Computational Prediction of Kinetic Rate Constants

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Report developed under SBIR/STTR contract for Topic# AF05-T010. The purpose of these efforts were to develop seamless, easy to use, efficient code to calculate electronic wave functions and potential energy surfaces of molecules and predict kinetic rate constants for reactions a priori. Given that an already existing software package, called POLYRATE, contained most of the capabilities desired for this Phase I, early on it was proposed to software was proposed to achieve the required level of calculations by marking modifications to an interface for models to be input into POLYRATE.

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1 EXECUTIVE SUMMARY

Several computer codes, some of them available commercially and others in the public domain, currently exist which can predict the electronic structure of molecules of interest. Similarly, several codes exist which can predict the kinetics and/or dynamics of a system given the electronic structure of the molecules involved. Several interfaces between some of these codes currently exist, however, none are seamless. They do not predict the likely error based on the level of quantum theory, nor do they account for the importance of small wells in the reaction entrance or exit channels.

SARA, Inc. has teamed with the University of Minnesota (U of Minn.), which has developed a means to minimize this disconnect, with an innovative and robust design. Based on the POLYRATE modifications developed by the computational chemistry group at the U of Minn. led by Professor Donald G. Truhlar, the redesigned POLYRATE program allows users to accurately predict the behavior of a chemically reacting system.

SARA, Inc. and the Department of Chemistry and Supercomputing Institute of the University of Minnesota – Minneapolis are proud to present the results of the Phase 1 efforts on computational predictions of kinetic rate constants. The purpose of these efforts were to develop seamless, easy to use, efficient code to calculate electronic wave functions and potential energy surfaces of molecules and to predict kinetic rate constants for reactions a priori. From these modifications to POLYRATE, we have demonstrated the capability to calculate kinetic rate constants for chemical reactions from inputs obtained by electronic structure theory with seamless integration of electronic structure and kinetics calculations as described in this final technical report and the accompanying technical papers.

2 TECHNICAL OBJECTIVES

Work on the project started in August 2005. Meetings took place between personnel from SARA, Inc. (Drs. Edward Patton and Dmitry Altshuler) and personnel from the University of Minnesota (U of Minn) (Drs. Don Truhlar and Stephen Klippenstein) with the kickoff meeting taking place on September 8-9, 2005. At this meeting, also attended by several U of Minn post doctoral associates, directions for the project and roles of participants were further clarified and remaining issues pertaining to the intellectual property agreement were resolved. Specific goals were set:

- to incorporate new kinds of dividing surfaces for barrierless association reactions into POLYRATE
- to develop improved error estimates for the reliability of the calculations
- to improve the treatment of anharmonicity
- to demonstrate the capability for convenient, efficient, and reliable direct dynamics
- to make generally useful improvements in POLYRATE and the methods used with POLYRATE
- to make the code portable under Linux

It was determined that the project would benefit from the work done by Dr. Klippenstein who had been working with Professor Truhlar on a related project on POLYRATE. Because of this, some of the subtasks initially planned were deemed not necessary, with the previous results being leveraged into this effort. Specifically, the original intent of these efforts had been to enhance POLYRATE in order to meet two of the three technical Phase I objectives:

- to include error estimates
- to add handling of certain additional types of chemical reactions.

When the proposal was written originally, it appeared that additional mathematical analysis would be needed.

But based on the previous work already performed by Dr. Klippenstein, this turned out not be the case. In the original plan there were four fundamental subtasks required to be accomplished before POLYRATE would be ready for demonstration: (1) preliminary design, (2) handling of barrierless reactions and reactions with potential wells must be added, (3) error estimates were to be added as a result of mathematical analysis, and (4) new equations were to be implemented in POLYRATE. It was determined that the subtasks (2) and (3) could, in fact, be incorporated into subtask (4) which it was at a savings in time and resources.

