prepared for publication in *Computer Physics Communications*
original manuscript October 8, 1997
revised November 4, 1997

ABCRATE: A Program for the Calculation of Atom-Diatom Reaction Rates

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Abstract. ABCRATE is a computer program for the calculation of atom-diatom chemical reaction rates for systems with collinear-dominated dynamics. The dynamical methods used are conventional or generalized transition state theory (GTST) and multidimensional semiclassical approximations for tunneling and nonclassical reflection. The GTST methods included in this version of the program are canonical and improved canonical variational transition state theory (VTST) and the canonical unified statistical (CUS) method. Rate constants may be calculated for canonical ensembles or for specific vibrational states of selected modes with translational, rotational, and other vibrational modes treated thermally. The potential energy surface required by the program may be a global or semiglobal analytic function. The reaction path is calculated as the path of steepest descent in mass-scaled coordinates from a collinear saddle point, and vibrations transverse to the reaction path are treated by curvilinear internal coordinates. The vibrational modes are quantized, and anharmonicity may be included by various options, including the WKB approximation for bond stretches and the centrifugal oscillator approximation through quartic terms for the curvilinear bend coordinate. Tunneling probabilities are calculated by a variety of semiclassical methods, in particular zero-curvature tunneling (ZCT), small-curvature tunneling (SCT), large-curvature tunneling (LCT), least-action tunneling (LAT), and the microcanonical optimized multidimensional tunneling (μOMT) methods.

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Keywords: chemical reaction rates — kinetics — tunneling — variational transition state theory

Program Summary

Title of program: ABCRATE

version: 10.0

Catalogue number: to be assigned by CPC

Program obtainable from: The program may be obtained with a non-profit license from the CPC Program Library, Queen's University of Belfast, N. Ireland (see order form in this issue.) It is also available at http://comp.chem.umn.edu/abcrate.

Licensing arrangements: Persons requesting the program for academic or non-profit use must sign the standard CPC non-profit use license (see license agreement printed in the first issue of every volume); or the license form is available at the URL mentioned above. Persons interested in a for-profit (commercial) license may also use the license form available at the URL mentioned above.

Computers on which this program has been tested: Cray Y-MP C90, Silicon Graphics IRIS Power Challenge L, and IBM RS/6000-550.

Operating systems under which the program has been tested: UNICOS 8.0.3 (Cray Y-MP C90), IRIX 6.2 (IRIS), and AIX 4.1 (IBM).

Word size: 64 bits

Program language used: ANSI-standard FORTRAN 77 with the INCLUDE extension

Disk storage for distributed program (in bytes):

FORTRAN files	680 909
other files	25 066 666
total	25 747 575

No. of bits in a single precision word (hardware): 64 on the Cray computers and 32 on the others.

Precision in which program executes: REAL*8 on all machines. (The code is written in double precision with generic FORTRAN function calls so it executes in REAL*8 mode on 32-bit workstations and on 64-bit workstations on which single precision is 32 bits. On Cray machines on which single precision in 64-bit words, the code should be compiled with double precision disabled so that it will execute in REAL*8 mode.)

Peripherals used: disk for input/output

No. of processors used: one

No. of lines in -

FORTRAN files:	18 066
ASCII manual:	1 892
C shell scripts	870
data and output for test runs:	305 457
total:	326 285

Keywords: chemical reaction rates, activation energy, stationary point analysis, reaction coordinate, anharmonicity, variational transition state theory, small-curvature tunneling, large-curvature tunneling, least-action ground-state tunneling.

Nature of the physical problem:

The program calculates bimolecular atom-diatom chemical reaction rates using global or semi-global analytical potential energy surfaces.

Method of solution:

Rate constants may be calculated by various versions of variational transition state theory or the unified statistical model, in either case with or without multidimensional semiclassical tunneling contributions. Rate constants may be calculated for canonical ensembles or for a special initial vibrational state with other modes thermalized. The semiclassical tunneling methods available in this version of the program are the minimum-energy-path semiclassical ground-state (MEPSAG) method, the centrifugal-dominant small-curvature semiclassical adiabatic ground-state (CD-SCSAG) method, the large curvature ground-state version-3 (LCG3) method, the least-action ground-state (LAG) method, and the microcanonical optimized multidimensional tunneling (μOMT) method. (The first four of these methods are usually abbreviated ZCT, SCT, LCT, and LAT, respectively.) The program can also be used to carry out stationary point analyses for transition states and conventional transition state theory rate constants. First the program optimizes the geometry of the reactant diatomic, the product diatomic, and the saddle point(s) (if any exist). The program is designed to handle zero to four saddle points. The reference path is found by following the path of steepest descent in a mass-scaled coordinate system from a collinear saddle point or from a pre-specified point in the asymptotic region (the latter option is for exoergic reactions with monotonically downhill reaction paths). Tunneling probabilities are calculated analytically by the Wigner method and semiclassically (six methods listed above) by numerical quadrature. The variational transition state of canonical variational theory and improved canonical variational theory is found by interpolation of data on a storage grid. Reverse reaction rates are determined by detailed balance.

