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## MORATE Manual

Program Version: 8.0/P8.0-M5.07 Program Version Date: September 4, 1998 Date of this manual update: September 4, 1998 Copyright 1998

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MORATE provides an interface between two other programs:

POLYRATE-version 8.0 by Y.-Y. Chuang, J. C. Corchado, P. L. Fast, J. Villa, E. L. Coitino, W.-P. Hu, Y.-P. Liu, G. C. Lynch, K. A. Nguyen, C. F. Jackels, M. Z. Gu, I. Rossi, S. Clayton, V. S. Melissas, R. Steckler, B. C. Garrett, A. D. Isaacson, and D. G. Truhlar Department of Chemistry and Supercomputer Institute University of Minnesota, Minneapolis, MN 55455-0431

and

MOPAC-version 5.07mn by J. J. P. Stewart, I. Rossi, W.-P. Hu, G. C. Lynch, Y.-P. Liu, and D. G. Truhlar Department of Chemistry and Supercomputer Institute University of Minnesota, Minneapolis, MN 55455-0431

Abstract: MORATE (Molecular Orbital RATE calculations) is a set of FORTRAN subprograms and Unix scripts for interfacing the POLYRATE dynamics program and the MOPAC electronic structure program for the purpose of direct dynamics calculations of gas-phase chemical reaction rates of polyatomic species (and also atoms and diatoms as special cases) using semiempirical molecular orbital theory to represent the potential energy of interaction and using POLYRATE for the dynamics. The interface is based on the POLYRATE hooks protocol. The dynamics 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 8.0 program for canonical or microcanonical ensembles or for specific vibrational states of selected modes with translational, rotational, and other vibrational modes treated thermally. Bimolecular and unimolecular reactions are included. Both single-level and dual-level modes are available. In single-level mode, potential energies and gradients can be calculated by any of the semiempirical molecular orbital methods in the MOPAC version 5.07mm package, in particular PM3, AM1, MNDO, and MINDO/3, and also by the NDDO-SRP method. In dual-level mode, these options are available for the lower-level part of the calculation, and higher-level data is read from an external file for VTST-IOC or ISPE calculations.

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## REFERENCES FOR MORATE PROGRAM:

Persons using MORATE should cite the MORATE, POLYRATE, and MOPAC packages. For example:

MORATE-version 8.0/P8.0-M5.07 by Y.-Y. Chuang, P. L. Fast, W.-P. Hu, G. C. Lynch, Y.-P. Liu, and D. G. Truhlar, University of Minnesota, Minneapolis, 1998 based on POLYRATE-version 8.0 by Y.-Y. Chuang, J. C. Corchad Corchado, P. L. Fast, J. Villa, E. L. Coitino, W.-H. Hu, Y. -P. Liu, G. C. Lynch, K. A. Nguyen, C. F. Jackels, M. Z. Gu, I. Rossi, S. Clayton, V. S. Melissas,

R. Steckler, B. C. Garrett, A. D. Isaacson, and D. G. Truhlar, University of Minnesota, Minneapolis, 1998 and MOPAC-version 5.07mn by J. Stewart, I. Rossi, W.-P. Hu, G. C. Lynch, Y. -P. Liu, and D. G. Truhlar University of Minnesota, Minneapolis, 1997.

Additional references for specific features of the calculations are given in the POLYRATE and MOPAC manuals and in Sections 1.A and 13 of this manual.

## USER AGREEMENT

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

- 1. 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 MORATE software or in any copyrights for the MORATE 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 (D.G.T.).
- Publications resulting from using this package or the POLYRATE or MOPAC subsystems used by this package will cite the corresponding program. The recommended references are given in the documentation (see above for the recommended reference for MORATE).
- 3. 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.
- 4. No consulting or maintenance services are guaranteed or implied.
- 5. The POLYRATE-8.0 and MOPAC-5.07mn codes required to use MORATE are covered by separate licenses. These licenses do not cover unchanged parts of MOPAC-5.0 or EF, which are available without licensing.

CONTACT INFORMATION

For more information or questions or problems with MORATE contact the principal investigator:

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## 1. INTRODUCTION

MORATE 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 multidimensional semiclassical tunneling probabilities using molecular orbital theory to represent the potential energy of interaction and its gradient wherever they are needed. The interface between MOPAC and MORATE is made by a series of FORTRAN subroutines called the MORATE hooks. This program version, 8.0/P8.0-M5.07, combines POLYRATE 8.0, which is a program for dynamical rate calculations, with the semiempirical electronic structure program MOPAC-version 5.07mn.

In the current version of the program, both unimolecular and bimolecular gas-phase reactions can be treated, and the maximum number of atoms can be reset by changing the parameters NATOMS, MAXHEV, and MAXLIT in the appropriate include files. More details of these parameters are given in Section 3 of this manual.

The analysis of reactants and products can be performed for up to two reactants and two products. The minimum-energy path (MEP) can be calculated by the Euler single-step (ES), Euler stabilization (ES1 or ES1\*), or Page-McIver (PM) methods. The MEP is always defined in mass-scaled coordinates and thus it is identical to what some persons call the IRC. Various anharmonicity options are available for the vibrational modes of the reactants, products, and/or generalized transition state species. The VTST rate constants can be computed using canonical variational theory (CVT), improved canonical variational theory (ICVT), or microcanonical variational theory (muVT). Conventional transition state theory (TST) may also be employed. The tunneling probabilities can be computed using the zerocurvature tunneling (ZCT) method, the centrifugal-dominant small-curvature tunneling (SCT)method, the large-curvature tunneling (LCT) method (version 3, including tunneling into excited states), and the microcanonical optimized multidimensional tunneling (muOMT) method.

In single-level mode, the MORATE program computes the rate constants either from energies and gradients calculated by semiempirical molecular orbital (MO) theory, or from a restart file which uses the reaction-path information from a previous calculation. In either case, the semiempirical MO methods that can be used to represent the potential energy surface are the same as those available in the MOPAC package, version 5.07mm, namely, MINDO/3, MNDO, AM1, PM3, and NDDO-SRP. The package also supports configuration interaction calculations based on semiempirical Hamiltonians.

In dual-level mode, MORATE computes the potential energy at the lower level by one of the options available for single-level calculations, and it reads the data needed for the high-level from a file assigned to FORTRAN unit fu50.

When we refer to the "potential", the "potential energy surface", or the "energy" in this manual, we mean the same thing, namely, the sum of the electronic energy and the nuclear repulsion energy.

## 1.A. General background references

The following references are recommended for general background. A more specific MORATE bibliography may be found in Section 13.

Generalized transition state theory:

1. "Variational Transition-State Theory," D. G. Truhlar and B. C. Garrett, Accounts of Chemical Research 13, 440-448 (1980).

2. "The Incorporation of Quantum Effects in Generalized Transition State Theory," D. G. Truhlar, A. D. Isaacson, R. T. Skodje, and B. C. Garrett, Journal of Physical Chemistry 86, 2252-2261 (1982). Erratum: 87, 4554 (1983).

3. "Generalized Transition State Theory," D. G. Truhlar, A. D. Isaacson, and B. C. Garrett, in Theory of Chemical Reaction Dynamics, edited by M. Baer (CRC Press, Boca Raton, FL, 1985), Vol. 4, pp. 65-137.

4. "Variational Transition State Theory," D. G. Truhlar and B. C. Garrett, in Annual Review of Physical Chemistry, Vol. 35, edited by B. S. Rabinovitch, J. M. Schurr, and H. L. Strauss (Annual Reviews, Inc., Palo Alto, California, 1984), pp. 159-189.

5. "Transition State Theory," M. M. Kreevoy and D. G. Truhlar, in Investigation of Rates and Mechanisms of Reactions, 4th edition, edited by C. F. Bernasconi (John Wiley and Sons, New York, 1986), Part 1, pp. 13-95. [Tech. Chem. (N.Y.), 4th ed., 6/Pt. 1, 13-95 (1986)].

6. "Dynamical Formulation of Transition State Theory: Variational Transition States and Semiclassical Tunneling," S. C. Tucker and D. G. Truhlar, in New Theoretical Concepts for Understanding Organic Reactions, edited by J. Bertrán and I. G. Csizmadia (Kluwer, Dordrecht, The Netherlands, 1989), pp. 291-346. [NATO ASI Ser. C 267, 291-346 (1989)]

7. "Direct Dynamics Method for the Calculation of Reaction Rates," D. G. Truhlar, in The Reaction Path in Chemistry: Current Approaches and Perspectives, edited by D. Heidrich (Kluwer, Dordrecht, 1995), pp. 229-255. [Understanding Chem. React. 16, 229-255 (1995).]

#### POLYRATE and MORATE:

1. "POLYRATE: A General Computer Program for Variational Transition State Theory and Semiclassical Tunneling Calculations of Chemical Reaction Rates," A. D. Isaacson, D. G. Truhlar, S. N. Rai, R. Steckler, G. C. Hancock, B. C. Garrett, and M. J. Redmon, Computer Physics Communications 47, 91-102 (1987).

2. "POLYRATE 4: A New Version of a Computer Program for the Calculation of Chemical Reaction Rates for Polyatomics," D.-h. Lu, T. N. Truong, V. S. Melissas, G. C. Lynch, Y.-P. Liu, B. C. Garrett, R. Steckler, A. D. Isaacson, S. N. Rai, G. C. Hancock, J. G. Lauderdale, T. Joseph, and D. G. Truhlar, Computer Physics Communications 71, 235-262 (1992).

3. "MORATE: A Program for Direct Dynamics Calculations of Chemical Reaction Rates by Semiempirical Molecular Orbital Theory," T. N. Truong, D.-h. Lu, G. C. Lynch, Y.-P. Liu, V. S. Melissas, J. J. P. Stewart, R. Steckler, B. C. Garrett, A. D. Isaacson, A. Gonzàlez-Lafont, S. N. Rai, G. C. Hancock, T. Joseph, and D. G. Truhlar, Computer Physics Communications 75, 143-159 (1993).

4. "POLYRATE-version 6.5 and MORATE-version 6.5/P6.5-M5.05. Two Computer Programs for the Calculation of Chemical Reaction Rates," W.-P. Hu, R. Steckler, G. C. Lynch, Y.-P. Liu, B. C. Garrett, A. D. Isaacson, D.-h. Lu, V. Melissas, I. Rossi, J. J. P. Stewart, and D. G. Truhlar, QCPE Bulletin 15, 32-36 (1995).

5. "POLYRATE 6.5: A New Version of Computer Program for the Calculation of Chemical Reaction Rates for Polyatomics," R. Steckler, W.-P. Hu, Y.-P. Liu, G. C. Lynch, B. C. Garrett, A. D. Isaacson, V. S. Melissas, D.-h. Lu, T. N. Truong, S. N. Rai, G. C. Hancock, J. G. Lauderdale, T. Joseph, and D. G. Truhlar, Computer Physis Communications 88, 341-343 (1995).

6. "MORATE 6.5: A New Version of Computer Program for Direct Dynamics Calculations of Chemical Reaction Rate Constants," W.-P. Hu, G. Reaction Rate Constants," W.-P. Hu, G. C. Lynch, Y.-P. Liu, I. Rossi, J. J. P. Stewart, R. Steckler, B. C. Garrett, A. D. Isaacson, D.-h. Lu, V. S. Melissas, and D. G. Truhlar, Computer Physics Communications 88, 344-346 (1995).

7. "Molecular Modeling of the Kinetic Isotope Effect for the [1,5]-Sigmatropic Rearrangement of cis-1,3-Pentadiene," Y.-P. Liu, G. C. Lynch, T. N. Truong, D.-h. Lu, D. G. Truhlar, and B. C. Garrett, Journal of the American Chemical Society 115, 2408-2415 (1993).

8. "Direct Dynamics Calculation of the Kinetic Isotope Effect for an Organic Hydrogen-Transfer Reaction, Including Corner-Cutting Tunneling in 21 Dimensions," Y.-P. Liu, D.-h. Lu, A. Gonzàlez-Lafont, D. G. Truhlar, and B. C. Garrett, Journal of the American Chemical Society 115, 7806-7817 (1993).

MOPAC:

1. "MOPAC: A Semiempirical Molecular Orbital Program," J. J. P. Stewart, Journal of Computer-Aided Molecular Design, Vol. 4, No. 1, 1-105 (1990).

2. "Semiempirical Molecular Orbital Methods," J. J. P. Stewart, Reviews in Computational Chemistry 1, 45-81 (1990).

#### FURTHER REFERENCES:

See Section 13.

## 2. ORGANIZATION OF THE MANUAL

This manual assumes that the user possesses manuals for POLYRATE-version 8.0, MOPAC-version 5.0, and MOPAC-version 5.07mm and that the user is familiar with the theory behind both POLYRATE and MOPAC.

In this manual, POLYRATE keywords (for example, EZERO) are in capital letters, whereas the values that these keywords take (for example, "calculate") are in double quotation marks. Section 3 discusses how to install MORATE. Some aspects of the interface of POLYRATE with the MOPAC semiempirical molecular orbital package are described in Section 4. Section 5 describes the program structure and the subprograms that make up the MORATE program, and it lists the files that comprise this version of MORATE. Section 6 describes the FORTRAN unit numbers used for the input and output. Section 7 contains selected details of some of the options available in this version of MORATE. Section 8 contains a description of the input required by the MORATE program. Section 9 describes the test runs that make up the test suite for this version of the program. Section 11 contains the timings for the test suite for this version of the code on all the machines on which it has been tested. Sections 12, 13, and 14 contain errata for the MORATE manuals, a bibliography, and information about MORATE versions.

Throughout this manual, we capitalize MORATE, POLYRATE, MOPAC, subprogram names, FORTRAN variables (except FORTRAN unit designators like fu6), MOPAC keywords, POLYRATE keywords, and acronyms in which every letter stands for a new word. File names (except SIZES.i and EXTERN.TR# files) and Unix commands are in lower case.

## 3. INSTALLATION

Notice that the licenses for POLYRATE and MOPAC5.07mn may be obtained via the internet, in particular from the URL: http://comp.chem.umn.edu

The MORATE8.0 package contains several compilation scripts (/morate8.0/src/moratecl.\*) for different platforms. The user of MORATE must obtain and install POLYRATE8.0 and MOPAC5.07mn before proceeding with MORATE. The MORATE scripts will look for the file .poly\_path8.0 for the location of the POLYRATE8.0 package and will ask the user to input the path of the MOPAC5.07mn source codes (e.g. /usr/chuang/mopac507mn/src).

One can carry out the installation by following the instructions in Section 3.C of this manual.

The program is distributed with the short output files for all the test runs in the test suite.