The preliminary design of the software modifications came out of that same meeting held on September 8-9, 2005 at the University of Minnesota. In addition, a Master Equation solver was determined at that time as feasible to be included. These enhancements would enable POLYRATE to handle reactions, other than the simple barrier. It was also determined that the U of Minn. investigators already had good handle on errors that occur in such calculations. The main source of such errors is in the calculation of potential energy surfaces. Estimates for these errors would be incorporated into POLYRATE.

2.1 Approach

The original POLYRATE software uses some modern versions of transition state theory (TST), such as canonical variational theory (CVT), improved canonical variational theory (ICVT), and microcanonical variational theory (μVT). These theories are described in journal articles and in a chapter of the upcoming volume in the *Comprehensive Chemical Kinetics* series, but are not widely known by non-experts. Enhancements in POLYRATE, implemented within the Phase I, include solving the Master Equation and treatment of barrierless reactions.

Prediction of reaction rates in chemical systems when the concentrations of the reactants vary over time is a difficult and challenging problem. While codes for this prediction have been developed, they are exceedingly complex. Yet, they require expertise at a level where they cannot be used by designers and engineers working on chemical or combustion processes. In addition, these codes do not provide good estimates of error, so even if a designer or engineer could use them, they would not know how accurate their predictions were. SARA, teamed with the University of Minnesota (U of Minn.) has provided an innovative and robust solution to this problem based on the POLYRATE code developed by the computational chemistry group at the U of Minn. The solution presented here is an enhancement of the POLYRATE program as needed to meet the stated requirements.

The intent of the project was to develop a computational tool usable by a chemist or a chemical engineer who is not an expert in chemical kinetics or quantum chemistry. It was, however, reasonable to assume that the potential user of the product had a solid one-year undergraduate course in physical chemistry. The user should, therefore, be familiar with the basic concepts and terminology of quantum chemistry, statistical mechanics and chemical kinetics. It would still be helpful for the user to have had a more mathematically sophisticated physical chemistry course and/or a modern course in chemical kinetics (e.g. based on the textbook by Steinfeld, Francisco, and Hase[1]), but it should not be a requirement.

2.2 Statement of the Problem

To review, in order to accurately predict the behavior of a chemically reacting system, it is critical to know how the reaction rate varies with the concentration (or partial pressure for gas-phase reactions) of the reactants. This, in turn, requires knowledge of a parameter called the reaction rate coefficient, which itself depends on temperature. Mathematically, the reaction rate coefficient, k, may be approximated by the well known Arrhenius equation:

$$k = Ae^{-E/RT},$$

where A is referred to as a pre-exponential factor, E is the activation energy, R is the gas constant, and T is temperature. Therefore, in order to have an approximation to the rate constant over a limited temperature range, calculate the reaction rate coefficient, it is, in fact, necessary to calculate two constants: A and E, hereafter referred to as Arrhenius parameters. In order to calculate a rate constant over a broad temperature range, one needs three or more parameters.

However, in order to calculate a rate constant over a <u>broad</u> temperature range, one needs a more complex model with at least three parameters, or possibly more. The team members at the University of Minnesota worked to develop a complex input model to address these additional parameters. This work was largely based on the existing POLYRATE program originally developed by U. of Minn. Phase I work has focused on extending the applicability of POLYRATE to a wider type of chemical reactions and on implementing error estimates in the calculations. Preliminary designs for the POLYRATE software interface determined that some previously developed code could be incorporated directly in POLYRATE.

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[1] Steinfeld, J.I., Francisco, J.S., and Hase, W.L. *Chemical Kinetics and Dynamics,* 2nd ed., Prentice Hall, 1999.

The most successful method for calculating rate constants goes back to the work of H. Eyring and his co-workers[2] and is known as Transition State Theory (TST), which has become a workhorse of chemical kinetics. TST provides mathematical equations for calculating rate constants and hence Arrhenius parameters. It is based on the structure of the so-called transition state between the reactants and the products, which, in theory, can be predicted from the structure of the reactants. For simple molecules and for the simplest version of the theory, as used by Eyring, these calculations on a qualitative basis can be carried out analytically by hand.