Restrictions on the complexity of the problem:

This code is applicable only to atom-diatom reactions with a collinear reaction path. The program has PARAMETER control for the maximum number of save points at which the reaction-path information is saved; this parameter is set in the INCLUDE file abc.inc. Large-curvature tunneling is available only with the minimum energy path as the reference path, *i.e.*, version 3.

Unusual features of the program:

A restart option is available in which the program writes properties it has calculated to disk files. There are three different independent sets of information which can be written: the properties for the minimum energy path, the WKB eigenenergies, and the one and three-dimensional transmission probabilities for the large–curvature tunneling methods. Subsequent runs of the program can read in one or all of these files and proceed without recomputing the information that has been input. The program is distributed with a documentation file in portable, searchable ASCII text format.

Typical running time:

The running time for ABCRATE ranges from a fraction of a second to several hours depending on the input parameters selected by the user. Timings for all of the test suite runs on three different platforms are given in the ASCII manual.

LONG WRITE-UP

1. Introduction

ABCRATE is a computer program for the calculation of atom-diatom bimolecular gas-phase chemical reaction rates with collinear-dominated reaction paths. The reaction rates are determined using conventional [1-4] and variational transition state theory [3-11] with multidimensional semiclassical tunneling coefficients [5,7,10,12-18]. These methods provide a conceptual framework for the interpretation of chemical reaction rates for atom-diatom as well as polyatomic systems.

Variational transition state theory (VTST) is a reaction-path method. It is based on separating the motions of the system along a reaction path from those transverse to it. In the present computer program the reaction path must be collinear, and it may be either the minimum-energy path, when that is collinear, or the lowest-energy collinear reaction path. To emphasize this generality in certain parts of the discussion, we call this path the reference path. The present program involves uncoupled treatment of the vibrational and rotational modes. Anharmonicity has proved to be an important consideration in VTST calculations, and several methods have been developed for the inclusion of anharmonic effects [5,19-22]. Tunneling effects have also proven to be an important factor in the determination of accurate reaction rates, especially for systems in which the transferring atom is a light atom such as hydrogen, leading to the development of one-dimensional [2,5,12,23] as well as multidimensional [5,7,10,12-18,22] methods for the determination of semiclassical transmission coefficients.

The application of variational transition state theory with multidimensional semiclassical tunneling coefficients to atom-diatom reactions has been successful in tests against experimental results, with the success limited more by the accuracy of the potential energy surface than by the accuracy of the dynamics. This is well confirmed for atom-diatom systems by calculations that could be tested against accurate quantum mechanical dynamics calculations for one [8,9,11,13,21,24] and three dimensions [11,22,25-30] for the same potential energy surface for a wide range of systems with a variety of mass combinations. A review of these tests is available [31]. (ABCRATE can carry out calculations not only for the real 3-D case, but also for the reduced dimensionality 1-D world in which all three atoms are forced to be collinear throughout the reaction.) These checks have provided an opportunity to test the approximations in VTST as well as in the semiclassical tunneling methods, and the success of those tests have engendered confidence in both the VTST and the semiclassical tunneling methods.

2. Overview

2.1. Dynamical methods

Variational transition state theory and multidimensional semiclassical tunneling methods are discussed in detail elsewhere [5-11,15,17,32], and only a brief overview is presented in this article.

In conventional transition state theory the reaction rate constant for a bimolecular reaction is given by [1-4]

$$k^{\ddagger}(T) = \frac{k_{\mathrm{B}}T}{h} K^{\ddagger,0} \exp\left(-\frac{\Delta G^{\ddagger,0}(T)}{RT} \right) \tag{1}$$

where k_{B} is Boltzmann's constant, T is the temperature, h is Planck's constant, $K^{\ddagger,0}$ is the reciprocal of the standard state concentration, $\Delta G^{\ddagger,0}(T)$ is the standard-state molar free energy of activation at temperature T, and R is the gas constant.

Symmetry is handled internally by the program. Symmetry of the reactant and/or product molecules is included by setting the symmetry number of the diatomic rotational partition function equal to 1 for heteronuclear diatoms or 2 for homonuclear diatoms, and hence symmetry is automatically included in $\Delta G^{\ddagger,0}(T)$ and the generalized quantity $\Delta G^{\mathrm{GT},0}(T,s)$ that occurs below.

The formulation of the rate constant in eq. (1) is based on the assumption that the net reaction rate in the forward direction at equilibrium equals the equilibrium flux in the direction of the products through the transition state, where the transition state is a surface in phase space that divides reactants from products and passes through the saddle point [5,32]. This definition assumes that the dividing surface through the saddle point is the dynamical bottleneck for the forward reaction [8]. This definition can be generalized if the dividing surface is not forced to pass through the saddle point.