The program is always distributed in the Unix tarred format, and upon issuing the command tar -xvf <filename>, the files which make up the distribution package (see Subsection 3.A) will be partitioned into the following structure:

	mc	orate8.0		
 check_test.jc check_all.jc	 doc	 src	 testr	 testo
morate8.0:	this director	y contains al	l the files	1
doc:	this director	y contains th	e present M	ORATE manual
src:	this director the job contr source codes	y contains al ol files need	l the sourc ed to compi	e code and all le and link the
testr:	this director	ry contains th	e sample te	st run files
testo:	this director for the test	ry contains al runs from Cra	l the short y C90	output files
check_test.jc:	a job control	file that ch	ecks a spec	ific test run
check_all.jc:	a job control	file that ch	ecks all th	e test runs

## 3.A. DESCRIPTION OF FILES IN RELEASE OF VERSION 8.0/P8.0-M5.07

Version 8.0/P8.0-M5.07 of the MORATE code consists of several files which may be classified according to the following categories:

1)	FORTRAN source code files	3	files
2)	Include files	4	files
3)	This manual	1	file
4)	Job control files	32	files
5)	Input for test runs	109	files
6)	MOPAC external data files	4	files
7)	Output for test runs	19	files

3.A.1 List of files in release of version 8.0

FORTRAN source code :

hooks.f m507drv.f morate.f

Include files:

param1.inc	param2.inc	param3.inc	param4.inc

Manual:

morate8.0.doc

Job control files (C shell scripts for compiling, linking, and running test runs):

check_test.jc	check_all.jc	run_all.jc	testr1.jc
testr2.jc	testr3.jc	testr4.jc	testr5.jc
testr6.jc	testr7.jc	testr8.jc	testr9.jc
testr10.jc	testr11.jc	testr12.jc	testr13.jc
testr14.jc	testr15.jc	testr16.jc	testr17.jc
testr18.jc	testr19.jc		
moratecl.590	moratecl.cray	moratecl.dec	moratecl.hp
moratecl.rs6k	moratecl.sgi	moratecl.sgi64	moratecl.sun
moratecl.linux	moratecl.604		

Input data files:

testr1.71	testr13.73	testr16.74	testr3.71	testr7.72
testr1.73	testr13.74	testr16.75	testr3.72	testr7.73
testr1.75	testr13.75	testr17.71	testr3.73	testr7.74
testr10.71	testr14.71	testr17.72	testr3.74	testr7.75
testr10.72	testr14.72	testr17.73	testr3.75	testr8.71
testr10.73	testr14.73	testr17.74	testr4.71	testr8.72
testr10.74	testrl4.74	testr17.75	testr4.72	testr8.73
testr10.75	testr14.75	testr18.71	testr4.73	testr8.74
testr11.75	testr15.71	testr18.72	testr4.74	testr8.75
testr12.71	testr15.72	testr18.73	testr4.75	testr9.71
testr12.72	testr15.73	testr18.75	testr5.71	testr9.72
testr12.73	testr15.74	testr2.71	testr5.72	testr9.73
testr12.74	testr15.75	testr2.72	testr5.73	testr9.74

testr12.75testr16.71testr2.73testr5.74testr9.75testr13.71testr16.72testr2.74testr5.75testr1.dattestr13.72testr16.73testr2.75testr7.71testr2.dattestr3.dattestr4.dattestr5.dattestr6.dattestr7.dattestr13.dattestr14.dattestr10.dattestr10.dattestr12.dattestr13.dattestr12.50testr14.50testr16.50testr3.50testr13.50testr15.50testr17.50testr8.50testr19.71testr19.72testr19.73testr19.74testr19.75testr19.76testr19.77testr19.dattestr19.51testr19.51

MOPAC external data files for NDDO-SRP test runs:

	EXTERN.TR4	EXTERN.TR7	EXTERN.TR8	EXTERN.TR15
--	------------	------------	------------	-------------

Output files:

testr1.fu15	testr5.fu15	testr8.fu14	testr10.fu15
testr2.fu15	testr6.fu15	testr8.fu15	testr11.fu15
testr3.fu15	testr7.fu14	testr9.ful4	testr12.fu15
testr4.fu15	testr7.fu15	testr9.fu15	testr13.fu15
testr14.fu15	testr15.fu15	testr16.fu15	testr17.fu15
testr18.fu15	testr19.fu15		

## 3.B. SPECIFYING THE SIZE OF THE MORATE EXECUTABLE FILE

A user can easily adjust the size of the executable file to be created by modifying the include files needed by the source code. A full description of how to carry out these modifications is given in subsection 3.C.

Dimensions in the MORATE program, like those in POLYRATE, are governed by an include file called param.inc; and the dimensions for the MOPAC5.07mm part are governed by the include file called SIZES.i. (This is a modified version of the SIZES include file that is distributed with the original MOPAC 5.0 code.) Note that the file SIZES.i and all references to it are case-sensitive when this program is used in a Unix or other case-sensitive environment.

As explained in Subsection 5.A.2 of the POLYRATE manual, any changes made to include files must be done consistently, and the code must be recompiled for the changes to become effective.

The include file param.inc may be modified as described in Section 5 of the POLYRATE manual. However, one must be wary of the value used for the maximum number of atoms, NATOMS, in this include file as it must be less than or equal to the sum of MAXHEV and MAXLIT in the include file SIZES.i. This sum sets the maximum number of atoms allowed in the MOPAC portion of the code.

The subroutines SURF and SETUP have the following line include 'param.inc'

which ensures that the variable NATOMS is correctly set in these subprograms. The MOPAC program also uses the variable NATOMS in the common block /GEOKST/; to avoid conflicts in the subprogram SETUP this MOPAC variable has been changed to MAXATM. This variable name change is only made in the subroutine SETUP as this is the only MORATE subroutine where both the MOPAC and POLYRATE variables NATOMS exist.

In the include file SIZES.i, the values of MAXHEV and MAXLIT may be modified as described in Section 11 of the MOPAC 5.0 manual. Note that, as mentioned above, MAXHEV + MAXLIT must be greater than or equal to the POLYRATE variable NATOMS. In the subprogram SETUP, a check is carried out to ensure that NATOMS is less than or equal to MAXHEV + MAXLIT before starting the full calculation.

The variables MAXHEV and MAXLIT are indirectly used to specify the values of certain variables which are used for array dimensioning. For example, the variable IPADD in the subroutine FORCE is defined as

IPADD = 2\*MORB2 + 2\*MAXORB - MAXPAR - MAXPA2

where

MAXORB = 4\*MAXHEV + MAXLIT MORB2 = MAXORB \* MAXORB MAXPAR = 3\*(MAXHEV + MAXLIT) MAXPA2 = MAXPAR \* MAXPAR

Because of this interdependency, the values of MAXHEV and MAXLIT chosen have to satisfy more than the conditions given in Section 11 of the MOPAC 5.0 manual. If proper values of MAXHEV and MAXLIT are not chosen so that variables like IPADD are greater than zero, the code will not compile successfully.

Another dimension which can be set in the include file SIZES.i allows the user to run either a "short" or a "long" version of MOPAC. This modification is also described, though briefly, in Section 11 of the MOPAC 5.0 manual. The "short" or the "long" version of MOPAC is determined by the values of the two parameters NMECI and NPULAY, which are then used to dimension various arrays in several MOPAC subroutines, for example, CIMAT(NMECI\*\*4) and MICROB(NMECI, 2\*NMECI\*\*3). The variable NMECI controls the sizes of arrays used in the configuration interaction calculations, and the variable NPULAY controls the sizes of arrays used in the CAMP-KING and PULAY converger routines. The CAMP-KING and PULAY convergers are automatically turned on if the initial iteration sequence fails to successfully generate self-consistency.

In the original include file SIZES the user could choose between the "short"

PARAMETER(NMECI=1, NPULAY=1)

or the "long"

PARAMETER(NMECI=10, NPULAY=MPACK)

version of MOPAC depending on which set of parameters was used. These parameter statements are the last two lines of the include file SIZES.i, and they must be commented out or uncommented depending on which set is required.

MORATE can be run with either the "short" or the "long" version of MOPAC, but running with the "short" version is risky because if the normal iteration sequence fails to converge the SCF process and the CAMP-KING and the PULAY convergers are turned on, the program will abort. If the user is confident that the SCF process for a particular system will converge with the initial iteration process, then MORATE can be run with the "short" version of MOPAC, and this significantly reduces the memory requirements of the code.

In the distributed version of MORATE, a new combination for the parameters NMECI and NPULAY has been added to the include file SIZES.i. This new combination, designed specifically for MORATE, is PARAMETER(NMECI=1, NPULAY=MPACK)

(this combination is not one of those provided in the MOPAC program). Using this combination, the memory requirements of the code are reduced significantly without running the risk of aborting in the SCF iteration process. This combination is the default in the current version of MORATE.

## 3.C. COMPILING AND LINKING THE SOURCE CODE

This subsection describes the use of the scripts provided for compiling and linking the MORATE-version 8.0 source code.

Nine scripts are included in the morate8.0/src directory:

moratecl.590	for IBM Power 2 series (Model 590)
moratecl.604	for IBM Power PC 604e
moratecl.cray	for Cray computers
moratecl.dec	for DEC alpha workstations
moratecl.hp	for HP workstations
moratecl.rs6k	for IBM RS/6000 workstations (Model 550)
moratecl.sgi	for SGI Indigo workstations
moratecl.sgi64	for SGI 64 bit Power Challenge L/R8000
moratecl.sun	for Sun SparcStations
moratecl.linux	for Linux (kernel 2.0.30)

Change the working directory to morate8.0/src, and choose the appropriate script from the list above for the type of machine you are working on, and then do the following: (Go to Step 2 if the machine being used is not a Cray Y-MP.)

Step 1: Uncomment the compilation lines for the POLYRATE subroutine files if the machine being used is a Cray Y-MP. In the distributed version of the script the statements for compiling POLYRATE subroutines on the Cray-2, Cray X-MP-EA, and Cray C90 are uncommented and those for the Cray Y-MP are commented out. If you wish to use the Y-MP version, uncomment the lines for the Y-MP and comment those for the Cray-2, Cray X-MP-EA, and Cray C90.

Step 2: Execute the script:

for example, if your machine is an IBM RS/6000 and you want to use paraml.inc as the MORATE parameter include file and the MOPAC507mn source codes are located in the /usr/chuang/mopac507mn.src directory, then you type:

moratecl.rs6k 1 /usr/chuang/mopac507mn/src <Return>

This script will copy, compile, and link all the necessary files to generate an executable called morate.exe in /src.

Use a different script name if a different type of machine is being used.

(Note: this script requires two arguments: (1) the number to indicate which param#.inc is used. And (2) the full path of the directory that contains the MOPAC507mn source codes.)

This will create a MORATE 8.0 executable file in the /morate8.0/src directory with the name morate.exe. Notice the arguments of these script files are different from those in version 7.2 and earlier.

# 3.D. COMPILING, LINKING, AND RUNNING THE TEST SUITE

MORATE-version 8.0 is distributed with four sample param.inc files. The sample param.inc files are paraml.inc, param2.inc, param3.inc, and param4.inc. The following chart lists the sample param.inc files which are applicable to each MORATE test run. (An X denotes that the include file at the top of that column is suitable for the test run on that line.)

									-
-		-		-	-		-		-
_	TEST RUN	_	param1.inc	_	param2.inc -	param3.i	nc –	param4.inc	_
_		_	-	_	-	-	_	-	_
									_
_		_		_	_		_		_
_	tootw1	_	v	_	_	v	_	v	_
-	LESLII	-	Δ	-	-	Δ	-	Λ	-
-		-		-	-		-		-
-	testr2	-	X	-	Х –	X	-	X	-
-		-		-	-		-		-
-	testr3,19	-	Х	-	Х –	Х	-		-
-		-		-	-		-		-
-	testr4,5	-	Х	-	Х –	Х	-		-
-		-		-	-		-		-
-	testr6	-	Х	-	Х –	Х	-		-
-		_		_	-		-		_
_	testr7	_	Х	_	-	Х	-		_
_		_		_	-		_		_
_	testr8	_	х	_	-	х	_		_
_		_		_	-		_		_
_	testra	_	v	_	v –		_		_
	LEBLIJ		А		Λ –				
-	10	_		-			-		_
-	testriu	-	X	-	Х –		-		-
-		-		-	-		-		-
-	testrll	-	Х	-	Х –		-		-
-		-		-	-		-		-
-	testr12,13	-	Х	-	Х –		-		-
-		-		-	-		-		-
-	testr14	-	Х	-	Х –	Х	-	Х	_
-		-		-	-		-		_
_	testr15,16	_	Х	_	Х –		-		_
_		_		_	-		-		_
_	testr17	_	х	_	х –		-		_
_		_		_			_		_
_	testr18	_	x	_	x –		_		_
_	CCDCLTO	_	22	_			_		_
									_

Eighteen job control files are provided for compiling and linking the source code for eighteen different types of machines. Eighteen job control files are provided for running the thirteen test runs that make up the test suite.

## 4. POTENTIAL ENERGY SURFACE FROM MOLECULAR ORBITAL THEORY

#### 4.A. INTERFACE

The interface between POLYRATE and MOPAC 5.07mn consists of four subroutines: MOPSET, MOPEG, MOPOPT, MOPHES. These subroutines, which are the MOPAC versions of the POLYRATE hooks, are in the file m507drv.f.

The primary subroutine for the interface between POLYRATE and MOPAC is MOPOPT. This subroutine, which is a modification of the main driver of MOPAC, sets up all the necessary parameters for the semiempirical molecular orbital calculation and reads the initial geometry. MOPOPT also calls the MOPAC 5.07mn optimization subroutines, such as FLEPO and EF, to optimize the geometry of a stationary point, if a geometry optimization is requested. In MORATE, the geometry optimizations for the reactants, products, and saddle point species are carried out by MOPAC 5.07mn routines only, and MOPOPT is called once for each molecular chemical species, i.e., once for each reactant and product and once for the saddle point.

The subroutine MOPEG evaluates the potential and its gradient as functions of the Cartesian coordinates of the atoms. It serves as a link between the POLYRATE and MOPAC 5.07mn programs, and it functions in the same way as in the case of an analytic potential energy surface used in POLYRATE. The subroutine MOPEG takes a set of Cartesians from POLYRATE, converts them to Angstroms, and passes this information to the MOPAC subroutine COMPFG which calculates the energy and gradient by self-consistent-field (SCF) method. The subroutine MOPEG then makes the necessary unit conversions and returns the energy and gradient to POLYRATE in atomic units.

The subroutine MOPHES returns to POLYRATE the Hessian matrix of the potential at a given point calculated using the MOPAC Hessian evaluation subroutine FMAT. This happens if MOPAC is specified in section \*SECOND of the input file. MOPAC uses an adaptive-stepsize scheme that in principle is more accurate than the one used in POLYRATE, but it is twice as expensive in terms of CPU time. In our experience the difference in the final results obtained using the two methods is quite small, if the stepsize for doing second derivatives is selected properly in POLYRATE. However, in some cases where the transition state has a very low-frequency vibrational mode, the calculated results can be very different across different platforms. Using the MOPAC second derivative option in this situation will give more consistent results on different computers.

The subroutine MOPSET sets up some common blocks needed by MOPAC and checks that certain MOPAC and POLYRATE arrays are dimensioned in a compatible way.