However, more complex cases and the full modern theory (to be called generalized TST or GTST), which is much more accurate, require numerical calculations with a computer. Kinetic calculations must, essentially, accomplish two tasks: Predict the structure of the transition state or, more generally, the part of the potential energy surface needed for the dynamics calculations and (2) calculate the rate constant itself, or, if one prefers to state the results that way, calculate the Arrhenius parameters, from the GTST equations. Both subjects are active fields of research, but they have progressed to the point where useful computer codes exist to calculate electronic structure of molecules, and useful computer codes which calculate rate constants or Arrhenius parameters from the known electronic structure of the molecules involved in the reaction also exist. There are interfaces between these two types of codes, but none are seamless, and the codes are not as user friendly as one would like.

Another drawback in the existing computational codes is lack of error estimates. In order to select the best computational method, it is necessary to know the error it may introduce. Furthermore, existing computational methods work better for simple barrier reactions than for reactions with chemically significant potential wells. To summarize, the following requirements should be met in order to make such computational codes more useful for chemical engineers:

- It should be possible to enter the formulas for the reacting molecules and obtain reaction rates without having to know the electronic structure of the molecules involved. If several reactions can occur between these reactants, it should be possible to predict rates for all of them.
- Since several methods are available for kinetics calculations, it is necessary to estimate an error involved in using each of them.

This work focused, therefore, on improvements to the usefulness of one of the available computational kinetics programs, POLYRATE, developed by Professor Truhlar's group at the University of Minnesota.

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[2] Glasstone, S., Laidler, K.J., and Eyring, H. *Theory of Rate Processes*, New York: McGraw-Hill, 1941.

2.3 POLYRATE Program

The POLYRATE[3] program has proven to be very successful in calculation of the Arrhenius parameters for a large class of chemical reactions. POLYRATE excels for the so-called simple barrier reactions[4], for which along with conventional TST it uses several varieties of the Generalized Transition State Theory (GTST)[5], also developed by Truhlar and his co-workers: Canonical Variational Theory (CVT), Improved Canonical Variational Theory (ICVT), and Microcanonical Variational Theory (μVT). These are all forms of Variational Transition State Theory[6] (VTST). There is a considerable amount of literature on these methods. Therefore, they are not described in depth here.

All varieties of the TST postulate the existence of the transition state (sometimes also called the activated complex), which acts as a potential barrier between the reactants and products. Arrhenius parameters in POLYRATE are calculated by finding the minimum energy path (MEP) across this barrier. As the name implies, this postulate is certainly true for simple barrier reactions. By their very nature, the computational methods in POLYRATE rely on the electronic structure of the molecules involved. In fact, POLYRATE can accept as input an electronic structure file. Therefore, at least for simple barrier reactions, this program already fulfils the first of the stated Phase I objectives – to demonstrate the capability to calculate kinetic rate constants for chemical reactions from inputs obtained by electronic structure theory. However, input files in POLYRATE must be built manually, which requires a considerable amount of labor.

The Phase 1 work focused, on one hand, on improving POLYRATE for reactions other than those of the simple barrier type, and, on the other hand, on estimating errors that may be present in computational algorithms. Phase 2 work will focus on eliminating the manual building of input files simplifying the interface between electronic structure theory and dynamics by better integrating POLYRATE with electronic structure tools developed by Professor Truhlar's group.

2.4 Enhancements to POLYRATE

Not all chemical reactions are of simple-barrier type. A common occurrence is that one or more potential wells lie along the reaction path. Should the system fall into such a well, it may become stabilized instead of decomposing into the reaction products or back into the reactants. Furthermore, it is possible for a system in such a well to isomerize into a system in another well (perhaps more than once) before decomposing into reactants or

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[3] Description of POLYRATE, including the complete manual, can be found at http://comp.chem.umn.edu/polyrate/

[4] Fernandez-Ramos, A., Miller, J.A., Klippenstein, S.J., and Truhlar, D.G. "Bimolecular Reactions", in *Comprehensive Chemical Kinetics*, R.W. Carr and M.R. Zachariah, eds., to be published. Simple barrier reactions and computational algorithms for them are described in Section 2.4. Other types of reactions are treated in Section 2.5.