If the reaction coordinate s is defined as the distance along the minimum energy path (MEP) from the saddle point such that $s = -\infty$ for the reactants and $s = +\infty$ for the products, then for each s a generalized transition state can be defined that intersects the MEP at s and is perpendicular to the MEP. Generalized transition state theory reaction rates at each s and T are given as [5,8-10,33,34]

$$k^{\mathrm{GT}}(T,s) = \frac{k_{\mathrm{B}}T}{h} K^{\ddagger,0} \exp\left(-\frac{\Delta G^{\mathrm{GT},0}(T,s)}{RT} \right) \tag{2}$$

where $\Delta G^{\mathrm{GT},0}(T,s)$ is the standard-state generalized free energy of activation for temperature T and location s. Note that the abbreviation GT has been used as a shortened representation of GTST. In ABCRATE the minimum energy path is defined as the collinear path of steepest descent from a collinear saddle point in mass-scaled coordinates [12].

Two levels of variational transition state theory are available in this program: canonical variational theory (CVT) [5,35] and improved canonical variational theory (ICVT) [6,7]. The CVT rate constant is defined as [5,35]

$$k^{\mathrm{CVT}}(T) = \min_{s} k^{\mathrm{GT}}(T,s) \tag{3}$$

and the ICVT rate is defined similarly [6,7,10].

The GT reaction rates are quantized by treating the modes orthogonal to the MEP quantum mechanically and by including a multiplicative transmission coefficient. The transmission coefficient accounts for quantum mechanical effects on the reaction coordinate, i.e., it accounts for tunneling, and special care is taken [7] to insure that the inclusion of tunneling effects is consistent with the rest of the VTST calculation.

The transmission coefficients can be determined using several different methods including the low-order Wigner method [2,23]. In this version of the program there is one zero-curvature tunneling (ZCT) method and one small-curvature tunneling (SCT) method; these are the minimum-energy-path semiclassical (MEPSA) method [7] and the centrifugal-dominant small-curvature semiclassical adiabatic (CD-SCSA) method [17,18], respectively. It should be pointed out that the original small-curvature semiclassical adiabatic (SCSA) method [36] and the CD-SCSA method [17,18] are identical for an atom-diatom collision with a collinear MEP. ABCRATE–version 10.0 also includes the least action (LA) tunneling method [15] and the large curvature version-3 (LC3) tunneling method [15] which are applicable to large-curvature systems. The microcanonical optimized multidimensional tunneling (μOMT) method [37] is also available in this version of the program. When the tunneling approximations are combined with the ground-state approximation we include the letter G, as in MEPSAG, CD-SCSAG, LCG3, and LAG. We will often use the abbreviations ZCT, SCT, LCT, and LAT for the MEPSA, CD-SCSA, LC3, and LA methods, respectively.

In the SCT method, tunneling initiates from the point where further motion along the reference path becomes classically forbidden. In the LA method, tunneling may initiate from any point in the classically accessible portion of the MEP, and the optimum tunneling path for each possible initiation point is chosen variationally from a one-parameter sequence of potential tunneling paths, varying smoothly between the MEP and a straight line in mass-scaled coordinates. The LC3 method is identical to the LA method except that the straight-line path is chosen for all initiation points. Earlier large-curvature tunneling methods [14,38] also used straight-line paths, but the initiation of the tunneling path was more complicated. Since the additional complication does not result in increased accuracy, the LC3 method is preferred to these earlier methods (LC1 and LC2). Hence LC1 and LC2, which were included in earlier versions of ABCRATE, have been removed in version 10.0.

The tunneling probabilities are combined with the overbarrier contributions using the "ground-state transmission coefficient" [7,8] approximation. In our earlier papers this was explicitly indicated by adding a G to the tunneling method acronym, as in CD-SCSAG, LCG3, and LAG. In later papers we abbreviate the CD-SCSAG and LCG3 methods as SCT, LCT, and LAT, respectively, for simplicity.

The SCT and the LCT methods are both more accurate than either the Wigner method or the ZCT method. The relative accuracy of either the SCT or the LCT methods depends on the curvature of the MEP in the tunneling region [11]; however for systems with intermediate curvature the LCT methods provide a better estimate of the tunneling [29,31].

The LCT and the SCT methods depend on the vibrationally adiabatic ground-state potential curve, $V_{\mathrm{a}}^{\mathrm{G}}$, which is defined as

$$V_{\mathrm{a}}^{\mathrm{G}} = V_{\mathrm{MEP}}(s) + \varepsilon^{\mathrm{G}}(s) \tag{4}$$

where V_{MEP} is the Born-Oppenheimer potential energy, and ε^{G} is the sum of the zero-point energies of the modes orthogonal to the MEP. For a one-dimensional calculation there is one mode orthogonal to the MEP, a symmetric stretch, and for a three dimensional calculation there are three modes, one stretch (which is the symmetric stretch for $D_{\infty h}$ generalized transition states) and a doubly degenerate vibrational bend. The eigenvalues for the stretch are determined by the harmonic approximation, by the Morse I approximation [5], or by the WKB approximation [21]. For the harmonic and Morse I approximations the local potential at each grid save point along the minimum energy path is fit to a harmonic or Morse curve, respectively. For the WKB approximation the calculation is carried out using the true potential energy curve without a power series expansion. The eigenvalues for the vibrational bend can be determined in one of four ways: harmonically, semiclassically, by the perturbation-variation approximation [19], or by the centrifugal oscillator approximation [22,39]. In all four cases the local bend potential at each save grid point is fit to a harmonic-quartic curve.