#### 4.B. ZERO OF ENERGY

In MOPAC the only difference between the so called heat of formation and the sum of the electronic energy and the nuclear repulsion energy is the choice of the zero of energy. In other words, MOPAC computes the heat of formation by adding a constant to the sum of the electronic and nuclear repulsion energies; this constant depends only on the number of each kind of atom. For example, the constant is the same for ethanol and dimethyl ether. Thus, in programming MORATE there was a choice between using the heat of formation or the sum of the electronic and nuclear repulsion energies for the potential energy surface, and these two choices would differ only in the zero pf energy. Hoever, MORATE actually uses a third choice for the zero of energy, by subtracting a constant EZERO from the heat of formation in kcal/mol as output by MOPAC. In particular, at the POLYRATE/MOPAC interface, MORATE immediately converts MOPAC heats of formation to POLYRATE potential energies in hartree atomic units using the MOPAC conversion factor, 1 hartree atomic unit = 627.503 kcal/mol, and it subtracts EZER0 (described below), in hartree atomic units, to change the zero of energy. (This means that any output from MOPAC subroutines has a different zero of energy from output from POLYRATE subroutines.)

As the above explanation makes clear, the term "heat of formation" in MOPAC is really a misnomer. In this manual, when we say heat of formation we are referring to these MOPAC heats of formation, i.e., to the sum of the electronic and nuclear repulsion energies with a specific choice of zero of energy. (The historical origin of this confusing language is that, in the original parameterization of the semiempirical molecular orbital parameters, differences of the sum of the electronic and nuclear repulsion energies were fit using differences of experimentally determined heats of formation, not because this is logical but rather because heats of formation are what was available.)

In the POLYRATE part of MORATE the variable EZERO always denotes the potential energy of reactants converted to hartree atomic units. It is necessary to understand this variable in order to understand the input options of the EZERO keyword in the GENERAL section of the unit fu5 input file. The following provides the necessary explanation.

EZERO refers to the potential energy of the single reactant for a unimolecular reaction or the sum of the potential energies of infinitely separated reactants for a bimolecular reaction. In the language of potential energy surfaces, EZERO denotes the potential energy of the reactant or reactants at their classical equilibrium geometries. In the language of electronic structure calculations, EZERO denotes the sum of the electronic and nuclear repulsion energies of the reactants (for ab initio calculations) or the sum of the "heats of formation" (for MOPAC).

In MORATE the user must ensure that EZERO is set equal to the sum of the heats of formation of the reactants of the system being studied. This can be accomplished in one of two ways: by setting the variable keyword EZERO to "calculate", or by giving a nonzero value to EZERO.

Setting the EZERO keyword to "calculate" causes the program to calculate EZERO. For a bimolecular reaction, this involves separate calls to MOPAC for each reactant and summing the heats of formation. To use this option it is necessary to include the \*REACT1 and \*REACT2 (for a bimolecular reaction) sections in unit fu5 input file. This causes the program to call SURF, which calls the appropriate MOPAC subroutines. To avoid this cost in cases where the reactants have been optimized in a previous run, the user may wish to set the EZERO keyword to "read" and provide the sum of the heats of formation in a.u. However, if the optimized geometries are used in the reactant cost of determining EZERO is negligible. The recommended method is to input the optimized geometries in the unit fu71 and fu72 input files and set the EZERO keyword to "calculate".

## 5. DESCRIPTION OF PROGRAM STRUCTURE AND SUBPROGRAMS

This section describes the program structure and the subprograms for the MORATE code.

## 5.A. DESCRIPTION OF PROGRAM STRUCTURE

As mentioned in the introduction, the MORATE program has two major options for obtaining the reaction-path information necessary for rate calculations. The first option is to calculate this information directly using semiempirical molecular orbital theory to represent the potential energy of interaction. The second option is to read it from a restart file which was saved from a previous MORATE run. These options are implemented in the MORATE program in precisely the same way as in the POLYRATE program. The next five paragraphs describe the use of these options either for a single-level calculation or for the lower level of a dual-level calculation.

First, the program reads the keyword input from different input files. Then the input options are analyzed for possible conflicts (i.e., unsupported combinations of options) in subroutine OPTION. If it is a restart run, the program reads the restart information in RESTOR, and the rate calculation proceeds as described in the POLYRATE manual. If the calculation is not a restart run, the geometry and the MEP-following information in the unit fu5 input file is used for the next stages of calculations.

Depending on the options chosen, the properties of the reactants, products, and generalized transition state are calculated next. MORATE differs from POLYRATE at this point in the calculation in that the optimization of the geometries is carried out in the MOPAC portion of the code and not within the POLYRATE subprograms that are used when the potential is a user-supplied analytic function.

For the reactants and/or the products, the equilibrium geometries and properties are optionally obtained in the subprogram DOREPR. It should be noted that in this version the force matrix can either be obtained directly from MOPAC or it can be calculated in POLYRATE routines from the numeric derivatives of the gradients obtained in MOPAC.

Next, the program optionally determines the saddle point geometry and properties. This is done in SADENG. The user must supply an approximate geometry of the saddle point in a MOPAC input data file, esp.fu75.

After determining the geometries and the properties for the reactants, products, and/or the saddle point, the program proceeds in the same way as described in the POLYRATE manual. The precise sequence of calculations depends on the combination of options chosen. Any further calculations of the energy and gradients needed by the POLYRATE subprograms are accomplished through calls to the interface subroutines ENERG and FIRST. These routines call the mopac-specific interface routine MOPEG. This routine converts the geometry from atomic units to Angstrom, and it calls the MOPAC subroutine COMPFG to determine the energy and the gradients. In the present version the subroutine COMPFG is called such that the energy calculations are done with a full SCF and the gradients are only calculated as required. The subroutine MOPEG then converts the energy and the gradients to atomic units and pass them back to ENERG and FIRST.

In dual-level mode, MORATE then reads the required data for the higher level from an external file assigned to FORTRAN unit fu50.

## 5.B. DESCRIPTION OF MORATE SUBPROGRAMS

This section discusses the subprograms used in MORATE. The first set of subprograms consists of the new routines created for the interface between POLYRATE and MOPAC. Descriptions of subroutines in the POLYRATE and MOPAC portions are already given in their individual manuals; thus only routines that were changed or included specifically for MORATE are discussed here.

The m507rv.f file is made up of four subprograms. The subprogram MOPEG calls the MOPAC subprograms to calculate the energy and the gradients. The subprogram MOPOPT is used to read the MOPAC input file and to optimize the geometry. The subprogram MOPHES calculates the force matrix from the gradients by central difference method with variable step sizes. The subprogram MOPSET checks the compatibility of system sizes allowed in POLYRATE and MORATE, and it performs some initialization.

## 6. INPUT/OUTPUT FILE USAGE

The program uses several files for input data, for storing restart information, and for output. The program explicitly opens and closes all files required for a given run, and the files are assumed to have the file names poly.fu# and esp.fu7#, where # denotes an integer. The file poly.fu# is assigned to FORTRAN I/O unit fu# which is defined in the include file param.inc (see the POLYRATE on-line manual). The files esp.fu7# are linked to the FORTRAN unit numbers fu71 through fu78. These unit numbers are also defined in the include file param.inc.

Because of these I/O specifications, at the beginning of any run all the MORATE input data files which have logical file names differing from poly.fu# or esp.fu7# must be linked or copied to the corresponding poly.fu# or esp.fu7# file. If the user wishes to assign different logical names to the output files, which are also poly.fu# files, these re-assignments must be carried out after the calculation has completed because all the files are closed at the end of the calculation.

- Unit Usage
- ful Reaction-path information for restarting the program
- fu2 Additional reaction-path information to be merged with that from unit=ful
- fu7 Output for merged reaction path information
- fu5 General POLYRATE input data
- fu6 Output (This is the full output file. Selected subsets of this output are also written to files poly.ful4 and poly.ful5.)
- ful4 Output table of dynamical bottleneck properties
- ful5 Output table of selected forward rate constants
- fu22 Detailed output for the LCT calculations
- fu25 Output table of energetic information along the MEP
- fu26 Output table of GTS frequency information along the MEP
- fu27 GTS geometry information in the XYZ input format of the XMOL program
- fu50 Additional input data for VTST-IOC calculations (also called duallevel mode or /// dynamics)
- fu51 Additional input data for VTST-ISPE calculations

- fu61 Information about the stationary points from POLYRATE calculation for the second restart option
- fu71 MOPAC input data for reactant 1
- fu72 MOPAC input data for reactant 2, if it exists
- fu73 MOPAC input data for product 1
- fu74 MOPAC input data for product 2, if it exists
- fu75 MOPAC input data for the saddle point or starting geometry
- fu76 reserved for use by electronic structure package interfaces in general, but not used by MORATE
- fu77 MOPAC input data for the wellr, if it exists
- fu78 MOPAC input data for the wellp, if it exists

Running the test runs

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To run the test run just type the name of the job control file at prompt:

For example: %testr1.jc

Note: This script creates a temporary subdirectory called testr1 in the current working directory is /morate8.0/testr/testr1. The calculation is carried out in this subdirectory. If this subdirectory already exists when the script is run, the script will move the existing testr1 subdirectory to /testr1\_old, write an error message in the long output file testr1.fu6, and continue. No error checking is carried out for the existence of the subdirectory testr1\_old.

To run the whole test suite, just type run\_all.jc. Note: to run the whole test suite, make sure that the morate.exe is compiled and linked with paraml.inc

To check the result of a test run, just type check\_test.jc #, where # is the number of the test run.

For example: %check\_test.jc 1

The differences will be listed in the file test1.chk.

To check the results for the whole test suite, just type check\_all.jc.

# 7. SELECTED DETAILS OF THE CALCULATION

The methods used by this program are described in detail in the POLYRATE and the MOPAC manuals and in the references within those manuals. See also the bibliography in Section 13 of the present manual. In the subsections below (7.A. and 7.B.) details of various MORATE options are discussed.

## 7.A. NDDO-SRP CALCULATIONS

Neglect-of-diatomic-differential-overlap (NDDO) molecular orbital theory with specfic reaction parameters (SRP) can be invoked in this program in the following way. An NDDO-SRP calculation can be invoked by using the MOPAC keyword EXTERNAL=filename in the esp.fu71 through esp.fu75 files. The parameters adjusted specifically for the given reaction should be defined in the file given in EXTERNAL=filename according to the guidelines in the MOPAC on-line manual. The EXTERNAL keyword need only be specified in the esp.fu71 through esp.fu78 files which contain the atoms whose parameters are being modified. However, if an esp.fu7# file contains the EXTERNAL keyword and the parameters for the atoms that make up the chemical species defined in that file are not being modified, the calculations for that chemical species will not be affected by the EXTERNAL keyword.

In MORATE-version 8.0, the EXTERNAL keyword can be used for any of the the hamiltonians in MOPAC-version 5.07mn, in particular for MINDO/3, MNDO, AM1, and PM3.

## 7.B. RESTART OPTION

The POLYRATE restart option (see Section 7.3. of the POLYRATE manual) is controlled by the RESTART keyword in the GENERAL section of the unit fu5 input file. This option is designed to allow calculations based on information stored on the save grid (the grid controlled by DELSV) in the restart file.

One of the simplest calculations which can be carried out with the restart flag is to calculate rate constants at temperatures different from those specified in the original run. If the restart calculation does not involve LCG3 tunneling calculations, then the only input file, other than the restart file, required for the calculation is the FORTRAN unit fu5 file. If the restart calculation does LCG3 tunneling, then the esp.fu75 file is also required; the esp.fu71 through esp.fu74 files are never required for a restart calculation.

This option can also be used to limit searches for variational transition states to localized ranges of s by using SLMG > SLM and/or SLPG < SLP, but SLM and SLP cannot be different from the values used in the run that created the restart file.

Perhaps the most powerful use of the restart option, however, is that a restart file used for LCG3 ground-state tunneling calculations can be used for LCG3 excited-state calculations. This means that the contribution to the LCG3 tunneling probabilities from excited states can be checked without calculating the MEP if the restart file is saved during the LCG3 ground-state calculation; this leads to significant savings in computer time.

A few additional points should be made with respect to the POLYRATE/MORATE restart option. First, with regard to tunneling calculations, if the restart run is required to do SCT tunneling calculations, then the run which created the restart file must also have done SCT calculations, and similarly for LCT calculations. Second, unlike a full calculation in which the MEP information is determined, there is no error-checking for a restart calculation. Therefore, if the restart file being used does not contain all the information needed for the calculation specified, no error messages will be printed, but the calculation will abort. Also, a VTST-IOC calculation can only be restarted with a restart file that was generated in a VTST-IOC calculation, since the unit fu50 file can only be read in a non-restart run.

## 8. DESCRIPTION OF INPUT DATA

The unit fu5 input file for MORATE is very similar to the unit fu5 input file for POLYRATE, but it has some different options. The fu5 input for MORATE is explained in the POLYRATE manual. MOPAC input is described in Subsection 8.A of this manual. This input is associated with the esp.fu71 through esp.fu78 input data files. All other input files for MORATE (e.g., unit fu40 and fu50) have the same formats as in POLYRATE, and detailed descriptions can be found in POLYRATE manual.

## 8.A. DESCRIPTION FOR esp.fu71 THROUGH esp.fu78 FILES

The data files esp.fu71 through esp.fu78 are MOPAC-type data files whose content and form are specified in the MOPAC manual. These data files are read by the subroutine ESPINT. Because of the interconnection with POLYRATE, certain issues must be considered when creating these data files.

The first issue which must be considered when creating these files is that 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 poly.fu5 file, and the order of the atoms in units fu71-fu74 must be consistent with the index specifications in the GEOM keyword in the REACT1, REACT2, PROD1, and PROD2 sections of the unit fu5 input file. And the units fu77 and fu78 must be consistent with the index specifications in the WELLR and WELLP sections.

Second, the method chosen for the semiempirical molecular orbital calculations for a given reaction must be the same in all the esp.fu71 through esp.fu78 files representing the species for that reaction. Also, the specification of the 1SCF keyword in files fu71-fu78 is optional. When this keyword is not included, an optimization will be carried out. When the geometry is already optimized, 1SCF may be specified to prevent an attempt at re-optimization. In general, though, this saves negligible time since for an optimized geometry, the gradient norm will be small and no optimization will be carried out even if 1SCF is not specified. However, the calculation proceeds by a different path through MOPAC routines when 1SCF is or is not specified, so the results will differ slightly due to the finite precision of the calculations. Generally speaking, it is not recommended to use the 1SCF keyword, especially in the fu75 file when there is a saddle point.

The esp.fu71 and esp.fu72 files specify information for the calculations on reactants, including geometry optimizations if desired. The esp.fu73 and esp.fu74 files specify analogous information for the products. The esp.fu75 file is used for the saddle point or starting geometry of the MEP as well as for all subsequent calls to MOPAC subprograms, in particular, for calculations at generalized transition states and at points in the nonadiabatic region of LCG3 calculations.

The file esp.fu75 requires further explanation. When there is a saddle point, the initial geometry in the esp.fu75 file should be the initial guess for the saddle point geometry, and any keywords related to geometry optimization will apply to this step. Other keywords, like SCFCRT, also apply to the subsequent calls to MOPAC subprograms. If there is a saddle point but it is already optimized, then the optimization with MOPAC is still used to obtain the geometry from esp.fu75 file. When there is no saddle point, the initial geometry in the esp.fu75 file should be the starting geometry for the MEP calculation, and the 1SCF keyword should be specified. In this case, too, the relevant keywords also apply to the calculations at further points along the reaction path.