[5] Truhlar, D.G., Isaacson, A.D., and Garrett, B.C. "Generalized Transition State Theory" in *The Theory of Chemical Reaction Dynamics*, M. Baer, ed., Boca Raton: CRC Press., 1985, Vol.4, pp.65-137.

[6] Truhlar, D.G. and Garrett, B.C. "Variational Transition State Theory" *Ann. Rev. Phys. Chem.,* 1984, Vol.35, pp.159-189.

products. It can also decompose into several sets or reaction products. There is also a possibility that a potential energy barrier, postulated in TST, is, in fact, absent. Barrierless reactions with multiple wells are a key class of reactions in practical applications.

2.4.1 Barrierless Reactions

VTST is applicable even to barrierless reactions[4]. However, the rigid-rotor harmonic-oscillator treatment of molecules turns out to be very inaccurate for transition states of such reactions. Therefore, it is necessary to introduce the treatment of anharmonicity into the calculations. This requires major changes including new coordinate systems to define the dividing surfaces.

At the same time, the absence of a barrier allows for some simplifications. One of them is that quantum tunneling effects are not very significant. Other applicable simplifications are described in depth in the above-cited reference[4]. Work included implementation of these calculations in POLYRATE as well an estimation of possible errors.

2.4.2 The Master Equation

Chemical reactions involving multiple wells or multiple sets of reaction products are studied using the statistical model governed by the master equation. In its most primitive form the master equation is written as

$$\frac{dn_i}{dt} = \sum_j \left[p_{ij} n_j(t) - p_{ji} n_i(t) \right],$$

where $n_i(t)$ is the population of the state i at the time t, and p_{ij} is the probability of transition from state j to state i. Essentially, the master equation describes a stochastic Markov process as long as the coefficients p_{ij} do not depend explicitly on time or the past history of the populations. This assumption is satisfied for all problems of interest. Furthermore, it is often adequate to assume that these coefficients do not depend on $n_i(t)$, which makes the equation linear.

Some alternative approaches to solving the Master Equation were pursued as part of this project. The importance of Markov processes in other areas of engineering and operations research led to the development of several algorithmic approaches for their analysis[7]. While most of these approaches dealt mainly with queuing theory and decision processes, the underlying mathematical methods may be applicable to any continuous-time Markov processes.

In addition, some alternative approaches to solving the master equation were be pursued as part of this project. The importance of Markov processes in other areas of engineering and operations research led to the development of several algorithmic approaches for

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[7] See, for example, Ross, S.M. *Applied Probability Models with Optimization Applications.* New York: Dover, 1992; Neuts, M.F. *Matrix-Geometric Solutions in Stochastic Models: An Algorithmic Approach.* New York: Dover, 1994; Tijms, H.C. *Stochastic Models: An Algorithmic Approach.* Chichester: John Wiley & Sons, 1994.

their analysis[8]. While most of these approaches deal mainly with queuing theory and decision processes, the underlying mathematical methods may be applicable to any continuous-time Markov processes.

2.4.3 Graphical User Interface (GUI)

Not all chemical reactions are of simple-barrier type. A common occurrence is that one or more potential wells lie along the reaction path. Should the system fall into such a well, it may become stabilized instead of decomposing into the reaction products or back into the reactants. Furthermore, it is possible for a system in such a well to isomerize into a system in another well (perhaps more than once) before decomposing into reactants or products. It can also decompose into several sets or reaction products. As discussed above, there is also a possibility that a potential energy barrier, postulated in TST, is, in fact, absent. Barrierless reactions with multiple wells are a key class of reactions in practical applications.