2.2 Program structure

The work carried out by the program consists of four major steps: data input, reaction-coordinate and vibrationally adiabatic potential calculation, calculation of the transmission coefficients, and calculation of the generalized free-energy-of-activation curves and the reaction rates. The program design is such that it can be stopped after the completion of any of these steps.

The subprogram DATAIN reads all the data and initializes all the variables. The masses that are read in dictate the direction of the reaction. After the data has been read in the energy for the dissociation of the system into three atoms is computed, and the equilibrium geometries and the Morse parameters for the asymptotic diatomics are determined in the subprogram GEOM. The saddle point geometry is then located in SADDLE, and a normal mode analysis is performed. After the saddle point calculation partition functions for the three stationary points are computed, and Wigner tunneling and conventional transition state theory calculations are carried out.

Next the minimum energy path is found by following the negative of the mass-scaled gradient of the potential in a mass-scaled coordinate system. The mass-scaled coordinate system used is

$$x = R_{\mathrm{AB}} + \mu_{\mathrm{BC}} R_{\mathrm{BC}} \tag{5}$$

$$y = \left(\frac{\mu_{BC}}{\mu} \right)^{1/2} R_{BC} \tag{6}$$

where R_{AB} is the A to B distance, R_{BC} is the bond length of the reactant diatomic BC, μ_{BC} is the reduced mass for the BC diatomic, and μ is the reduced mass of relative translation of A with respect to BC. The MEP calculation is started at the saddle point along the normal coordinate for the unbound motion and is followed in the direction of reactants and products. If a well exists along the MEP, the reaction coordinate calculation is stopped at the bottom of the well, and the calculation is restarted at the closest asymptotic geometry and followed back to the well. If the calculation is successful, i.e., if the calculation returns to the bottom of the well, the two segments are joined into one continuous MEP. For systems with more than one saddle point a single continuous MEP is determined by sequentially starting at each saddle point and computing segments in both directions; the MEP is checked to ensure that the wells between the saddle points connect the adjacent saddle point. The program can determine a MEP containing up to four different saddle points. The driver for the MEP calculation is the subprogram RPATH.

The negative of the mass-scaled gradient is followed using a fixed step size DEL. At intervals DELSV along the MEP, the local potential orthogonal to the MEP is fit to a Morse potential using the Morse I approximation [5] for the stretching motion, and to a quartic-quadratic potential for the bending motion [20]. The values of the coordinates, the potential energy, the Morse and bending parameters, the mass-scaled gradient vector, the moment of inertia, and the curvature of the reaction coordinate are stored in arrays in common blocks. At the end of the reaction coordinate calculation the grid of stored information can be written to the file abc.1 which is linked to FORTRAN unit 1, and this information can be used for subsequent calculations for the same reaction without recalculating the reaction coordinate information.

After the reaction coordinate calculation the vibrationally adiabatic potential energies are calculated on the same storage grid used in the MEP calculation in the subprogram ADIAB. The maximum of the vibrationally adiabatic potential curve is determined by an iterative process. First a quadratic fit is carried out using the maximum on the storage grid and one point on either side of the maximum. New reaction coordinate information is determined for the maximum of the quadratic fit and for one point on either side of the new maximum by interpolating the distance along the MEP and the geometry along the MEP on the storage grid. These three new points are used to obtain a new quadratic fit and the procedure repeated up to a maximum of ten times or until the relative difference between the old and the new maxima is less than a tolerance value of $1.0 \times 10^{-6}\ E_{\mathrm{h}}$. The vibrationally adiabatic potential curve is determined by carrying out a cubic spline fit of the vibrationally adiabatic energies, including the new point generated for the location of the maximum. The spline fit is carried out in the subprogram SPL1D1.

The next step in the calculation is the determination of the transmission coefficients, all of which are computed semiclassically with parabolic uniformization in the subprogram KAPVA. In this version of the program the ZCT and the SCT methods are adiabatic methods which use the spline fit of the vibrationally adiabatic potential curve, and the LCT methods are nonadiabatic methods which use the vibrationally adiabatic potential within the adiabatic region and the Born-Oppenheimer potential within the non-adiabatic region. For all three types of tunneling methods, the ground-state transmission coefficient for the ICVT reaction rate is given by [7,10]

$$\kappa(T) = \frac{\int_{E^{\mathrm{RG}}}^{\infty} \mathrm{d}E e^{-\beta E} P^{\mathrm{G}}(E)}{\int_{V_{\mathrm{a}}^{\mathrm{AG}}}^{\infty} \mathrm{d}E e^{-\beta E}} \tag{7}$$

where $\beta = \dfrac{1}{k_{\mathrm{B}}T}$, $P^{\mathrm{G}}(E)$ is the semiclassical ground-state transmission probability, E^{RG} is the vibrationally adiabatic ground-state energy of the reactants, and $V_{\mathrm{a}}^{\mathrm{AG}}$ is the maximum of the vibrationally adiabatic ground-state potential curve, i.e.,

$$V_{\mathrm{a}}^{\mathrm{AG}} = \max_{s} V_{\mathrm{a}}^{\mathrm{G}}(s). \tag{8}$$

The integrals in eq. (7) are evaluated using repeated Kronrod quadrature [40] in NSEG segments with quadratures of size NQ and 2*NQ+1. The variables NSEG and NQ are input variables that the user is allowed to control.