## 8.B. DESCRIPTION OF OTHER INPUT

Units fu29 and fu40 are not supported in the MORATE package, even though they can be used in POLYRATE. This means that neither the IVTST-0 nor the IVTST-1 method is allowed in MORATE via fu29. Furthermore, the external electronic structure input file fu40 cannot be used for single-level or dual-level calculations in MORATE.

# 9. DESCRIPTION OF SAMPLE TEST RUNS

The input and short output data files for the eighteen test runs are included in the MORATE distribution package. In a few cases, some of the input data files (such as those that are used as esp.fu71 through esp.fu75 files) are the same for two or more test runs. In such cases the file is included more than once, with different names, e.g., testr2.71 and testr7.71, for the convenience of the new user and to ensure that each test run package is complete.

The results obtained on different Cray computers or on workstations are not always identical to the full number of digits printed (due to round-off, SCF convergence, etc.), especially if there are any low-frequency modes. In all cases, the distributed versions of the ful4 and ful5 files for this version of MORATE are from runs on the Cray C90 computer.

The reactions involved in the examples are:

TR1:	CH	H.		CF	I		
	/ H2C=CH	\\ Сн СНЗ	->	// CH   CH3	\ CH=C	IH2	(symmetric 1,5-hydrogen shift reaction; TST rate constants only)
TR2:	CD3	+ CH4	->	CD3H	+ C	н3	(TST rate constants only with hindered internal rotor anharmonicity)
TR3:	Cl-	+ CH3Cl	->	CH3C]	L + C	21- 2	(symmetric SN2 reaction; M1-IOC calculation)
TR4:	Cl-	+ CH3BR	->	CH3C]	L + E	8r-	(exoergic SN2 reaction; forward rates for an NDDO-SRP calculation at 2 temperatures
TR5:	Cl-	+ CH3BR	->	CH3C]	L + E	Br-	(exoergic SN2 reaction; forward rates calculation at 2 temperatures)
TR6:	Cl-	+ CH3BR	->	CH3C]	L + E	8r-	(forward and reverse rates at six temperatures from a restart of the NDDO-SRP calculation of TR4)
TR7:	 H3C-C-Cl   H	+ CF3CH2C	)	> CH20	снсн3	+ CF	3CH2OH + Cl- (forward rates for an NDDO-SRP calculation)
TR8:	CH4 + 0	-> CH3 -	- OH				(forward rates for an NDDO-SRP CUS calculation)

TR9:	CD3 + CH4	-> CD3H + CH3		(forward and reverse rates with LCG3 tunneling)
TR10:	Br + CH4	-> HBr + CH3		(forward and reverse rates with LCG3 tunneling)
TR11:	Br + CH4	-> HBr + CH3		(forward and reverse rates with LCG3 tunneling, including excited final states, from a restart calculation of TR10)
TR12:	CH4 + OH	-> CH3 + H2O	LCG3	(VTST-IOC calculation including tunneling)
TR13:	CH4 + OH	-> CH3 + H2O		(VTST-IOC calculation including LCG3 tunneling)
TR14:	CH3Cl + F-(H	120) -> CH3F + Cl-(	(H2O)	(TST and TST-IOC calculations)
TR15:	CF3 + CD3H	-> CF3H + CD3	calcu tunne	(NDDO-SRP and NDDO-SRP-IOC lations including LCG3 ling)
TR16:	CF3 + CD3H	-> CF3H + CD3		(VTST-IOC calculations including LCG3 tunneling)
TR17:	N2H2 + H ->	N2H + H2		(ICL-ECKART calculation with AM1 surface)
TR18:	HBr + C2H2 -	-> CHBrCH2		(Redundant curvilinear internal coordinates with AM1 surface)
TR19:	Cl- + CH3Cl	-> CH3Cl + Cl-		(symmetric SN2 reaction with
weits;				AM1 VTST-ISPE calculation with VRPE reaction path following)

Note: Since TR6 and TR11 are restart calculations, they need unit ful files produced by the previous test runs as input. So, TR4 must be run prior to TR6, and TR10 must be run prior to TR11.

9.1. Test run 1

H3C-CH=CH-CH=CH2 -> H2C=CH-CH=CH-CH3

TST rate constants only

Potential:PM3MEP:noRODS:noVibrations:harmonic rectilinearDynamics:TSTTunneling:noDual Level:no

This sample input is for a conventional transition state theory calculation for the 1,5-hydrogen shift in the cis-1,3-pentadiene molecule using a PM3 potential energy surface. The harmonic approximation is assumed for all normal modes and generalized normal modes. Neither the MEP nor any transmission coefficients are calculated. Conventional transition state theory (TST) rate constants are calculated at seven temperatures. The activation energy is calculated for the interval 460-480K.

MORATE I/O Files MORATE Filenames input data for reactant 1 testr1.71 esp.fu71 testr1.73 esp.fu73 input data for product 1 testr1.75 esp.fu75 input data for the saddle point testr1.dat poly.fu5 input data for MORATE testr1.fu6 poly.fu6 long output file testr1.fu15 poly.ful5 summary output file

9.2. Test run 2

CD3 + CH4 -> CD3H + CH3

TST rate constants only with hindered internal rotation anharmonicity

Potential:MNDOMEP:noRODS:noVibrations:harmonic rectilinearDynamics:TSTTunneling:noDual Level:no

This sample input is for an MNDO direct dynamics calculation for the CD3 + CH4  $\rightarrow$  CD3H + CH3 reaction. The lowest frequency mode of the saddle point is treated as a hindered internal rotation. Only conventional transition state theory rate constants are computed.

(Note: In versions prior to 7.0, this test run also treated the lowest-frequency mode as a hindered internal rotator. Beginning with POLYRATE-version 7.0, anharmonicities not supported with the TST-only option. This capability might be added back in a later version.)

MORATE I/O Files

MORATE Filenames

esp.fu71 testr2.71 input data for reactant 1 testr2.72 esp.fu72 input data for reactant 2 testr2.73 esp.fu73 input data for product 1 testr2.74 esp.fu74 input data for product 2 testr2.75 esp.fu75 input data for the saddle point testr2.dat input data for MORATE poly.fu5 testr2.fu6 poly.fu6 long output file testr2.fu15 poly.fu15 summary output file

9.3. Test run 3
----Cl- + CH3Cl -> CH3Cl + Cl- AM1 harmonic TST and CVT rate constants
Potential : AM1 (low-level)
MEP : Page-McIver
RODS : no
Vibrations : harmonic rectilinear
Dynamics : TST, CVT, ICVT
Tunneling : SCT
Dual Level : ICA for vibrations, ECKART for VMEP

This sample input is for an AM1 and an AM1-IOC direct dynamics calculation on the Cl- + CH3Cl -> CH3Cl + Cl- SN2 reaction. All normal modes and generalized normal modes are treated using the harmonic approximation. The Page-McIver integration method is used with a gradient step size of 1.E-2 bohr to follow the MEP, and a save step size of 2.0E-2 bohr is used between generalized normal mode analyses. Both MEPSAG and CD-SCSAG tunneling corrections are computed, and both CVT and ICVT rate constants are calculated at three temperatures. Derivatives of the gradient with respect to the reaction coordinate, as required for the CD-SCSAG calculation, are found by a quadratic fit. Accurate data for the VTST-IOC calculations are obtained from J. Phys. Chem. 93, 8138 (1989).

Note: In the poly.fu5 input data file the masses of the species in this reaction are arranged in the following order: C, Cl, Cl, H, H, H. The indices used for the reactant and product specifications in the poly.fu5 file correspond to the order of the masses; i.e. reactant 1 is Cl-, which is index 2, reactant 2 is CH3Cl, represented by indices 1, 3, 4, 5, and 6, and similarly for the products. The esp.fu71 through esp.fu75 files must be consistent with the representation used for the species in the poly.fu5 file. For example, esp.fu71, which represents reactant 1, must be a MOPAC-type input data file for Cl-.

MORATE Filenames

MORATE I/O Files

testr3.71	esp.fu71	input data for reactant 1
testr3.72	esp.fu72	input data for reactant 2
testr3.73	esp.fu73	input data for product 1
testr3.74	esp.fu74	input data for product 2
testr3.75	esp.fu75	input data for the saddle point
testr3.dat	poly.fu5	input data for MORATE
testr3.fu6	poly.fu6	long output file
testr3.fu15	poly.fu15	summary output file
testr3.50	poly.fu50	additional input data for the VTST-IOC
	calc	ulation

9.4. Test run 4

EXTERN.TR4

Cl- + CH3Br -> CH3Cl + Br-

NDDO-SRP harmonic TST and CVT rate constants

Potential:AM1-SRPMEP:Page-McIverRODS:noVibrations:harmonic redundant curvilinearDynamics:TST, CVTTunneling:noDual Level:no

This sample input is for an NDDO-SRP direct dynamics calculation on the Cl- + CH3Br -> CH3Cl + Br- excergic SN2 reaction. The AM1 parameters are modified by using the keyword EXTERNAL in the esp.fu71 through esp.fu75 files. The new NDDO parameters are passed to MOPAC via the files EXTERN.TR# where # is an integer corresponding the to MORATE test run number. All normal modes and generalized normal modes are treated using the harmonic approximation. The Page-McIver integration method with cubic starting algorithm is used. A gradient step size of 5.E-3 bohr is used to follow the MEP, and a save step size of 1.0E-2 bohr is used between generalized normal mode analyses. A restart file containing reaction-path information is written to unit ful for use in test run 5. No tunneling corrections are computed, and only forward CVT reaction rate constants are calculated at two temperatures. The only difference between test run 4 and 5 is that test run 4 is based on NDDO-SRP and test run 5 is based on AM1.

MORATE I/O Files	MORATE Filena	ames
testr4.71 testr4.72 testr4.73 testr4.74	esp.fu71 esp.fu72 esp.fu73 esp.fu74	input data for reactant 1 input data for reactant 2 input data for product 1 input data for product 2
testr4.75	esp.fu75	input data for the saddle point
testr4.dat	poly.fu5	input data for MORATE
testr4.fu6	poly.fu6	long output file
testr4.ful	poly.ful	reaction path information
testr4.fu15	poly.fu15	summary output file
NDDO-SRP File		

external parameters for Cl, Br, and C

9.5. Test run 5
----Cl- + CH3Br -> CH3Cl + Br- AM1 harmonic TST and CVT rate constants
Potential : AM1
MEP : Page-McIver
RODS : no
Vibrations : harmonic redundant curvilinear
Dynamics : TST, CVT
Tunneling : no
Dual Level : no

This sample input is for an AM1 direct dynamics calculation on the Cl- + CH3Br -> CH3Cl + Br- excergic SN2 reaction. All normal modes and generalized normal modes are treated using the harmonic approximation with redundant curvilinear coordinates. The Page-McIver integration method with cubic starting algorithm is used. A gradient step size of 5.E-3 bohr is used to follow the MEP, and a save step size of 1.0E-2 bohr is used between generalized normal mode analyses. A restart file containing reaction-path information is written to unit ful for use in test run 5. No tunneling corrections are computed, and only forward CVT reaction rate constants are calculated at two temperatures. The only difference between test run 4 and 5 is that test run 4 is based on NDDO-SRP and test run 5 is based on AM1.

MORATE I/O Files

MORATE Filenames

testr5.71	esp.fu71	input data for reactant 1
testr5.72	esp.fu72	input data for reactant 2
testr5.73	esp.fu73	input data for product 1
testr5.74	esp.fu74	input data for product 2
testr5.75	esp.fu75	input data for the saddle point
testr5.dat	poly.fu5	input data for MORATE
testr5.fu6	poly.fu6	long output file
testr5.ful	poly.ful	reaction path information
testr5.fu15	poly.fu15	summary output file

9.6. Test run 6 ------Cl- + CH3Br -> CH3Cl + Br- NDDO-SRP restart calculation Potential : AM1-SRP MEP : restart test run 5 RODS : no Vibrations : harmonic redundant curvilinear Dynamics : TST, CVT Tunneling : no Dual Level : no

This sample input is for an AM1 NDDO-SRP direct dynamics calculation on the Cl- + CH3Br -> CH3Cl + Br- excergic SN2 reaction. The reaction-path information is read from a restart file on unit ful. The restart file must be created by running test run 4 prior to running test run 6. The reaction rate constants are calculated for the forward and the reverse directions, and the rate constants are calculated at six temperatures. All other parameters are the same as those in the previous test run.

MORATE I/O Files	MORATE File	names
testr6.dat	poly.fu5	input data for MORATE
testr4.ful	poly.ful	reaction path information
		(input data for a restart
		calculation)
testr6.fu6	poly.fu6	long output file
testr6.fu15	poly.fu15	summary output file

9.7. Test run 7

CH3CHClCH3 + CF3CH2O- -> CH2CHCH3 + CF3CH2OH + Cl-NDDO-SRP forward reaction rate calculation

Potential: AM1-SRPMEP: EulerRODS: noVibrations: harmonic rectilinearDynamics: TST, CVTTunneling: noDual Level: no

This sample input is for an NDDO-SRP direct dynamics calculation for the E2 reaction CH3CHClCH3 + CF3CH2O- -> CH2CHCH3 + CF3CH2OH + Cl-. The AM1 parameters are modified by using the keyword EXTERNAL in the esp.fu71 through esp.fu75 files. The new NDDO parameters are passed to MOPAC via the files EXTERN.TR# where # is an integer corresponding the to MORATE test run number. All normal modes and generalized normal modes are treated using the harmonic approximation. The Euler intergration method is used. A gradient step size of 2.E-3 bohr is used to follow the MEP, and a save step size of 1.0E-2 bohr is used between generalized normal mode analyses. No tunneling contributions are computed, and only forward CVT reaction rate constants are calculated at three temperatures. The only difference between test run 7 and 8 is that test run 7 is based on NDDO-SRP and test run 8 is based on AM1.

MORATE I/O Files	MORATE Filena	ames
testr7.71 testr7.72 testr7.73 testr7.74	esp.fu71 esp.fu72 esp.fu73 esp.fu74	input data for reactant 1 input data for reactant 2 input data for product 1 input data for product 2
testr7.75	esp.fu75	input data for the saddle point
testr7.dat testr7.fu6 testr7.fu15	poly.fu5 poly.fu6 poly.fu15	input data for MORATE long output file summary output file
NDDO-SRP File		
EXTERN.TR7	external para	ameters for Cl, F, and C

9.8. Test run 8

CH4 + O -> CH3 + OH

PM3 forward reaction rate calculation

Potential: PM3-SRP (low-level)MEP: Page-McIverRODS: yesVibrations: harmonic rectilinearDynamics: TST, CVT, CUSTunneling: ZCT, SCT, LCT, muOMTDual Level: ICL for vibrations, ECKART for VMEP

This sample input is for the reaction CH4 + O -> CH3 + OH. All generalized normal modes are treated using the harmonic approximation with redundant internal coordinates. The Page-McIver intergration method is used for calculating the reaction path with a gradient step size of 1.E-2 bohr with the RODS (re-orient the dividing surface) option on. The hessian/gradient step ratio is 40. Zero-, small-, and large-curvature tunneling calculations are carried with this reaction. The reaction rate is evaluated with TST, CVT, CVT, and CUS methods. An external NDDO-SRP file is read in as EXTERN.TR8.

