/truhlar/index.htm#software>. Fill out and return the license forms and you will be given a password to download the programs.
- There is no fee for POLYRATE and GAUSSRATE.
- *Gaussian 03* must be licensed from Gaussian, Inc.

Installation (continued)

- Once the POLYRATE and GAUSSRATE programs have been acquired, install POLYRATE first.

```
[~]% gunzip polyrate9.7.tar.gz
```

```
[~]% tar -xvf polyrate9.7.tar
```

- Go to the POLYRATE directory and run the "configure" script

```
[~]% cd polyrate9.7
```

```
[~/polyrate9.7]% ./configure
```

```
Welcome to POLYRATE 9.7!
```

```
Do you want POLYRATE 9.7 to be your  
new default version of POLYRATE? [yes]:
```

```
...[displays information about the OS and compiler]
```

```
Do the options chosen above look OK? [yes]:
```

```
...installing // ...creating Makefile // ...done with Makefile
```

```
---- POLYRATE INSTALLATION COMPLETE ----
```

This script generates a file called Makefile in ~/polyrate9.7/src/ directory

Installation (Continued)

- POLYRATE is now installed, then install GAUSSRATE

```
[~/polyrate9.7]% gunzip gaussrate9.7.tar.gz
```

```
[~/polyrate9.7]% tar -xvf gaussrate9.7.tar
```

- Go to the `gaussrate` directory and edit the ```shuttle``` script.

The 'shuttle' script needs to be told where the *Gaussian 03* executable file is to be located

```
set gausspath=/usr/local/g03/g03.d01/g03/
```

- Run the ```configure``` script under `gaussrate` directory to install and compile the program.

```
[~/polyrate9.7]% cd gaussrate
```

```
[~/polyrate9.7/gaussrate]% ./configure
```

- Now installation is completed and you are ready to run test runs.

GAUSSRATE Input Files

- .dat file:
 - This is the main input file for POLYRATE routines.
 - The keywords in this file are explained in the POLYRATE manual.
 - A few keywords related to how the implicit PES is obtained can also be found in the GAUSSRATE manual.
- .70 file
 - Information needed by POLYRATE to generate *Gaussian 03* input files
- .71 - .78 files
 - *Gaussian 03 input files*, which are called to optimize geometries of reactants, products, saddle points, and wells, if Gaussian is used to optimize geometries.

Organization of .dat input file

- There are 12 sections for the .dat file
 - *GENERAL
 - *ENERGETICS
 - *SECOND
 - *OPTIMIZATION
 - *REACT1 *REACT2 *PROD1 *PROD2 *WELLR *WELLP
 - *START
 - *PATH
 - *TUNNEL
 - *RATE
- There are three types of keywords
 - Switch (on or off)
 - Variable (keywords followed by numerical value)
 - List
 - LEVEL1KEYWORD
 - LEVEL2KEYWORDA
 - LEVEL2KEYWORDB
 - END

Example of .dat input file

*GENERAL

TITLE

OH + H2 -> H2O + H Gaussrate test
calculation

END

ATOMS

1 H
2 O
3 H
4 H

END

NOSUPERMOL

INPUNIT ANG #default
OUTUNIT ANG #default

*OPTIMIZATION

OPTMIN

OHOOK

OPTTS

OHOOK

*SECOND

HESSCAL

HHOOK

*REACT1

INITGEO

HOOKS

GEOM

1

2

END

SPECIES

LINRP

end of react1 section

*REACT2

.....

*PROD1

.....

*PROD2

.....

*START

.....

Example of .dat input file (continued)

*PATH

SSTEP	0.002
INH	9
NSTEPS	99999
RPM	ESD

SRANGE

SLP	2.0
SLM	-2.0

END

*TUNNEL

ZCT
SCT

*RATE

BOTHK	
SIGMAF	2
SIGMAR	2

TST
CVT

TEMP

298.0
400.0
667.0
1000.
1500.

END

Example of .70 file for GAUSSRATE

***GRGENERAL**

GRRESTART

***GRCOMMON**

GRENER

%mem=200mb

#MPWPW91/6-31+G(d,p) SCF=(tight,xqc) FCHK

UNITS=AU NOSYMM IOP=(3/76=0572004280)

Integral(UltraFine)

END

GRFIRST

..... FORCE

END

GRSEC

..... FREQ=NORAMAN

END

***GRREACT1**

CHARGE 0

MULTIPLICITY 2

***GRREACT2**

CHARGE 0

MULTIPLICITY 1

***GRPROD1**

.....