For conventional transition state theory and canonical variational transition state theory (CVT), the determination of the tunneling probabilities is similar to the definition in eq. (7). The term $V_{\mathrm{a}}^{\mathrm{AG}}$ in eq. (7) would be replaced by

$$V_{\mathrm{a}}^{\ddagger,\mathrm{G}} = V_{\mathrm{a}}^{\mathrm{G}}(s = 0) \tag{9}$$

for conventional transition state theory, and by $V_{\mathrm{a}}^{\mathrm{G}}\left[s_{*}^{\mathrm{CVT}}(T)\right]$ for CVT, where s_{*}^{CVT} is the location of the CVT transition state at a given temperature *T*. After the transmission coefficients have been calculated the one- and three-dimensional LCT transmission probabilities are written to the files abc.11 and abc.12 which are linked to FORTRAN units 11 and 12, respectively; these probabilities can also be used in subsequent calculations for the same reaction.

The final portion of the calculation involves the determination of the reaction rates. The generalized free-energy-of-activation profile is calculated on the grid of stored reaction-coordinate information, which is also the grid of stored vibrationally adiabatic energies. The maximum of the generalized free-energy-of-activation curve for a given temperature is the CVT transition state; this maximum is determined by the same iterative procedure used to determine the maximum of the vibrationally adiabatic potential curve. After the CVT transition state is located, the ICVT transition state is located, the reaction rates are computed, and the reaction coordinate information for both transition states is summarized in the long output file. This procedure is repeated for each temperature. After the reaction rates are determined Arrhenius activation parameters are optionally calculated at pairs of temperatures specified in the input. Finally a summary of the transmission coefficients, the reaction rates, and the Arrhenius parameters is listed at the end of the long output file. The properties of the dynamical bottlenecks (variational transition states) and summaries of the reaction rates are written to the long output file and also respectively to files abc.21 and abc.22, which are linked to FORTRAN units 21 and 22.

3. Distribution

The distribution of version 10.0 of the ABCRATE program contains 212 files, consisting of 4 major parts—the program source code, the ASCII manual, C shell scripts for compiling, linking, running, and verifying the test suite, and all the files needed for the test runs. The files for the test runs consists of source code for the potential energy surfaces used in the test suite, input data files, and the short (abc.20, abc.21, and abc.22) and long output files for all 10 test runs. In general, the user supplies the source code for the potential energy surface in the form described in the ASCII manual.

ABCRATE–version 10.0 includes a test suite of 10 test runs designed to test most of the capabilities of the code. Extensive discussion of running and verifying the test suite as well as more detailed descriptions of the test suite runs and references to the potential energy surfaces used is given in the ASCII manual.

The ASCII manual provides additional information on the program structure, and options, as well as a detailed description of the input data file.

4. Test run input and output

An example of an input file and one of the short output files, abc.22, for one of the test suite runs (test run no. 1) is given at the end of this article. The format of the input file is explained in detail in the ASCII manual.

5. Comparison to other programs

ABCRATE may be compared to a previous version, VTST, and contrasted to other programs, POLYRATE, MORATE, and GAUSSRATE, for variational transition state calculations with semiclassical tunneling contributions.

The only previously distributed version of ABCRATE was version 5, which was called VTST [41]. This older version carried out calculations based on the methods of Refs. [7] and [36]. The present version has a large number of enhancements and additional capabilities, the most important of which are probably large-curvature tunneling [14–16], least-action tunneling [15], WKB anharmonicity in stretches [21], the centrifugal oscillator method for bending anharmonicity [22], and the microcanonical optimized multidimensional tunneling approximation [37].

We may also contrast ABCRATE to POLYRATE [42,43], MORATE [44,45], and GAUSSRATE [46]. Whereas ABCRATE is applicable only to gas-phase atom-diatom reactions with a collinear reaction path or at least a collinear reference path, those three programs may be applied to both unimolecular and bimolecular gas-phase reactions with an arbitrary number of atoms, and POLYRATE may also be applied to reactions at gas-solid interfaces. ABCRATE always uses curvilinear coordinates, whereas POLYRATE, MORATE, and GAUSSRATE have options for using either rectilinear or curvilinear coordinates. For the special case of bimolecular atom-diatom reactions, ABCRATE has two special capabilities that are not contained in any of the three polyatomic programs, namely least-action tunneling and centrifugal oscillator anharmonicity, both of which allow more accurate calculations than would be possible with the polyatomic codes.