MORATE I/O Files

MORATE Filenames

esp.fu71	input data for reactant 1
esp.fu72	input data for reactant 2
esp.fu73	input data for product 1
esp.fu74	input data for product 2
esp.fu75	input data for the saddle point
poly.fu5	input data for MORATE
poly.fu6	long output file
poly.fu15	summary output file
poly.fu50	input data for the
	VTST-IOC calculation
	esp.fu71 esp.fu72 esp.fu73 esp.fu74 esp.fu75 poly.fu5 poly.fu6 poly.fu15 poly.fu50

9.9. Test run 9
----CD3 + CH4 -> CD3H + CH3 LCG3 ground-state-to-ground-state
Potential : MNDO
Vibrations : harmonic redundant curvilinear
MEP : Euler-Stabilization
RODS : no
Dynamics : TST, CVT
Tunneling : ZCT, SCT, LCT, muOMT
Dual Level : no

This sample input is for an MNDO direct dynamics calculation for the CD3 + CH4 -> CD3H + CH3 reaction. All normal modes and generalized normal modes are treated using the harmonic approximation. The Euler integrator is used. A gradient step size of 4.E-3 bohr is used to follow the MEP, and a save step size of 1.6E-2 bohr is used between generalized normal mode analyses. Zero-(ZCT), small-(SCT), and large-(LCT) curvature tunneling contributions are computed, and both forward and reverse reaction rate constants are calculated. In the LCG3 calculations, only ground-state-to-ground-state tunneling processes are included.

MORATE I/O Files MORATE Filenames testr9.71 input data for reactant 1 esp.fu71 esp.fu72 testr9.72 input data for reactant 2 testr9.73 esp.fu73 input data for product 1 testr9.74 esp.fu74 input data for product 2 testr9.75 esp.fu75 input data for the saddle point testr9.dat poly.fu5 input data for MORATE testr9.fu6 poly.fu6 long output file testr9.ful4 poly.ful4 summary output file testr9.fu15 poly.fu15 summary output file

9.10. Test run 10

Br + CH4 -> HBr + CH3

LCG3 ground-state-to-ground-state

Potential:MNDOMEP:Euler-StabilizationRODS:noVibrations:harmonic redundant curvilinearDynamics:TST, CVTTunneling:ZCT, SCT, LCT, muOMTDual Level:no

This sample input is for an MNDO direct dynamics calculation for the Br + CH4 -> BrH + CH3 reaction. All normal modes and generalized normal modes are treated using the harmonic approximation. The Euler stabilizationversion 1 (ES1) method integrator is used. A gradient step size of 1.E-3 bohr is used to follow the MEP, and a save step size of 2.0E-2 bohr is used between generalized normal mode analyses. A generalized normal mode analysis is also performed at eighty-six special save points. Zero-(ZCT), small-(SCT), and large-(LCT) curvature ground-state tunneling contributions are computed, and both forward and reverse reaction rate constants are calculated. In the LCG3 calculations, only groundstate-to-ground-state processes are included. A restart file containing reaction-path information is written to unit ful for use in test run 11.

MORATE I/O Files

MORATE Filenames

testr10.71	esp.fu71	input data for reactant 1
testr10.72	esp.fu72	input data for reactant 2
testr10.73	esp.fu73	input data for product 1
testr10.74	esp.fu74	input data for product 2
testr10.75	esp.fu75	input data for the saddle point
testr10.dat	poly.fu5	input data for MORATE
testr10.fu6	poly.fu6	long output file
testr10.ful	poly.ful	reaction path information
testr10.fu14	poly.ful4	summary output file
testr10.fu15	poly.fu15	summary output file

9.11. Test run 11

Br + CH4 -> HBr + CH3

LCG3 with tunneling into excited states

Potential: MNDOMEP: restart from test run 10RODS: noVibrations: harmonic redundant curvilinearDynamics: TST, CVTTunneling: ZCT, SCT, LCT, muOMTDual Level: no

This sample input is for an MNDO direct dynamics calculation for the Br + CH4 -> BrH + CH3 reaction. This calculation is a restart calculation which uses the reaction path information in the restart file generated by test run 10. The parameters are the same as for test run 8 except for the large-curvature tunneling option which is set to include all accessible product excited states. This directs the program to carry out tunneling calculations for ground-state transmission coefficients by the ZCT, SCT, and LCG3 methods and to include excited final states in the LCG3 calculation. For the LCG3 calculation, the program determines the highest excited state which is accessible in the LCG3 exit arrangement, and probabilities for tunneling into those excited states are included in the LCG3 calculation. There is approximately a 10% increase in the LCG3 kappa factors in this calculation versus those from test run 10.

Note that the reaction as written is endoergic. Therefore the code treats HBr + CH3 as the LCG3 entrance arrangement, in which only the ground state is included in tunneling calculations, and it treats Br + CH4 as the LCG3 exit arrangement, in which excited states are considered as well. The forward transmission coefficient is set equal to the backward one because of microscopic reversibility.

MORATE I/O Files	MORATE Filen	ames
testr11.75 testr10.ful	esp.fu75 poly.fu1	input data for the saddle point reaction path information (input data for a restart calculation)
testr11.dat	poly.fu5	input data for MORATE
testr11.fu6	poly.fu6	long output file
testr11.fu14	poly.ful4	summary output file
testrl1.ful5	poly.fu15	summary output file

9.12. Test run 12

CH4 + OH -> CH3 + H2O

LCG3 tunneling

Potential:PM3 (low-level)MEP:Page-McIverRODS:noVibrations:harmonic rectilinear with one hindered-rotor modeDynamics:TST, CVTTunneling:ZCT, SCT, LCT, muOMTDual Level:ICA for vibrations, original interpolation method for VMEP

This sample input is for a PM3 and a PM3-IOC direct dynamics calculation for the CH4 + OH -> CH3 + H2O reaction. The lowest vibrational mode of the generalized transition state is treated as a hindered rotator. All other modes are treated using the harmonic approximation. A gradient step size of 2.E-3 bohr is used to follow the MEP, and a save step size of 1.E-2 bohr is used between generalized normal mode analyses. Zero-, small-, and largecurvature tunneling corrections are computed. The forward reaction rate constants are calculated at 15 temperatures.

MORATE I/O Files	MORATE Filena	ames
testr12.71	esp.fu71	input data for reactant 1
testr12.72	esp.fu/2	input data for reactant 2
testr12.73	esp.iu/3	input data for product 1
testr12.74	esp.fu/4	input data for product 2
testr12.75	esp.fu75	input data for the saddle point
testr12.dat	poly.fu5	input data for MORATE
testr12.fu6	poly.fu6	long output file
testr12.fu15	poly.fu15	summary output file
testr12.50	poly.fu50	input data for the
	VTST-I	OC calculation

9.13. Test run 13

CH4 + OH -> CH3 + H2O

LCG3 tunneling

Potential:PM3 (low-level)MEP:Page-McIverRODS:noVibrations:harmonic redundant curvilinear with one hindered-rotor modeDynamics:TST, CVTTunneling:ZCT, SCT, LCT, muOMTDual Level:ICA for vibrations, original interpolation method for VMEP

This sample input is for a PM3 and a PM3-IOC direct dynamics calculation for the CH4 + OH -> CH3 + H2O reaction. The lowest vibrational mode of the generalized transition state is treated as a hindered rotator. All other modes are treated using the harmonic approximation. A gradient step size of 2.E-3 bohr is used to follow the MEP, and a save step size of 1.E-2 bohr is used between generalized normal mode analyses. Zero-, small-, and largecurvature tunneling corrections are computed. The forward reaction rate constants are calculated at 15 temperatures.

MORATE I/O Files	MORATE File	names
testr13.71	esp.fu71	input data for reactant 1
testr13.72	esp.fu72	input data for reactant 2
testr13.73	esp.fu73	input data for product 1
testr13.74	esp.fu74	input data for product 2
testr13.75	esp.fu75	input data for the saddle point
testr13.dat	poly.fu5	input data for MORATE
testr13.fu6	poly.fu6	long output file
testr13.fu15	poly.fu15	summary output file
testr13.50	poly.fu50	input data for the
		VTST-IOC calculation

9.14. Test run 14 ------CH3Cl + F-(H2O) -> CH3F + Cl-(H2O) TST and TST-IOC calculations Potential : PM3 (low-level) MEP : no RODS : no Vibrations : harmonic rectilinear Dynamics : TST Tunneling : no Dual Level : ICA for vibrations and original interpolation method for VMEP

This sample input is for a PM3 and a PM3-IOC TST calculation for the CH3Cl +  $F-(H2O) \rightarrow CH3F + Cl-(H2O)$  reaction. The TST-IOC calculation is a special case of the VTST-IOC calculation, where all the reactant and saddle point properties are replaced by high-level ab initio calculations (in this case, MP2/aug-cc-pVDZ calculations). All modes are treated using the harmonic approximation. The forward reaction rate constants are calculated at 3 temperatures.

MORATE I/O Files	MORATE Filen	ames
testr14.71	esp.fu71	input data for reactant 1
testr14.73	esp.fu72 esp.fu73	input data for product 1
testr14.74	esp.fu74	input data for product 2
testr14.dat	poly.fu5	input data for MORATE
testr14.fu6	poly.fu6	long output file
testr14.fu15	poly.fu15	summary output file
testr14.50	poly.fu50	input data for the
	TST-IC	DC calculation

9.15. Test run 15 \_\_\_\_\_ CF3 + CD3H -> CF3H + CD3 LCG3 tunneling Potential : MNDO-SRP (low-level) MEP : Page-McIver RODS : no Vibrations : rectilinear, harmonic with one hindered-rotor mode Dynamics : TST, CVT Tunneling : ZCT, SCT, LCT, muOMT Dual Level : ICA for vibrations and original interpolation method for VMEP

This sample input is for an MNDO-SRP and an MNDO-SRP-IOC direct dynamics calculation for the CF3 + CD3H -> CF3H + CD3 reaction. The SRP parameter is chosen to reproduce the experimental excergicity. The high-level surface is chosen to be the AM1-SRP-2 surface from J. Am. Chem. Soc. 115, 7806 (1993). The lowest vibrational mode of the generalized transition state is treated as a hindered rotator. All other modes are treated using the harmonic approximation. A gradient step size of 5.E-3 bohr is used to follow the MEP from s = -3.00 bohr to s = 3.00 bohr, and a save step size of 3.E-2bohr is used between generalized normal mode analyses. Zero-, small-, and large curvature tunneling (ground-state to ground-state) corrections are computed. The forward reaction rate constants are calculated at 11 temperatures. The only difference between test run 15 and 16 is that test run 15 is based on NDDO-SRP and test run 16 is based on MNDO.

MORATE I/O Files testr15.71 input data for reactant 1 esp.fu71 testr15.72 esp.fu72 input data for reactant 2 testr15.73 esp.fu73 input data for product 1 testr15.74 esp.fu74 input data for product 2 testr15.75 esp.fu75 input data for the saddle point testr15.dat poly.fu5 input data for MORATE testr15.fu6 poly.fu6 long output file testr15.fu15 poly.ful5 summary output file poly.fu50 input data for the testr15.50 VTST-IOC calculation

MORATE Filenames

9.16. Test run 16 ------CF3 + CD3H -> CF3H + CD3 LCG3 tunneling Potential : MNDO (low-level) MEP : Page-McIver RODS : no Vibrations : rectilinear, harmonic with one hindered-rotor mode Dynamics : TST, CVT Tunneling : ZCT, SCT, LCT, muOMT Dual Level : ICA for vibrations and original interpolation method for VMEP

This sample input is for a VTST-IOC direct dynamics calculations for the CF3 + CD3H -> CF3H + CD3 reaction. The high-level surface is chosen to be the AMI-SRP-2 surface from J. Am. Chem. Soc. 115, 7806 (1993). The lowest vibrational mode of the generalized transition state is treated as a hindered rotator. All other modes are treated using the harmonic approximation. A gradient step size of 5.E-3 bohr is used to follow the MEP from s = -3.00 bohr to s = 3.00 bohr, and a save step size of 3.E-2 bohr is used between generalized normal mode analyses. Zero-, small-, and large curvature tunneling (ground-state to ground-state) corrections are computed. The forward reaction rate constants are calculated at 11 temperatures. The only difference between test run 15 and 16 is that test run 15 is based on NDDO-SRP and test run 16 is based on MNDO.

MORATE I/O Files

MORATE Filenames

testr16.72 input data for reactant 2 esp.fu72 testr16.73 esp.fu73 input data for product 1 testr16.74 esp.fu74 input data for product 2 testr16.75 esp.fu75 input data for the saddle point testr16.dat poly.fu5 input data for MORATE testr16.fu6 poly.fu6 long output file testr16.fu15 poly.fu15 summary output file testr16.50 poly.fu50 input data for the VTST-IOC calculation

9.17. Test run 17

N2H2+ H -> N2H + H2

ICL-ECKART calculation in curvilinear internal coordinates

Potential: AM1 (low-level)MEP: Page-McIverRODS: noVibrations: harmonic nonredundant curvilinearDynamics: TST, CVTTunneling: ZCT, SCT, LCT, muOMTDual Level: ICL for vibrations and ECKART interpolation for VMEP

This sample input is for an AM1 and an AM1-ICL-ECKART direct dynamics calculation for the N2H2 + H -> N2H + H2 reaction. The high-level information is taken from J. Chem. Phys. 104, 6298 (1994). Also, the curvilinear internal coordinates are used to obtain better low-frequency modes. Both gradient and save steps are 0.01 bohr with the MEP followed from -1.0 to 0.4 bohr. Zero-, small, and large curvatures tunneling corrections are computed. The forward reaction rate constants are calculated at 9 temperatures with symmetry number equals to 2.

MORATE I/O Files

MORATE Filenames

testr17.71 testr17.72 testr17.73 testr17.74 testr17.75 testr17.dat testr17.fu6 testr17.fu15 testr17.50 esp.fu71 input data for reactant 1 esp.fu72 input data for reactant 2 esp.fu73 input data for product 1 esp.fu74 input data for product 2 esp.fu75 input data for the saddle point poly.fu5 input data for MORATE poly.fu6 long output file poly.fu15 summary output file poly.fu50 input data for the VTST-IOC calculation

9.18. Test run 18

HBr+ C2H2 -> CHBrCH2

AM1 calculation in redundant internal coordinates

Potential: AM1MEP: Page-McIverRODS: noVibrations: harmonic redundant curvilinearDynamics: TST, CVTTunneling: ZCT, SCT, LCT, muOMTDual Level: no

This sample input is for an AM1 direct dynamics calculation for the HBr + C2H2 -> CHBrCH2 reaction. The harmonic vibrational frequencies are evaluated with the redundant internal coordinates option (curv3). The MEP is followed from -3.3 to 1.5 bohr. The gradient step is 0.01 bohr and the save step is 0.02 bohr. Zero-, small-, and large- curvature tunneling contributions are computed. The forward rate constants are calculated at 9 temperatures.