To access these newer levels of complexity being built into POLYRATE, a sequence of GUI screens were designed. Each screen was designed to contain necessary menu options with the available new choices. Chemical species (both reactants and products) could be entered by drawing their structures with a mouse. For instance, if the user decides to calculate potential energy from scratch, the calculation could be accomplished by a seamless interface with one of the electronic structure packages developed by the University of Minnesota, e.g., GAMESSPLUSRATE, which, in turn, calls GAMESSPLUS, another package developed by the University of Minnesota.

It is of importance to note that no specialized, expert-level knowledge of PES is needed to provide input for this section. Progress was also made on making POLYRATE portable, to run under LINUX, specifically, under g77 compiler, the standard compiler for LINUX platforms. Based on analysis and assessment of electronic structure tools also developed by the same group at the University of Minnesota, the final deliverable of the Phase I will be a system-level specification of the new integrated tool. Phase II work will proceed to actually design, test and implement the tool from this specification.

At the same time, it was decided that it would be unreasonable not to give the user an option to select the computational approach. In fact, the user may want to try more than one such approach in order to compare the results. Furthermore, while POLYRATE gives the user options for various treatments of anharmonicity and tunneling, it was decided that it was unreasonable to take these options away for the sake of simplifying the usability of the product. Therefore, it seemed that the best option was to allow the user to select a computational approach from the available choices, but to include, with the software, a comprehensive description of these methods. Such a description should probably take the form of an advanced textbook, rather than just a software reference

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[8] See, for example, Ross, S.M. *Applied Probability Models with Optimization Applications*. New York: Dover, 1992; Neuts, M.F. *Matrix-Geometric Solutions in Stochastic Models: An Algorithmic Approach.* New York: Dover, 1994; Tijms, H.C. *Stochastic Models: An Algorithmic Approach.* Chichester: John Wiley & Sons, 1994.

manual and would be aimed, as stated earlier, at a reader with a solid undergraduate coursework in physical chemistry.

Presently, in order to use POLYRATE, the user must manually build an input file. In the final Phase 2 form, this will be replaced by a sequence of screens. Each screen will contain menu options with available choices. Chemical species (both reactants and products) will be entered by drawing their structures with a mouse.

3 RESULTS

The following subsections describe how the POLYRATE input files will be built, based on this Phase 1 software design. The modifications to the algorithms that were developed for this effort and the references to the papers under which these results are given in detail. Electronic copies of all papers being generated and citing these results will be included on CD-ROM and furnished to the Government. To seamlessly access these modifications as part of the entire POLYRATE program, the subsequent sections of this report detail the modified GUI designed to access both existing and new modes of the software. These sections are written from the internal point of view, i.e., they are organized around the sections and keywords of the existing POLYRATE main input file.

3.1 Bimolecular reactions

Initial modifications to the algorithms dealt with the theoretical and computational modeling of bimolecular reactions, especially with generally applicable methods for kinetics (i.e., overall rates as opposed to detailed dynamics). These included a basic theoretical framework that could be used for gas-phase thermal reactions, gas-phase microcanonical and state-selected reactions, and condensed-phase chemical reactions.

The treatment of gas-phase thermal reactions included separate discussions of simple direct reactions over a barrier, which usually have tight transition states and reactions proceeding over a chemical potential well, which now can have a number of additional complications, such as barrierless addition potentials (which generally have loose, flexible transition states), competitive reaction pathways, isomerizations between multiple wells, and pressure-dependent energy transfer processes.