POLYRATE, like ABCRATE, requires an analytic potential energy function with gradients. MORATE and GAUSSRATE, however, are direct dynamics [47] codes in which all energy and gradient information is generated as needed by electronic structure calculations. POLYRATE, MORATE, and GAUSSRATE all have capabilities for VTST-IC [48] and IVTST [49] calculations that are not supported by ABCRATE.

6. Concluding remarks

The ABCRATE program is designed for the determination of atom-diatom gas-phase reaction rates. It uses a global or semi-global representation of the Born-Oppenheimer potential energy surface of the system; this potential energy surface must be supplied by the user. The dynamics are represented by conventional and variational transition state theory with multidimensional semiclassical tunneling contributions.

7. Acknowledgment

This work was supported in part by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences under grant DE-FG02-86ER13579 (principal investigator: D. G. Truhlar) and contract number DE-AC06-76RL0 1830 with Battelle Memorial Institute, which operates the Pacific Northwest National Laboratory.

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TEST RUN INPUT

```
D + H2  (DMBE potential, test run dh2tr1)
WKB stretches, perturb.-var. bends, write out LAG probs. and WKB energies
         D    H    H
     3671.297           1837.153            1837.153
 4 3 2 1 4 3 6 4 0 0   0 0 0 0 0 1
    4   40    4   40    4   40    1   0.02      10    3  0.10E-07
    4   40    0    0
        1.875              1.4008
    1
        2.30               1.78
        0.00               0.0               0.0            0.00
       -3.0                2.0
        0.00010            0.0010            0.999999          0.000008
        0.00001            0.00001          -3.0               2.00
    3    5.0      20.     0    0        0.0               0.0        0  0  0
    8   50    0    0    0    0
   200.0   300.0   400.0   500.0   600.0  1000.0  1500.0  2400.0
 F     F
    2
    1    4    2    6
    1    1    1    1    1
    2
    0.0
    1
    0.0
    2
    0.0
    1
    0.0
    2
    0.0
    0
```

TEST RUN OUTPUT

```
Mon Oct  6 10:39:03 1997
    D + H2  (DMBE potential, test run dh2tr1)
WKB stretches, Pertubation variation bends, write out LAG and WKB

   TST methods:
   TST  - transition state theory
          (dividing surface at saddle point)
   CVT  - canonical variational transition state theory
   ICVT - improved canonical variational transition state theory
   CUS  - canonical unified statistical model
   AG   - adiabatic ground-state
          (dividing surface at maximum of ground-state adiabatic potential

   Tunneling methods:
   MEPSAG    - minimum-energy-path semiclassical adiabatic ground-state method
   CD-SCSAG  - small-curvature semiclassical adiabatic ground-state method
   LAG       - least-action ground-state method
   LCG3      - large-curvature ground-state method
   muOMT     - microcanonical optimized multidimensional tunneling method


       Forward rate constants for 1D reaction (units of cm/molecule-sec)

        T(K)      TST         TST         TST         TST         TST         TST
                              MEPSAG      CD-SCSAG    LAG         LCG3        muOMT
        200.000  1.3875E-02  2.1612E-02  9.1686E-02  1.1172E-01  6.5499E-02  9.5951E-02
        300.000  2.6276E+00  2.8203E+00  5.4171E+00  6.1908E+00  5.2418E+00  5.8275E+00
        400.000  3.7788E+01  3.7033E+01  5.3692E+01  6.0064E+01  5.5454E+01  5.8150E+01
        500.000  1.9261E+02  1.8327E+02  2.3284E+02  2.5729E+02  2.4530E+02  2.5204E+02
        600.000  5.8340E+02  5.4961E+02  6.4949E+02  7.1107E+02  6.8840E+02  7.0076E+02
       1000.000  6.0561E+03  5.7190E+03  6.0758E+03  6.4904E+03  6.4091E+03  6.4504E+03
       1500.000  2.2670E+04  2.1667E+04  2.2260E+04  2.3374E+04  2.3218E+04  2.3294E+04
       2400.000  7.1834E+04  6.9601E+04  7.0339E+04  7.2703E+04  7.2448E+04  7.2569E+04

        T(K)      CVT         CVT         CVT         CVT         CVT         CVT
                              MEPSAG      CD-SCSAG    LAG         LCG3        muOMT
        200.000  8.8938E-03  2.1612E-02  9.1685E-02  1.1172E-01  6.5498E-02  9.5951E-02
        300.000  1.9529E+00  2.8196E+00  5.4158E+00  6.1893E+00  5.2406E+00  5.8262E+00
        400.000  3.0198E+01  3.6965E+01  5.3593E+01  5.9953E+01  5.5351E+01  5.8043E+01
        500.000  1.6023E+02  1.8214E+02  2.3141E+02  2.5571E+02  2.4379E+02  2.5049E+02
        600.000  4.9624E+02  5.4219E+02  6.4072E+02  7.0147E+02  6.7910E+02  6.9130E+02
       1000.000  5.2019E+03  5.3576E+03  5.6919E+03  6.0802E+03  6.0041E+03  6.0428E+03
       1500.000  1.8627E+04  1.8707E+04  1.9218E+04  2.0180E+04  2.0045E+04  2.0111E+04
       2400.000  5.3881E+04  5.2913E+04  5.3474E+04  5.5271E+04  5.5077E+04  5.5169E+04

        T(K)      ICVT        ICVT        ICVT        ICVT        ICVT        ICVT
                              MEPSAG      CD-SCSAG    LAG         LCG3        muOMT
        200.000  8.8938E-03  2.1612E-02  9.1685E-02  1.1172E-01  6.5498E-02  9.5951E-02
        300.000  1.9529E+00  2.8196E+00  5.4158E+00  6.1893E+00  5.2405E+00  5.8261E+00
        400.000  3.0195E+01  3.6962E+01  5.3589E+01  5.9948E+01  5.5346E+01  5.8038E+01
        500.000  1.6013E+02  1.8204E+02  2.3128E+02  2.5556E+02  2.4365E+02  2.5034E+02
        600.000  4.9531E+02  5.4119E+02  6.3954E+02  7.0017E+02  6.7785E+02  6.9002E+02
       1000.000  5.1229E+03  5.2877E+03  5.6177E+03  6.0010E+03  5.9258E+03  5.9641E+03
       1500.000  1.8005E+04  1.8260E+04  1.8759E+04  1.9698E+04  1.9566E+04  1.9631E+04
       2400.000  5.1270E+04  5.1552E+04  5.2098E+04  5.3849E+04  5.3660E+04  5.3749E+04

        T(K)      CUS         CUS         CUS         CUS         CUS         CUS
                              MEPSAG      CD-SCSAG    LAG         LCG3        muOMT
        200.000  8.8938E-03  2.1612E-02  9.1685E-02  1.1172E-01  6.5498E-02  9.5951E-02
        300.000  1.9529E+00  2.8196E+00  5.4158E+00  6.1893E+00  5.2406E+00  5.8262E+00
        400.000  3.0198E+01  3.6965E+01  5.3593E+01  5.9953E+01  5.5351E+01  5.8043E+01
        500.000  1.6023E+02  1.8214E+02  2.3141E+02  2.5571E+02  2.4379E+02  2.5049E+02
```