MORATE I/O Files

MORATE Filenames

testr18.71	esp.fu71	input data for reactant 1
testr18.72	esp.fu72	input data for reactant 2
testr18.73	esp.fu73	input data for product 1
testr18.75	esp.fu75	input data for the saddle point
testr18.dat	poly.fu5	input data for MORATE
testr18.fu6	poly.fu6	long output file
testr18.fu15	poly.fu15	summary output file

9.3. Test run 19
----Cl- + CH3Cl -> CH3Cl + Cl- AM1 harmonic TST and CVT rate constants
Potential : AM1 (low-level)
MEP : VRPE
RODS : no
Vibrations : harmonic rectilinear
Dynamics : TST, CVT, ICVT
Tunneling : SCT
Dual Level : ISPE

This sample input is for an AM1 and an AM1 VTST-ISPE direct dynamics calculation on the Cl- + CH3Cl -> CH3Cl + Cl- SN2 reaction. All normal modes and generalized normal modes are treated using the harmonic approximation. The VRPE integration method is used with a gradient step size of 1.E-2 bohr to follow the MEP, and a save step size of 2.0E-2 bohr is used between generalized normal mode analyses. Both MEPSAG and CD-SCSAG tunneling corrections are computed, and both CVT and ICVT rate constants are calculated at three temperatures. Derivatives of the gradient with respect to the reaction coordinate, as required for the CD-SCSAG calculation, are found by a quadratic fit. For the VTST-ISPE calculation, the energies of the two turning points at the representative tunneling energy of the SCT at 300 K are evaluated at the MP2/6-31G\*\* level.

MORATE I/O Files MORATE Filenames testr19.71 esp.fu71 input data for reactant 1 testr19.72 esp.fu72 input data for reactant 2 testr19.73 esp.fu73 input data for product 1 testr19.74 esp.fu74 input data for product 2 testr19.75 esp.fu75 input data for the saddle point testr19.77 esp.fu77 input data for the wellr esp.fu78 input data for the wellp testr19.78 testr19.dat poly.fu5 input data for MORATE testr19.fu6 poly.fu6 long output file testr19.fu15 poly.fu15 summary output file testr19.51 input data for the VTST-ISPE poly.fu51 calculation

10. COMPUTERS AND OPERATING SYSTEMS ON WHICH MORATE HAS BEEN TESTED

Version 1.6	VAX 11/780 (VMS version 4.3)
Version 2.0	Cray-2 (UNICOS 5.0)
Versions 4.2-4.4	Cray-2 and Cray X-MP-EA (UNICOS 6.1)
Version 4.5	Cray-2 and Cray X-MP-EA (UNICOS 6.1)
	Cray Y-MP (UNICOS 6.1.6)
Version 5.0	Cray-2 (UNICOS 6.1), CRAY X-MP-EA (UNICOS 7.C.2), Cray Y-MP (UNICOS 6.1.7), Cray C90 (UNICOS 7.C.2)
Version 5.1	Crav-2 (UNICOS 7.0.5), CRAY X-MP-EA (UNICOS 7.C.2),
	Cray C90 (UNICOS 7.C.2)
Version 6.2	Cray-2 (UNICOS 7.0.5), CRAY X-MP-EA (UNICOS 7.C.2),
	Cray C90 (UNICOS 7.C.2),
	IBM RS/6000 model 550 (AIX 3.2.5)
	Silicon Graphics IRIS-Indigo R4000 (IRIX 5.2)
Version 6.2.1	CRAY X-MP-EA (UNICOS 7.C.3), Cray C90 (UNICOS 7.C.3),
	IBM RS/6000 model 550 (AIX 3.2.5),
	Silicon Graphics IRIS-Indigo R4000 (IRIX 5.2)
Version 6.5	CRAY X-MP-EA (UNICOS 7.C.3), Cray C90 (UNICOS 7.C.3),
	IBM RS/6000 model 550 (AIX 3.2.5),
	Silicon Graphics IRIS-Indigo R4000 (IRIX 5.2),
	Sun SparcStation IPX (SunOS 4.1.2)
Versions 7.2-7.3	Cray C90 (UNICOS 8.0.3),
	IBM RS/6000 models 550 and 590 (AIX $4.1$ ),
	Silicon Graphics Power Challenge L/R8000 (IRIX 6.2)
Versions 7.4-7.5	Cray C90 (UNICOS 8.0.3),
	IBM RS/6000 model 590 (AIX 4.1),
	Silicon Graphics Power Challenge R10000 (IRIX 6.2),
	Dell Dimension XPSPro200n (RedHat 4.2, Linux kernel 2.0.30)
Version 7.8-7.9.1	Cray C90 (UNICOS 8.0.3),
	IBM RS/6000 model 590 (AIX 4.1)
	Silicon Graphics Origin 200 (IRIX 6.4),
	Dell Dimension XPSPro200n (RedHat 4.2, Linux kernel 2.0.30)
Version 8.0	IBM SP with PowerPC 604e (AIX 4.3),
	Silicon Graphics Indigo2 R10000 (IRIX 6.2),
	Dual Intel Pentium II 333 MHz (Linux kernel 2.0.33)

# 11. TEST RUN TIMINGS

Here are the timings for the test runs. These timing are measured with the Unix time command.

The following timings (in seconds) apply to version 8.0:

		IBMSP604	e SGI-Indig	02* Linux**
run	1	23 0	10 4	31 3
run	2	5.0 6.6	3 5	9 4
run	3	31.6	17.1	46.1
run	4	82 1	82 0	104 7
run	5	82.2	45.6	105.6
run	6	0.0	0.0	0.0
run	7	1605.5	541.1	2108.3
run	8	76.9	33.3	106.8
run	9	748.2	349.7	1017.1
run	10	1303.4	669.3	1690.0
run	11	27.6	14.5	38.1
run	12	779.5	326.3	998.4
run	13	805.0	328.0	1027.9
run	14	3.4	1.7	5.1
run	15	1771.7	644.9	2240.2
run	16	1465.2	556.3	1876.7
run	17	102.5	50.9	140.3
run	18	27.4	138.4	345.3
run	19	135.4	69.1	224.8
	run run run run run run run run run run	run 1 run 2 run 3 run 4 run 5 run 6 run 7 run 8 run 9 run 10 run 11 run 12 run 13 run 14 run 15 run 16 run 17 run 18 run 19	run 1       23.0         run 2       6.6         run 3       31.6         run 4       82.1         run 5       82.2         run 6       0.0         run 7       1605.5         run 8       76.9         run 10       1303.4         run 11       27.6         run 12       779.5         run 13       805.0         run 14       3.4         run 15       1771.7         run 16       1465.2         run 17       102.5         run 18       27.4         run 19       135.4	IBMSP604eSGI-Indigrun 123.010.4run 26.63.5run 331.617.1run 482.182.0run 582.245.6run 60.00.0run 71605.5541.1run 876.933.3run 9748.2349.7run 101303.4669.3run 1127.614.5run 12779.5326.3run 13805.0328.0run 143.41.7run 151771.7644.9run 161465.2556.3run 17102.550.9run 1827.4138.4run 19135.469.1

<sup>\*</sup> SGI-Indigo2 means SGI Indigo2 with R10000

\*\* Linux runs were carried out on the following IBM-compatible PC: Dual Pentium II 333 MHz with LINUX kernel 2.0.33.

# 12. ERRATA

This section contains selected errata for the MORATE manuals.

- 12.A. Errata for the version 4.2 manual
- 1. Page 8-1, the reaction for TR2: CH3 + CD4 -> CH3D + CD3 should be CD3 + CH4 -> CD3H + CH3.
- 12.B. Errata for the version 5.1 manual
- 1. Page 6-4, there shouldn't be an X on the param2.inc column and testr1 row in the table, i.e., param2.inc is not suitable for testr2.

#### 13. BIBLIOGRAPHY

See Section 1.A for general background references.

## 13.A. MORATE publications

1. "MORATE: A Program for Direct Dynamics Calculations of Chemical Reaction Rates by Semiempirical Molecular Orbital Theory," T. N. Truong, D.-h. Lu, G. C. Lynch, Y.-P. Liu, V. S. Melissas, J. J. P. Stewart, R. Steckler, B. C. Garrett, A. D. Isaacson, A. Gonzalez-Lafont, S. N. Rai, G. C. Hancock, T. Joseph, and D. G. Truhlar, Computer Physics Communications 75, 143-159 (1993).

This article describes the first library version, namely, version 4.5/P4.5-M5.03, which is catalog no. ACLM in the Computer Physics Communications Program Library, Department of Applied Mathematics and Theoretical Physics, Queen's University, Belfast, Northern Ireland.

2. "MORATE: A Program for Direct Dynamics Calculations of Chemical Reaction Rates by Semiempirical Molecular Orbital Theory (version 6.5)", W.-P. Hu, G. C. Lynch, Y.-P. Liu, I. Rossi, J. J. P. Stewart, R. Steckler, B. C. Garrett, A. D. Isaacson, D.-h. Lu, V. S. Melissas, and D. G. Truhlar, QCPE Bulletin, 15, 26-27 (1995).

This is the first listing of MORATE in the Quantum Chemistry Program Exchange. It describes version 6.5/P6.5-M5.05, which is catalog no. 666 in the QCPE Program Library, Indiana University, Bloomington.

3. "MORATE 6.5: A New version of a Computer Program for Direct Dynamics Calculations of Chemical Reaction Rate Constants", W.-P. Hu, G. C. Lynch, Y.-P. Liu, I. Rossi, J. J. P. Stewart, R. Steckler, B. C. Garrett, A. D. Isaacson, D.-h. Lu, V. S. Melissas, and D. G. Truhlar, Computer Physics Communications, 88, 341-343 (1995).

This is a new version announcement for MORATE-version 6.5/P6.5-M5.05 in the Computer Physics Communications Program Library.

The recommended references to read for an introduction to MORATE version 8.0 are the POLYRATE version 8.0 manual and Reference 3 in section 13.C. of this manual.

The recommended references to cite are given on page iv.

13.B. Publications based on MORATE

1. "Direct Dynamics Calculations with Neglect of Diatomic Differential Overlap Molecular Orbital Theory with Specific Reaction Parameters," A. Gonzalez-Lafont, T. N. Truong, and D. G. Truhlar, Journal of Physical Chemistry 95, 4618-4627 (1991).

2. "Temperature Dependence of the Kinetic Isotope Effect for a Gas-Phase SN2 Reaction: Cl- + CH3Br," A. A. Viggiano, J. Paschkewitz, R. A. Morris, J. F. Paulson, A. Gonzalez-Lafont, and D. G. Truhlar, Journal of the American Chemical Society 113, 9404-9405 (1991).

3. "Variational Transition State Theory with Multidimensional Semiclassical Ground-State Transmission Coefficients: Applications to Secondary Deuterium Kinetic Isotope Effects in Reactions Involving Methane and Chloromethane," D. G. Truhlar, D.-h. Lu, S. C. Tucker, X. G. Zhao, A. Gonzalez-Lafont, T. N. Truong, D. Maurice, Y-.P. Liu, and G. C. Lynch, American Chemical Society Symposium Series 502, 16-36 (1992).

4. "Molecular Modeling of the Kinetic Isotope Effect for the [1,5]-Sigmatropic Rearrangement of cis-1,3-Pentadiene," Y.-P. Liu, G. C. Lynch, T. N. Truong, D.-h. Lu, D. G. Truhlar, and B. C. Garrett, Journal of the American Chemical Society 115, 2408-2415 (1993).

5. "Direct Dynamics Calculation of the Kinetic Isotope Effect for an Organic Hydrogen-Transfer Reaction, Including Corner-Cutting Tunneling in 21 Dimensions," Y.-P. Liu, D.-h. Lu, A. Gonzalez-Lafont, D. G. Truhlar, and B. C. Garrett, Journal of the American Chemical Society 115, 7806-7817 (1993).

6. "Variational Transition State Theory and Semiclassical Tunneling Calculations with Interpolated Corrections: A New Approach to Interfacing Electronic Structure Theory and Dynamics for Organic Reactions," W.-P. Hu, Y.-P. Liu, and D. G. Truhlar, Journal of the Chemical Society Faraday Transactions 90, 1715-1725 (1994).

7. General Discussion: tunneling effects in hydride transfer reactions, Y.-P. Liu and D. G. Truhlar, Journal of the Chemical Society Faraday Transactions 90, 1735-1737 (1994).

8. "Modeling Transition State Solvation at the Single-Molecule Level: Test of Correlated Ab Initio Predictions Against Experiment for the Gas-Phase SN2 Reaction of Microhydrated Fluoride with Methyl Chloride," W.-P. Hu and D. G. Truhlar, Journal of the American Chemical Society 116, 7797-7800 (1994).

9. "Dual-Level Reaction-Path Dynamics (The /// Approach to VTST with Semiclassical Tunneling). Application to OH + NH3 -> H2O + NH," J. C. Corchado, J. Espinosa-Garcia, W.-P. Hu, I. Rossi, and D. G. Truhlar, Journal of Physical Chemistry 99, 687-694 (1995).

10. "Deuterium Kinetic Isotope Effects and their Temperature Dependence in the Gas-Phase SN2 Reactions X - + CH3Y -> CH3X + Y - (X,Y=Cl,Br,I)," W.-P. Hu and D. G. Truhlar, Journal of the American Chemical Society 117, 10726-10734 (1995).

11. "Factors Affecting Competitive Ion-Molecule Reactions: ClO- + C2H5Cl and C2D5Cl via E2 and SN2 Channels," W.-P. Hu and D. G. Truhlar, Journal of the American Chemical Society 118, 860-869 (1996).

12. "Molecular Modeling of Combustion Kinetics. The Abstraction of Primary and Secondary Hydrogens by Hydroxyl Radical," W.-P. Hu, I. Rossi, J. C. Corchado, and D. G. Truhlar, Journal of Physical Chemistry A 101, 6911-6921 (1997).

 "Reaction-Path Dynamics with Harmonic Vibrational Frequencies in Curvilinear Internal Coordinates: H + trans-N2H2 -> N2H + H2,"
 Y.-Y. Chuang, and D. G. Truhlar, Journal of Chemical Physics 107, 83-89 (1997).

14. "Improved Dual-Level Direct Dynamics Method for Reaction Rate Calculations with Inclusion of Multidimensional Tunneling Effects and Validation for the Reaction H with trans-N2H2," Y.-Y. Chuang, and D. G. Truhlar, Journal of Physical Chemistry, Journal of Physical Chemistry A 101, 3808-3814 (1997).

15. "Reaction-Path Dynamics in Redundant Internal Coordinates," Y.-Y. Chuang, and D. G. Truhlar, Journal of Physical Chemistry A 102, 242-247 (1998).

16. "Dual-Level Direct Dynamics Calculations of the Reaction Rates for a Jahn-Teller Reaction: Hydrogen Abstraction from CH4 or CD4 by O(3P)", J. C. Corchado, J. Espinosa-Garcia, O. Roberto-Neto, Y.-Y. Chuang, and D. G. Truhlar, Journal of Physical Chemistry A, in press.