With a heavy emphasis on thermal reactions using (generalized) transition state theory (TST) including multidimensional tunneling, we showed that this provides the best available method to calculate thermal rate constants for all but the very simplest systems. Work on state-selective reactions and product state distributions included an introduction to the theory of electronically nonadiabatic reactions and coupled potential energy surfaces, as required for modeling photochemical and chemiluminescent reactions. For bimolecular reactions in liquid solution, we considered diffusion control and equilibrium and nonequilibrium solvation. From these results, there has been great progress in our ability to model the kinetics of bimolecular reactions. This derives from:

- improved methods for generating and using reactive potential energy surfaces, especially implicit potential energy surfaces generated by direct dynamics
- improved dynamical algorithms, including practical methods for finding variational transition states, well-validated multidimensional methods for including tunneling, and master equation methods for treating nonequilibrium distributions, especially in multi-well, multi-arrangement reactions
- efficient methods for interfacing both of the above.

We anticipate continued improvements in the theoretical development for extending POLYRATE to further barrierless reactions and reactions with potential wells[9].

3.2 Transition states with wide-amplitude motion

Practical approximation schemes for calculating partition functions of torsional modes were tested against accurate quantum mechanical results for H_2O_2 and six isotopically substituted hydrogen peroxides. The schemes were classified on the basis of the type and amount of information that is required. First, approximate one-dimensional hindered-rotator partition functions were benchmarked against exact one-dimensional torsion results obtained by eigenvalue summation. The approximate one-dimensional methods tested in this stage included schemes that only require the equilibrium geometries and frequencies, schemes that also required the barrier heights of internal rotation, and schemes that required the whole one-dimensional torsional potential. Then, three classes of approximate full-dimensional vibrational-rotational partition functions were calculated and were compared with the accurate full-dimensional path integral partition functions. These three classes were:

- separable approximations combining harmonic oscillator-rigid rotator models with the one-dimensional torsion schemes
- almost-separable approximations in which the nonseparable zero-point energy was used to correct the separable approximations
- improved nonseparable Pitzer–Gwinn-type methods in which approaches of type 1 were used as reference methods in the Pitzer–Gwinn approach.

The effectiveness of these methods for the calculation of isotope effects was studied. Based on the results of these studies, the best schemes of each type were recommended in Reference 9 for further use on systems where a corresponding amount of information is available.

Neither the heights nor spacings of the torsion barriers are equal for the torsional motion in H_2O_2 so the system is an excellent case to use in testing methods intended for general problems. H_2O_2 is also the only system with a torsion of any kind for which accurate, full-dimensional quantal partition functions have been published for use as benchmarks.

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[9] "Modeling the Kinetics of Bimolecular Reactions," A. Fernández-Ramos, J. A. Miller, S. J. Klippenstein, and D. G. Truhlar, Chemical Reviews 106, 4518-4584 (2006).

Twenty-two methods for calculating partition functions of one-dimensional torsional potentials were examined. If the potential can be easily represented in a low-order Fourier series, the Hamiltonian takes the form of a banded matrix with analytically determinable matrix elements; for many applications such systems can often be affordably diagonalized and partition functions obtained via direct eigenvalue summation.

When this approach is not feasible, but one can still afford to perform a numerical quadrature over the torsion coordinate, the Torsional Displaced-Points Path Integral method- with Harmonic Sampling (TDPPI-HS) is the method of choice. If the potential is only known at the locations of the barriers and minima, then the segmented reference Pitzer–Gwinn scheme or the Segmented Reference potential version of the TDPPI-HS (SR-TDPPI-HS), (which requires accurate integration involving only the segmented reference potential), are the most appropriate methods from among those considered here. For systems where only the geometries and frequencies are known, the CT-Cω method is best option. We also point out that the usual manner of applying the harmonic approximation would be in error by approximately a factor of 2, but once one recognizes the issue, this error is easily corrected without requiring additional data.