600.000	4.9624E+02	5.4219E+02	6.4072E+02	7.0147E+02	6.7910E+02	6.9130E+02
1000.000	5.2019E+03	5.3576E+03	5.6919E+03	6.0802E+03	6.0041E+03	6.0428E+03
1500.000	1.8627E+04	1.8707E+04	1.9218E+04	2.0180E+04	2.0045E+04	2.0111E+04
2400.000	5.0019E+04	4.9120E+04	4.9641E+04	5.1309E+04	5.1129E+04	5.1214E+04

T(K)	AG	AG MEPSAG	AG CD-SCSAG	AG LAG	AG LCG3	AG muOMT
200.000	8.8938E-03	2.1612E-02	9.1685E-02	1.1172E-01	6.5498E-02	9.5951E-02
300.000	1.9529E+00	2.8196E+00	5.4158E+00	6.1893E+00	5.2406E+00	5.8262E+00
400.000	3.0198E+01	3.6965E+01	5.3593E+01	5.9953E+01	5.5351E+01	5.8043E+01
500.000	1.6023E+02	1.8214E+02	2.3141E+02	2.5571E+02	2.4379E+02	2.5049E+02
600.000	4.9627E+02	5.4224E+02	6.4077E+02	7.0153E+02	6.7916E+02	6.9136E+02
1000.000	5.2169E+03	5.3847E+03	5.7207E+03	6.1111E+03	6.0345E+03	6.0735E+03
1500.000	1.8959E+04	1.9228E+04	1.9753E+04	2.0742E+04	2.0604E+04	2.0671E+04
2400.000	5.7172E+04	5.7487E+04	5.8096E+04	6.0049E+04	5.9838E+04	5.9938E+04

Forward rate constants for 3D reaction (units of cc/molecule-sec)

T(K)	TST	TST MEPSAG	TST CD-SCSAG	TST LAG	TST LCG3	TST muOMT
200.000	5.3950E-20	1.6453E-19	1.7434E-18	2.1958E-18	1.1249E-18	1.7614E-18
300.000	6.1089E-17	8.6072E-17	2.6422E-16	2.7177E-16	2.2854E-16	2.7154E-16
400.000	2.0531E-15	2.3574E-15	4.5156E-15	4.5004E-15	4.2116E-15	4.7151E-15
500.000	1.7272E-14	1.8302E-14	2.7939E-14	2.7966E-14	2.7067E-14	2.9479E-14
600.000	7.3355E-14	7.4843E-14	1.0070E-13	1.0169E-13	9.9768E-14	1.0683E-13
1000.000	1.5885E-12	1.5560E-12	1.7344E-12	1.7822E-12	1.7732E-12	1.8400E-12
1500.000	9.4207E-12	9.1932E-12	9.6504E-12	9.9305E-12	9.9091E-12	1.0140E-11
2400.000	4.7616E-11	4.6662E-11	4.7557E-11	4.8695E-11	4.8649E-11	4.9312E-11