# 13.C. General references for Variational Transition State Theory and Semiclassical Tunneling Approximations

1. "Criterion of Minimum State Density in the Transition State Theory of Bimolecular Reactions," B. C. Garrett and D. G. Truhlar, Journal of Chemical Physics 70, 1593-1598 (1979).

2. "Variational Transition-State Theory," D. G. Truhlar and B. C. Garrett, Accounts of Chemical Research 13, 440-448 (1980).

3. "Generalized Transition State Theory," D. G. Truhlar, A. D. Isaacson, and B. C. Garrett, in: Theory of Chemical Reaction Dynamics, edited by M. Baer (CRC Press, Boca Raton, FL, 1985), Vol. 4, pp. 65-137.

4. "Variational Transition State Theory," D. G. Truhlar and B. C. Garrett, Annual Review of Physical Chemistry 35, 159-189 (1984).

5. "Transition State Theory," M. M. Kreevoy and D. G. Truhlar, in Investigation of Rates and Mechanisms of Reactions, 4th edition, edited by C. F. Bernasconi (Vol. 6 of "Techniques of Chemistry," edited by A. Weissberger; John Wiley and Sons, New York, 1986), Part 1. pp. 13-95.

6. "Dynamical Formulation of Transition State Theory: Variational Transition States and Semiclassical Tunneling," S. C. Tucker and D. G. Truhlar, in: New Theoretical Concepts for Understanding Organic Reactions, edited by J. Bertran and I. G. Csizmadia (NATO ASI Series C, Vol. 267, Kluwer, Dordrecht, The Netherlands, 1989), pp. 291-346.

7. "POLYRATE 4: A New Version of a Computer Program for the Calculation of Chemical Reaction Rates for Polyatomics," D.-h. Lu, T. N. Truong, V. S. Melissas, G. C. Lynch, Y.-P. Liu, B. C. Garrett, R. Steckler, A. D. Isaacson, S. N. Rai, G. C. Hancock, J. G. Lauderdale, T. Joseph, and D. G. Truhlar, Computer Physics Communications 71, 235-262 (1992).

8. "Direct Dynamics Methods for the Calculation of Reaction Rates," D. G. Truhlar, in The Reaction Path in Chemistry: Current Approaches and Perspectives, edited by D. Heidrich (Kluwer, Dordrecht, 1995), pp. 229-255. 14. MORATE VERSIONS

14.A. Explanation of version number

In the MORATE version number, the first number (i.e., the part before the virgule) refers to the version of the MORATE package and is unique. That is, this number changes if the interface changes or if the POLYRATE and/or the MOPAC part changes. The second and third numbers refer to the versions of POLYRATE and MOPAC, respectively, upon which the given version of MORATE is built. In particular, in the version number 8.0/P8.0-M5.07, the first 8.0 is the version number of the whole package, including the interface, P8.0 specifies that the version of POLYRATE is 8.0, and M5.07 specifies that the version of MORATE is based on MOPAC version 5.07mn.

Because the first number is unique, it is sufficient to just say MORATE-version 8.0, but the longer version number (8.0/P8.0-M5.07) is more informative.

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

14.2 MORATE versions and authors

In the list below, if we list several versions in succession and then a set of authors, it means the authors are the same for all those versions. Through version 6.5, MORATE was distributed as a complete package containing POLYRATE and MOPAC. Beginning with version 7.2, MORATE is the interface, and the user must obtain POLYRATE and MOPAC separately.

MORATE-version 1.6/P1.6-M4.0 (1989)

T. N. Truong, J. J. P. Stewart, B. C. Garrett, R. Steckler,

A. D. Isaacson, S. N. Rai, G. Hancock, T. Joseph, and

D. G. Truhlar.

MORATE-version 2.0/P2.0-M5.01 (August 1990)

T. N. Truong, D.-h. Lu, J. J. P. Stewart, B. C. Garrett,

R. Steckler, A. D. Isaacson, S. N. Rai, G. Hancock, T. Joseph,

V. S. Melissas, and D. G. Truhlar.

Notes: (1) MOPAC-version 5.01mm is a local modification by Minnesota Supercomputer Center Inc. for the Cray computers.

MORATE-version 2.1/P2.1-M5.01 (October 1990)

T. N. Truong, D.-h. Lu, J. J. P. Stewart, B. C. Garrett,

R. Steckler, A. D. Isaacson, S. N. Rai, G. Hancock, T. Joseph,

V. S. Melissas, and D. G. Truhlar.

MORATE-version 2.5/P2.5-M5.01 (November 1990)

T. N. Truong, D.-h. Lu, J. J. P. Stewart, B. C. Garrett,

R. Steckler, A. D. Isaacson, S. N. Rai, G. Hancock, T. Joseph,

V. S. Melissas, and D. G. Truhlar.

MORATE 8.0/P8.0-M5.07

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Note: MORATE-version 2.5 was used for the calculations in

A. A. Viggiano, J. S. Paschkewitz, R. A. Morris, J. F. Paulson, A. Gonzalez-Lafont, and D. G. Truhlar, "Temperature Dependence of the Kinetic Isotope Effect for

a Gas-Phase SN2 Reaction: Cl- + CH3Br, " Journal of the

American Chemical Society, 113, 9404-9405 (1991).

MORATE-version 2.6/P2.6-M5.01 (March 1991)

MORATE-version 2.6.1/P2.6.1-M5.01 (June 1991)

T. N. Truong, D.-h. Lu, J. J. P. Stewart, B. C. Garrett,

R. Steckler, A. D. Isaacson, S. N. Rai, G. Hancock, T. Joseph,

V. S. Melissas, and D. G. Truhlar.

MORATE-version 3.0/P3.0-M5.01 (July 1991)

MORATE-version 3.0.1/P3.0.1-M5.01 (August 1991)

MORATE-version 3.0.7/P3.0.7-M5.01 (December 1991)

MORATE-version 3.9.1/P3.9.1-M5.01 (December 1991)

MORATE-version 3.9.2/P3.9.2-M5.01 (December 1991)

T. N. Truong, D.-h. Lu, Y.-P. Liu, G. C. Lynch, V. S. Melissas,

J. J. P. Stewart, B. C. Garrett, R. Steckler, A. D. Isaacson,

S. N. Rai, G. Hancock, T. Joseph, A. Gonzalez-Lafont, and D. G. Truhlar.

MORATE-version 4.2/P4.2-M5.02 (May 1992)

T. N. Truong, D.-h. Lu, G. C. Lynch, Y.-P. Liu, V. S. Melissas,

J. J. P. Stewart, B. C. Garrett, R. Steckler, A. D. Isaacson, A. Gonzalez-Lafont, S. N. Rai, G. Hancock, T. Joseph, and

D. G. Truhlar.

Notes: (1) MOPAC-version 5.02mn is a modification of MOPAC-version 5.01mn made specifically for this version of MORATE.

(2) The authors are grateful to Wei-Ping Hu for assistance in preparing this version of MORATE.

MORATE-version 4.4/P4.4-M5.03 (August 1992)

T. N. Truong, D.-h. Lu, G. C. Lynch, Y.-P. Liu, V. S. Melissas,

J. J. P. Stewart, B. C. Garrett, R. Steckler, A. D. Isaacson, A. Gonzalez-Lafont, S. N. Rai, G. Hancock, T. Joseph, and

D. G. Truhlar.

Note: MOPAC-version 5.03mn is a modification of MOPAC-version 5.02mn made specifically for MORATE.

MORATE-version 4.5/P4.5.1-M5.03 (September 1992)

T. N. Truong, D.-h. Lu, G. C. Lynch, Y.-P. Liu, V. S. Melissas,

J. J. P. Stewart, B. C. Garrett, R. Steckler, A. D. Isaacson,

A. Gonzalez-Lafont, S. N. Rai, G. Hancock, T. Joseph, and

D. G. Truhlar.

Note: MORATE-version 4.5 was the first distributed version of MORATE. MORATE-version 5.0/P5.0.1-M5.04 (June 1993)

G. C. Lynch, Y.-P. Liu, W.-P. Hu, T. N. Truong, D.-h. Lu,

V. S. Melissas, J. J. P. Stewart, B. C. Garrett, R. Steckler,

A. D. Isaacson, A. Gonzalez-Lafont, S. N. Rai, G. Hancock,

T. Joseph, and D. G. Truhlar.

Note: MOPAC-version 5.04mn is a modification of MOPAC-version 5.03mn made specifically for MORATE.

MORATE-version 5.1/P5.1-M5.04 (December 1993) G. C. Lynch, Y.-P. Liu, W.-P. Hu, T. N. Truong, D.-h. Lu, V. S. Melissas, J. J. P. Stewart, B. C. Garrett, R. Steckler, A. D. Isaacson, A. Gonzalez-Lafont, S. N. Rai, G. Hancock, T. Joseph, and D. G. Truhlar. MORATE-version 6.2/P6.2-M5.05 (August 1994) W.-P. Hu, G. C. Lynch, Y.-P. Liu, I. Rossi, J. J. P. Stewart, R. Steckler, B. C. Garrett, A. D. Isaacson, T. N. Truong, D.-h. Lu, A. Gonzalez-Lafont, V. S. Melissas, S. N. Rai, G. Hancock, T. Joseph, and D. G. Truhlar. Note: MOPAC-version 5.05mn is a modification of MOPAC-version 5.04mn. This version of MOPAC can be used independently, or it can be used in MORATE. MORATE-version 6.2.1/P6.2.1-M5.05 (November 1994) MORATE-version 6.3/P6.2.1-M5.05 (November 1994) W.-P. Hu, G. C. Lynch, Y.-P. Liu, I. Rossi, J. J. P. Stewart, R. Steckler, B. C. Garrett, A. D. Isaacson, T. N. Truong, D.-h. Lu, A. Gonzalez-Lafont, V. S. Melissas, S. N. Rai, G. Hancock, T. Joseph, and D. G. Truhlar. MORATE-version 6.5/P6.5-M5.05 (February 1995) W.-P. Hu, G. C. Lynch, Y.-P. Liu, I. Rossi, J. J. P. Stewart, R. Steckler, B. C. Garrett, A. D. Isaacson, D.-h. Lu, V. S. Melissas, and D. G. Truhlar. MORATE-version 7.2/P7.2-M5.05 (March 1997) Y.-Y. Chuang, W.-P. Hu, G. C. Lynch, Y.-P. Liu, and D. G. Truhlar. MORATE-version 7.3/P7.3-M5.05 (June 1997) MORATE-version 7.4/P7.4-M5.05 (August 1997) Y.-Y. Chuang, P. L. Fast, W.-P. Hu, G. C. Lynch, Y.-P. Liu, and D. G. Truhlar. MORATE-version 7.5/P7.4-M5.06 (September 1997) Y.-Y. Chuang, P. L. Fast, W.-P. Hu, G. C. Lynch, Y.-P. Liu, and D. G. Truhlar. Note: MORATE-version 7.5 is a modification of MORATE-version 7.4 in which only the MOPAC part and the interface changes; it is based on the same version of POLYRATE. MORATE-version 7.8/P7.8-M5.07 (December 1997) MORATE-version 7.8.1/P7.8.1-M5.07 (February 1998) MORATE-version 7.9/P7.9-M5.07 (March 1998) MORATE-version 7.9.1/P7.9.1-M5.07 (April 1998) MORATE-version 8.0/P8.0-M5.07 (September 1998) Y.-Y. Chuang, P. L. Fast, W.-P. Hu, G. C. Lynch, Y.-P. Liu, and D. G. Truhlar.

## 14.3 MORATE REVISION HISTORY

This section contains the MORATE revision history beginning with version 2.0. Updates involved in incorporating a new version of POLYRATE are summarized in the POLYRATE manual.

Version 2.0/P2.0-M5.01 (August 1990)

1. This version of MORATE was created to incorporate new versions of POLYRATE and MOPAC.

Version 2.1/P2.1-M5.01 (October 1990)

1. This version was created to incorporate the new version of POLYRATE.

Version 2.5/P2.5-M5.01 (November 1990)

1. This version was created to incorporate the new version of POLYRATE.

Version 2.6/P2.6-M5.01 (March 1991)

1. This version was created to incorporate the new version of POLYRATE.

Version 2.6.1/P2.6.1-M5.01 (June 1991)

## 1. In subprogram MAIN:

This subprogram has been modified so that MORATE can be correctly run using the restart option. This error existed since version 1.6. This bug fix enables the use of the restart option with LCG3 calculations that sample the vibrationally nonadiabatic region.

# 2. In subprogram REDGEO:

Minor modifications were introduced to allow the user to choose the anharmonicity option LGS(5) = 21 at the saddle point. This bug existed since version 1.6.

Version 3.0/P3.0-M5.01 (July 1991)

- 1. This version was created to incorporate the new version of POLYRATE.
- 2. In subprogram READ5: For MORATE calculations the LGS(33) option is no longer supported.

Version 3.0.1/P3.0.1-M5.01 (August 1991)

1. This version was created to incorporate the new version of POLYRATE.

Version 3.0.7/P3.0.7-M5.01 (December 1991)

1. This version was created to incorporate the new version of POLYRATE.

Version 3.9.1/P3.9.1-M5.01 (December 1991)

1. This version was created to incorporate the new version of POLYRATE.

Version 3.9.2/P3.9.2-M5.01 (December 1991)

1. This version was created to incorporate the new version of POLYRATE.

Version 4.2/P4.2-M5.02 (May 1992)

- 1. This version was created to incorporate new versions of POLYRATE and  $\ensuremath{\operatorname{\mathsf{MOPAC}}}$  .
- In version 5.02mn of MOPAC, all the subprograms have been returned to the original form, which used the include extension and the include file SIZES. This was done so as to make dimension changes much easier in MORATE. (In version 5.01 of MOPAC the statements which made up the include file SIZES are explicitly included in all subprograms.)
- 3. All the parameter statements and common blocks which were used for passing information, other than the energy V, the coordinates X, and the gradients DX, between POLYRATE and MOPAC have been removed from the POLYRATE subprograms and placed in the include file morate.inc. This include file is needed when compiling the subprograms that make up the poly\_mod.f file.
- 4. In subprogram SURF:

The zero of energy is subtracted from the total energy in all of the POLYRATE subprograms which call SURF, and not in the subprogram SURF. This change is in accord with POLYRATE-version 4.2 and causes only minor differences between calculations made with this version and previous versions of MORATE.

5. In subprogram READ5:

A new option has been added which allows the user to input the zero of energy in kcal/mol. This option uses LGS2(4) and the variable EZOTMP. This zero of energy (in hartree atomic units) will be echoed to the unit ful restart file if the option is chosen to have the restart information saved. Note that the format of this option allows old input data files to be used by this version of MORATE, but the conversion constant used to convert EZOTMP from kcal/mol to atomic units is the conversion constant in POLYRATE-version 4.2. Old input restart files will not be compatible with this version of MORATE because the zero of energy was not saved in old restart data files.