Zero-point energy (ZPE) anharmonicity has a large effect on the accuracy of approximate partition function estimates. If the accurate ZPE is taken into account, separable approximation partition functions using the most accurate torsion treatment and harmonic treatments for the remaining degrees of freedom agree with accurate QM partition functions to within a mean accuracy of 9%. If no ZPE anharmonicity correction is used, the mean accuracy of the separable treatment drops to 23%. We also presented a simple modification of the multidimensional Pitzer–Gwinn approximation, denoted the improved-reference Pitzer–Gwinn (IRPG) approximation, that includes an accurate treatment of a 1D torsional model instead of a harmonic treatment in the quantum correction to the full-dimensional classical phase-space integral. When an accurate ZPE correction is also employed, the IRPG method provides substantial improvements compared with the standard Pitzer–Gwinn approximation with the worst errors for H_2O_2 being only 1%[10].

3.3 Direct dynamic calculations

Further modifications included an efficient method for interfacing POLYRATE with direct dynamics calculations, which is an important element in making the package easier to use by nonspecialists. Multiconfiguration molecular mechanics (MCMM) is a general algorithm for constructing potential energy surfaces for reactive systems%[11].

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[10] "Statistical Thermodynamics of Bond Torsional Modes. Tests of Separable, and Almost-Separable, and Pitzer-Gwinn Approximations," B. A. Ellingson,, V. A. Lynch, B. A. Ellingson, S. L. Mielke, and D. G. Truhlar, Journal of Chemical Physics 125, 84305/1-17 (2006).

[11] Kim, Y.; Corchado, J. C.; Villa, J.; Xing, J. and Truhlar, D. G. J. Chem. Phys. 2000, 112, 2718).

Our results show how the performance of the MCMM method can be improved by adopting improved molecular mechanics parameters. We carried out calculations of reaction rate constants using variational transition state theory with optimized multidimensional tunneling on the MCMM potential energy surfaces for three hydrogen transfer reactions, and we compared the results to direct dynamics. We found that the MCMM method with as little as one electronic structure Hessian can describe the dynamically important regions of the ground-electronic state potential energy surface, including the corner-cutting-tunneling region of the reaction swath, with practical accuracy[12].

3.4 Error Estimates

In conjunction with the above referenced results, we also added mathematically based error estimates. We used three small sets of barrier heights for heavy-atom transfer, nucleophilic substitution, and unimolecular and association reactions as benchmarks for comparing and developing theoretical methods. The data sets were chosen to be statistically representative subsets of the NHTBH38/04 database. Each data set consists of 6 barrier heights; we called these small benchmark suites HATBH6, NSBH6, and UABH6. Benchmark values were tabulated for 204 combinations of theory level and basis set. The theory levels studied includes single-level wave function theory like Hartree-Fork, Miller-Plesset perturbation theory, quadratic configuration interaction, and coupled cluster theory; they also included multicoefficient correlation methods, local and hybrid density functional theory, and semiempirical molecular orbital methods. The three new representative data sets were combined with a previous representative data set for hydrogen-transfer reactions to form a new compact but diverse and representative data set called DBH24.

Comparison of a large number of methods for their performance on DBH24 leads us to recommend the following methods for barrier height calculations, in order of decreasing cost: G3SX, BMC-CCSD, PWB6K, BB1K, M06-L, MPW1K, HF/MIDI!, and PM3. The three small but representative data sets, HATBH6, NSBH6, and UABH6, were identified for the barrier heights of heavy-atom transfer, nucleophilic substitution, and unimolecular and association reactions, respectively. They were representative of the full data set within 12% (HAT), 9% (NS), and 11% (UA), respectively. We combined these data sets with a previous small representative data set for hydrogen-transfer reactions to create a diverse representative data set of zero-point-exclusive barrier heights called DBH24. Assessment of methods with 16 DBH24 showed that DFT and multilevel methods have much better performance-to-cost ratios than single-level WFT methods. The best N6 method was BMC-CCSD, and its cost was an order of magnitude smaller than the best N7 methods, although it is almost as accurate. The two best N4 methods, PWB6K and BB1K, outperformed the best N5 method MC3BB. The best local DFT method was M06-L.