***GRPROD2**

.....

***GRSTART**

.....

Example of .70 file for JAGUARATE

***JRGENERAL**

JRRESTART

***JRREACT1**

JRENER

&gen **isymm=0** dftname=m05 **iunit=0** basis=6-
31+G** multip=2 noauto=4 &
END

JRFIRST

&gen igeopt=-1 &
END

JRSEC

&gen ifreq=1 igeopt=-1 &
END

***JRREACT2**

.....

***JRPROD1**

.....

***JRPROD2**

.....

***JRSTART**

.....

***JRPATH**

.....

Selected Output Files

- .fu6 Full output file; selected subsets of this file are also written to files *.fu14 and *.fu15
- .fu14 Output table of dynamical bottleneck properties
- .fu15 Output table of selected forward rate constants
- .fu61 Information of stationary points

For information about the other output files, please see the POLYRATE manual, available without fee or license in PDF form at <http://comp.chem.umn.edu/polyrate>

Run Gaussrate - *.jc file

```
#!/bin/csh -f
# Usage ./oh3tr1.jc
set name = oh3tr1
#
if ($#argv != 0) then
    set actdir = `pwd`
    set wrkdir = $argv[1]
else
    set actdir = `pwd`
    set wrkdir = $actdir/$name
check:
    if (-e $wrkdir) then
        set tmp = $wrkdir/$name
        set wrkdir = $tmp
        goto check
    endif
    mkdir $wrkdir
endif
# Go to working directory
cd $wrkdir
#
# Set the name of the executable
#
set polydir = `cat ~/.poly_path`
set exedir = $polydir/exe
set exe = $exedir/gaussrate.exe
# Delete the fu# files left previously if any
rm poly.fu* >& /dev/null
```

```
# Copy the data files to POLYRATE filenames.
if (-e esp.fu81) then
    /bin/rm esp.fu81
endif
if (-e shuttle) goto input
cp $exedir/shuttle $wrkdir/shuttle
input:
cp $actdir/$name.dat poly.fu5
cp $actdir/$name.70 esp.fu70
cp $actdir/$name.75 esp.fu75
#
# Execute program & write system message to .time
file
(time $exe) >& $actdir/$name.time
echo " " >> $actdir/$name.time
#
# Copy the output files to appropriate filenames
mv poly.fu6 $actdir/$name.fu6
mv poly.fu15 $actdir/$name.fu15
mv esp.fu84 $actdir/$name.rst
mv esp.fu61 $actdir/$name.fu61
#
if (-e $actdir/GRTEMPFILES) goto exist
mkdir $actdir/GRTEMPFILES
exist:
mv * $actdir/GRTEMPFILES
cd $actdir
rm -rf $wrkdir
exit
```

Advice on Application

- Check whether the results are reasonable and do not suffer from numerical problems, instabilities, or errors. It is recommended to check the results in this order:
 - Reactant properties (i.e., geometries and frequencies)
 - Product properties and energy of reaction
 - Saddle point properties, including barrier height and magnitude of imaginary frequency
 - Conventional transition state theory without tunneling (TST)
 - Canonical variational transition state theory (CVT) with zero-curvature tunneling (CVT/ZCT)
 - CVT with small-curvature tunneling (CVT/SCT)
 - CVT with large-curvature tunneling limited to ground vibrational state (CVT/LCT(0))
 - CVT with full LCT and microcanonical optimized multidimensional tunneling (μ OMT) (CVT/LCT and CVT/ μ OMT)

- Vibrational frequency calculations
 - Use curvilinear coordinates (Keyword: `Coord CURV3` in `*PATH` section of the `*.dat` file).
 - When using a DFT method, the `ultrafine` grid for integration should be used.
 - Frequency scaling is recommended (http://comp.chem.umn.edu/database/freq_scale.htm) (keyword: `FREQSCALE`).

Advice on Application (continued)

- A common error of GAUSSRATE:
“Error reading Gaussian 03/98/94 checkpoint file” in fu6 output file
 - Check esp.fu82 in the GRTEMPFILES subdirectory
 - If this file exists, GAUSSRATE has performed *Gaussian 03* calculations, but something went wrong in *Gaussian 03*.
 - If this file does not exist, GAUSSRATE did not start any *Gaussian 03* calculation. Check `shuttle` script to see if the `gausspath` is set correctly.
 - Check the `.time` file. This file contains any information that the system wrote to the standard output during the run.