6. The user can now supply a value for the variable DERSTP in the POLYRATE portion of the input data. This allows the user to use a quadratic fit calculation for the second derivatives of the potential (LGS(25) = 1). In the previous versions of MORATE this variable was not read in, and therefore it had a default value of zero.

- 7. A new option (LGS(4) = 3) has been installed. This option controls the writing to unit fu6 of the bond orders and charges calculated by MOPAC. This enhancement required changes in the following subprograms: MAIN, PATH, POLYAT, and SADDLE. This enhancement will cause small differences in the output produced by this version of the code from output from previous versions of MORATE.
- 8. Format statements were modified so that calculations with NATOMS set larger than 15 atoms can be handled. This involved changes in the subprograms PATH and RESTOR.

Version 4.4/P4.4-M5.03 (August 1992)

- 1. This version was created to incorporate new versions of POLYRATE and  $\ensuremath{\operatorname{\mathsf{MOPAC}}}$  .
- In version 5.03 of MOPAC, the blockdata file has been modified to include all the AM1 and PM3 parameters that are currently available in MOPAC-version 6.0. Save statements have been added to all the subprograms in m503\_mod.f and m503\_unmod.f.
- 3. A bug in the subprogram FIOPEN has been corrected. This bug caused the program to open fort.35 instead of morate.35 for a restart run. This bug was introduceded in version 4.2.
- 4. Save statements have been added to the subprograms ENERGY and SURF in the file interface.f.

Version 4.5/P4.5.1-M5.03 (September 1992)

- 1. This version was created to incorporate a new version of POLYRATE with an improved POLYRATE interface for electronic structure packages.
- 2. The subprogram HEADER in the file interface.f has been renamed HEADR.
- 3. The subprogram FIOPEN from the POLYRATE program is now used to open all the files (except the files linked to FORTRAN units fu5 and fu6) for a MORATE calculation. The interface.f file no longer contains a FIOPEN subprogram. The new FIOPEN subprogram opens files with filenames poly.fu# for all the files except those linked to FORTRAN units fu31 through fu35. The C shell scripts for running the test runs have been modified to reflect these changes.
- 4. The FORTRAN statements "INCLUDE morate.inc" in the poly\_mod.f subprograms have been changed to "INCLUDE esp.inc". The information in the include file has not been changed; only the referencing name has changed. The moratecl.jc C shell script has been modified to reflect this change.
- 5. The FORTRAN units 31 through 35 have been changed to FORTRAN units fu31 through fu35, and these fu3# units are defined in the param.inc include file. The open statements for these files have also been changed to open files with filenames esp.fu3# instead of morate.3#. The C shell scripts for running the test runs have been modified to reflect these changes.

6. In subprogram READ5:

Read statements in this subprogram have been modified to allow the user to input a value for the variable D3LX. D3LX is the step size used in evaluating the third derivatives of the potential with respect to the coordinates when these third derivatives are needed (only when the cubic starting algorithm is used). If D3LX is set equal to zero, it defaults to the value of DLX.

7. The compatibility check for the parameter NSDM has been expanded to include a check for NSPEC. This check causes a warning to be printed to the file linked to FORTRAN unit fu6, but it does not stop the calculation. The calculation will proceed until NSDM save grid points are stored and then the MEP calculation will stop; therefore, the MEP integration may not reach the limits set by SLM and SLP. This modification involved the subprogram READ5. The user is still responsible for ensuring that NSDM is large enough when extrapolation and/or NSPEC .NE. 0 are used.

Version 5.0/P5.0.1-M5.04 (June 1993)

- 1. The program has been modified so that the link between POLYRATE and MOPAC is more modular. The subprograms SETUP and SURF have been restructured; this restructuring results in three new subprograms SETUP, ESPINT, and ESPOPT. Also, the include file esp.inc has been removed from this version of the program.
- 2. Three new subprograms have been introduced in this version of the program. These new subprograms are described below.

a) Subprogram SETUP:

This subprogram has the same name as the subprogram in the previous versions of the program, but in this version of the code this subprogram checks the values of the variables N3TM, NATOMS, and NUMATM and exits. This subprogram does not carry out any calculations.

- b) Subprogram ESPINT: This subprogram initializes the subprograms for the electronic structure package, in this case MOPAC, for each chemical species. The input geometry is read and the array containing the Cartesian coordinates is initialized with the input geometry. The variable NUMCAL is also initialized in this subprogram.
- c) Subprogram ESPOPT: This subprogram uses the optimization routines in the electronic structure program, MOPAC in this case, to optimize the input geometry for each chemical species. This subprogram assumes that the subprogram ESPINT has been called to read the initial geometry and to initialize the electronic structure subprograms.
- 3. In subprogram MAIN:

A check comparing the value of NATOMS to the MOPAC variable NUMATM has been moved from this subprogram and placed in the interface subprogram SETUP.

- 4. In the subprogram REACT: The program has been modified such that for an atomic species the subprograms ESPINT and SURF are called and ESPOPT is not called. The result of this change is that the MOPAC heat of formation information for the atomic species is not printed in the long output file.
- 5. The include file SIZES has been renamed SIZES.i and all the FORTRAN statements modified accordingly. This change was made because the utility ANSITAPE, which is used to write VAX COPY format tapes on Unix machines, does not handle files without extensions.
- 6. The bond order and bond charges information has been suppressed in this version of the program. If this information is needed the user will need to modify the subprogram SURF to compute this information in conjunction with the extra potential information feature described in Section 8 of the POLYRATE-version 5.0.1 manual.
- 7. The program has been improved such that it can do SRP calculations with all the semiempirical MO methods available in MOPAC version 5.03 or 5.04.

Version 5.1/P5.1-M5.04 (December 1993)

- This version consists of the same MOPAC and interface versions as in MORATE-version 5.0 and is based on a new version of POLYRATE, version 5.1, which includes the VTST-IOC method published in the Faraday Symposium. The version in 5.0 was a preliminary one that is not recommended for further use.
- 2. Two new test runs, test run 11 and test run 12, have been added. The input data for test runs 3 and 6 have been changed because of the changes in the VTST-IOC method.
- 3. Three utility programs hrotor.f, findl.f, and findb.f have been included in this version. See sections 14.C and 14.D of the POLYRATE-version 5.1 on-line manual for details.

Version 6.2/P6.2-M5.05 (August 1994)

- 1. This version is based on POLYRATE-version 6.2 and MOPAC-version 5.05mn. The major changes from the previous versions in these two programs are summarized in the revision history sections of the POLYRATE 6.2 and MOPAC 5.05mn manuals.
- 2. The test run input files have been converted to keyword input format.
- 3. The distribution package of this version of MORATE also includes a complete version of MOPAC 5.05mn which can be used as a stand-alone program. An on-line manual for MOPAC 5.05mn is also included in the distribution package.

- 4. This version of MORATE and MOPAC 5.05mm have been made more portable. These two programs can now not only run on a Cray computer but also on an IBM RS/6000 or an IRIS Indigo machine. Many machinedependent files have been added to the distribution package.
- 5. The compiling and linking process has been simplified by using just one script (instead of three in previous versions) for a certain type of computer. This script also automatically makes a MOPAC 5.05mn executable file.

Version 6.2.1/P6.2.1-M5.05 (November 1994)

1. This version is based on POLYRATE-version 6.2.1 which is a bug-fix version of POLYRATE-version 6.2. The interface and MOPAC parts of the code have not been changed.

Version 6.3/P6.2.1-M5.05 (November 1994)

1. Three new scripts, check\_all.jc, check\_test.jc, and run\_all.jc, have been included in the distribution package.

Version 6.5/P6.5-M5.05 (February 1995)

 This version is based on POLYRATE-version 6.5 which has a prototype modular interface to obtain potential energy surface data from analytical potential energy surfaces or electronic structure calculation packages. The old interface (interface.f) has been replaced by the new POLYRATE interface (hooks.f) which is designed to linked to various electronic structure calculation packages and which is a first step toward a completely

modular interface. A new file m506drv.f which contains MOPAC-specific potential energy routines has been added in the distribution package.

- 2. This version has been tested on Sun workstations, and some machine-specific routines have been added in the distribution package.
- 3. This version supports the option of getting hessians directly from the MOPAC program rather than calculating them in POLYRATE from MOPAC gradients. This option has been used in test runs 2 and 4 in the distribution package.

Version 7.2/P7.2-M5.05 (March 1997)

1. This version is based on POLYRATE-version 7.2 and MOPAC-version 5.05mn. The major changes from the previous version of POLYRATE are summarized in the revision history section of the POLYRATE 7.2 manual. For example version 7.2 of POLYRATE allows users to use nonredundant curvilinear internal coordinates and the improved VTST-IOC scheme with the ICL and ECKART options.

- 2. Beginning with version 7.2, MORATE itself consists of only the interface routines and routines that must be changed to complete the interface; POLYRATE and MOPAC must be obtained separately.
- 3. A new example is added (test run 13).
- 4. Since anharmonicity is no longer supported with TST-only calculations, the input file of test run 2 has been modified.
- 5. A new keyword EZUNIT is introduced, and the input data files of test runs testr2, testr3, testr6, testr7, and testr8 are modified according to this change.

Version 7.3/P7.3-M5.05 (June 1997)

- 1. This version is based on POLYRATE-version 7.3 and MOPAC-version 5.05mn. The major changes from the previous version of POLYRATE are summarized in the revision history section of the POLYRATE 7.3 manual.
- 2. In hooks.f:

The INITG variable was added to account for the new keyword INITGEO which was added to the POLYRATE 7.3 program. For MORATE the INITGEO keyword is required to have the value "hooks". This is NOT the default value, and therefore the user must take care to add this keyword and value to the REACT1, REACT2, PROD1, PROD2, and START sections of the \*.dat input file. See the POLYRATE 7.3 manual for a detailed description of this new keyword. All testruns have been modified to account for this change in the POLYRATE program.

- 3. A new keyword NOSUPERMOL and its negation SUPERMOL have been added and are described in detail in the POLYRATE 7.3 manual. The following MORATE testrun input data files have been modified accordingly: testr1.dat, testr2.dat, testr3.dat, testr4.dat, testr6.dat, testr7.dat, testr8.dat, testr10.dat, testr11.dat, testr12.dat, testr13.dat.
- 4. The FORTRAN file units fu31-fu35 have been changed to FORTRAN file units fu71-fu75 for consistency with a new file numbering scheme introduced at this time to promote consistency across interfaces. The test runs and scripts have been updated for this change.

Version 7.4/P7.4-M5.05 (August 1997)

- 1. This version is based on POLYRATE-version 7.4 and MOPAC-version 5.05mn. The major changes from the previous version of POLYRATE are summarized in the revision history section of the POLYRATE 7.4 manual.
- A new test run, testr18, has been added for the HBr + C2H2 -> CH2CHBr reaction in redundant internal coordinates. New test runs (testr5, testr8, testr13, and testr16) are added.
- 3. The parameter POLYMX has been removed from subroutine mopset in m505drv.f.

Version 7.5/P7.4-M5.06 (September 1997)

- 1. This version is based on POLYRATE-version 7.4 and MOPAC-version 5.06mn.
- 2. The script moratecl.linux has been added to allow MORATE to run under the Linux operating system.
- 3. The subprogram m505drv.f has been renamed m506drv.f to be consistent with the updated MOPAC 5.06mn.
- 4. The testr16.75 geometry has been changed to a more converged geometry so that the results for the testr16 testrun are consistent across all the supported platforms.

Version 7.8/P7.8-M5.07 (December 1997)

- 1. This version is based on POLYRATE-version 7.8 and MOPAC-version 5.07mn.
- 2. The subprogram m506drv.f has been renamed m507drv.f to be consistent with the updated MOPAC 5.07mn.
- 3. The testr8 has been removed and replaced with a new reaction, CH4 + 0.

Version 7.8.1/P7.8.1-M5.07 (February 1998)

1. This version is based on POLYRATE-version 7.8.1, which is a bug-fix version of POLYRATE-version 7.8. The interface and MOPAC parts of the code have not been changed.

Version 7.9/P7.9-M5.07 (March 1998)

1. This version is based on POLYRATE-version 7.9 and MOPAC-version 5.07mn.

Version 7.9.1/P7.9.1-M5.07 (April 1998)

1. This version is based on POLYRATE-version 7.9.1, which is a bug-fix version of POLYRATE-version 7.9. The interface and MOPAC parts of the code have not been changed.

Version 8.0/P8.0-M5.07 (September 1998)

- 1. This version is based on POLYRATE-version 8.0 and MOPAC-version 5.07mn.
- 2. A new testrun, testr19, is add to serve as an example of the VTST-ISPE and VRPE options.
- 3. A new compiling script moratecl.604 is added for the IBM PowerPC 604 machines.

# 14.4 INPUT FILE COMPATIBILITY

Because of the introduction of keyword input format in POLYRATE-version 6.0 and its refinement in version 6.5, all restart files and input files (except those linked to FORTRAN units fu71-fu75) created before version 6.5 are not upgrade-compatible. Also, beginning with version 7.2, the keyword EZUNIT is required if the energy is read in kcal/mol. Beginning with version 7.4, the INITGEO and NOSUPERMOL keywords are required. Please refer to the POLYRATE manual for a description changes in POLYRATE, which also affect MORATE.

## 14.5 MORATE MANUAL REVISION HISTORY

manual for version	2.0	Aug.	10,	1990
manual for version	4.2	May	25,	1992
manual for version	4.4	Sept.	16,	1992
manual for version	4.5	Nov.	16,	1992
manual for version	5.0	Jun.	16,	1993
Revised manual for	version 5.0	Nov.	30,	1993
manual for version	5.1	Jan.	13,	1994
manual for version	6.2	Aug.	29,	1994
manual for version	6.2.1	Nov.	30,	1994
manual for version	6.5	Mar.	23,	1995
manual for version	7.2	Mar.	28,	1997
manual for version	7.3	Jun.	20,	1997
manual for version	7.4	Aug.	28,	1997
manual for version	7.5	Sept.	25,	1997
manual for version	7.8	Dec.	9,	1997
manual for version	7.8.1	Dec.	4,	1998
manual for version	7.9	Mar.	27,	1998
manual for version	7.9.1	Apr.	15,	1998
manual for version	8.0	Sep.	4,	1998

Note: The MORATE distribution (see Section 3.A) through version 6.5 included the POLYRATE, MOPAC5.0, and MOPAC5.05mm manuals as well as a MORATE manual. Beginning with version 7.2 of MORATE, we assume that the POLYRATE and MOPAC5.07mm manuals were obtained with with the POLYRATE and MOPAC5.07mm packages, respectively.

All MORATE manuals are in the form of an ASCII documentation file.

## 15. MORATE ACKNOWLEDGMENTS

MORATE is a modular interface of POLYRATE with MOPAC. The authors of the current version of MORATE acknowledge the following coauthors of earlier versions of MORATE: Bruce C. Garrett, Angels Gonzalez-Lafont, Gene C. Hancock, Alan D. Isaacson, Tomi Joseph, Da-hong Lu, Vasilios Melissas, Sacchida N. Rai, Rozeanne Steckler, James J. P. Stewart, and Thanh Truong.

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