T(K)	CVT	CVT MEPSAG	CVT CD-SCSAG	CVT LAG	CVT LCG3	CVT muOMT
200.000	3.9455E-20	1.6907E-19	1.7915E-18	2.2564E-18	1.1559E-18	1.8100E-18
300.000	5.0060E-17	8.8368E-17	2.7127E-16	2.7902E-16	2.3464E-16	2.7879E-16
400.000	1.7791E-15	2.4154E-15	4.6267E-15	4.6111E-15	4.3152E-15	4.8311E-15
500.000	1.5440E-14	1.8681E-14	2.8518E-14	2.8546E-14	2.7628E-14	3.0090E-14
600.000	6.6757E-14	7.6008E-14	1.0227E-13	1.0327E-13	1.0132E-13	1.0849E-13
1000.000	1.4722E-12	1.5419E-12	1.7187E-12	1.7660E-12	1.7571E-12	1.8233E-12
1500.000	8.6226E-12	8.8061E-12	9.2440E-12	9.5124E-12	9.4919E-12	9.7129E-12
2400.000	4.2073E-11	4.2322E-11	4.3134E-11	4.4166E-11	4.4125E-11	4.4726E-11

T(K)	ICVT	ICVT MEPSAG	ICVT CD-SCSAG	ICVT LAG	ICVT LCG3	ICVT muOMT
200.000	3.9452E-20	1.6928E-19	1.7938E-18	2.2592E-18	1.1573E-18	1.8123E-18
300.000	5.0056E-17	8.8556E-17	2.7185E-16	2.7962E-16	2.3514E-16	2.7938E-16
400.000	1.7790E-15	2.4229E-15	4.6411E-15	4.6255E-15	4.3286E-15	4.8462E-15
500.000	1.5439E-14	1.8754E-14	2.8628E-14	2.8657E-14	2.7735E-14	3.0207E-14
600.000	6.6753E-14	7.6317E-14	1.0268E-13	1.0369E-13	1.0173E-13	1.0894E-13
1000.000	1.4722E-12	1.5440E-12	1.7211E-12	1.7685E-12	1.7595E-12	1.8259E-12
1500.000	8.6226E-12	8.8064E-12	9.2443E-12	9.5126E-12	9.4921E-12	9.7131E-12
2400.000	4.2073E-11	4.2421E-11	4.3235E-11	4.4269E-11	4.4228E-11	4.4830E-11

T(K)	CUS	CUS MEPSAG	CUS CD-SCSAG	CUS LAG	CUS LCG3	CUS muOMT
200.000	3.9455E-20	1.6907E-19	1.7915E-18	2.2564E-18	1.1559E-18	1.8100E-18
300.000	5.0060E-17	8.8368E-17	2.7127E-16	2.7902E-16	2.3464E-16	2.7879E-16
400.000	1.7790E-15	2.4152E-15	4.6265E-15	4.6109E-15	4.3150E-15	4.8309E-15
500.000	1.5439E-14	1.8680E-14	2.8515E-14	2.8544E-14	2.7625E-14	3.0088E-14
600.000	6.6749E-14	7.5999E-14	1.0225E-13	1.0326E-13	1.0131E-13	1.0848E-13
1000.000	1.4717E-12	1.5413E-12	1.7181E-12	1.7655E-12	1.7565E-12	1.8227E-12
1500.000	8.3889E-12	8.5674E-12	8.9935E-12	9.2545E-12	9.2346E-12	9.4496E-12
2400.000	3.8405E-11	3.8632E-11	3.9374E-11	4.0315E-11	4.0278E-11	4.0826E-11

T(K)	AG	AG MEPSAG	AG CD-SCSAG	AG LAG	AG LCG3	AG muOMT
200.000	3.9509E-20	1.6953E-19	1.7964E-18	2.2625E-18	1.1590E-18	1.8149E-18
300.000	5.0176E-17	8.8768E-17	2.7250E-16	2.8029E-16	2.3570E-16	2.8005E-16
400.000	1.7854E-15	2.4316E-15	4.6578E-15	4.6421E-15	4.3442E-15	4.8637E-15
500.000	1.5511E-14	1.8842E-14	2.8762E-14	2.8791E-14	2.7865E-14	3.0348E-14
600.000	6.7101E-14	7.6714E-14	1.0322E-13	1.0423E-13	1.0226E-13	1.0950E-13
1000.000	1.4757E-12	1.5477E-12	1.7252E-12	1.7727E-12	1.7637E-12	1.8302E-12
1500.000	8.6232E-12	8.8070E-12	9.2449E-12	9.5133E-12	9.4928E-12	9.7138E-12
2400.000	4.2421E-11	4.2772E-11	4.3592E-11	4.4635E-11	4.4593E-11	4.5201E-11