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[12] "Optimizing the Performance of the Multiconfiguration Molecular Mechanics Method," O. Tishchenko and D. G. Truhlar, Journal of Physical Chemistry A, in press. (Proofs returned to ACS Publications on Oct. 31, 2006).

The MG3S basis set gave the best performance for DFT methods among the tested basis sets[13].

4 Modified POLYRATE Program: Test software

This section details the final version of the modified POLYRATE software that was coded to implement the improvements described above. A GUI was designed based upon the user's response to input to the questions on the *GENERAL INFORMATION* screen unless stated otherwise. Additionally, this screen will also prompt the user to enter the number of the reactants and products.

4.1.1 General Section

TITLE Keyword

This keyword is used to give the title for the computation run. It will be filled from the user free-form input.

ATOMS Keyword

This keyword will be filled in automatically from the information the user provides about the reactants (see GEOM keyword in 0).

CHECK Keyword

This keyword specifies if the input is checked for consistency prior to beginning the calculation. Current default is OFF, but in the new product this keyword will always be set to ON.

CLASSVIB Keyword

This keyword specifies if vibrational partition functions are calculated classically. It will be set to NOCLASSVIB (current default), indicating that all vibrations are treated as quantized.

DL Keyword

This keyword determines if dual-level interpolated corrections are done. It will always be set to *none.*

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[13] "Representative Benchmark Suites for Barrier Heights of Diverse Reaction Types and Assessment of Electronic Structure Methods for Thermochemical Kinetics," J. Zheng, Y. Zhao, and D. G. Truhlar, Journal of Chemical Theory and Computation, in press. (accepted Nov. 13, 2006)

ICOPT Keyword

This keyword sets options for interpolated optimized corrections. It will not be used in the new product.

GEOMUNIT Keyword

This keyword specifies the unit for the geometries. It will be filled from the user input in the pull-down menu.

IVTST0 and IVTST1 Keywords

TBD.

MDMOVIE Keyword

This keyword determines if the user wants to use the calculation results in an animation. The default is OFF, but the option to turn it on will be provided.

RESTART Keyword

This keyword directs the program to use already existing files and/or save some files for future use. All such options will be available in the new product.

SUPERMOL Keyword

This keyword indicates if the supermolecule mode is used. It is relevant only if the potential energy is calculated from scratch (see below) and will always be set to default, which is ON.

WRITE62, WRITEFU30, and WRITEFU31 Keywords

These keywords determine if certain files are written out for future use. All these options will be available in the new product.

4.1.2 Energetics Section

This section will be built from the user input to the questions in the *GENERAL INFORMATION* screen, just like the GENERAL section. It is used to specify the method for computing the potential energy surfaces (PES). The choices are to calculate from scratch using the so-called hooks or to use already existing file saved in previous calculations. These options will be available in the new product.

If the user decides to calculate potential energy from scratch, the calculation will be accomplished by a seamless interface with one of the electronic structure packages developed by the University of Minnesota, e.g., GAMESSPLUSRATE, which, in turn, calls GAMESSPLUS, another package developed by the University of Minnesota.

It is of importance to note that no specialized, expert-level knowledge of PES is needed to provide input for this section. Nevertheless, some knowledge of PES is needed for understanding of transition state theories. Therefore, treatment comparable to Chapter 7 of the reference 1 above will be given in the accompanying tutorial handbook.

4.1.3 Ancillary Section

This section contains information about the method for computing the Hessian. It is relevant only if the PES calculations are performed from scratch using the hooks. If it is, indeed, the case, this section will be built automatically using the current defaults.

4.1.4 Optimization Section

Like the Ancillary Section, this section is relevant only if the PES calculations are performed from scratch. In such cases, an *OPTIMIZATION* screen will appear with default values pre-filled. The user will have an option to override any of the default values. The parameters in this section have more to do with numerical mathematics than with chemical kinetics. In most cases user will most likely let the default values stand.

4.1.5 REACT, PROD, WELL, and START Sections

These sections describe the geometry and (optionally) other quantum-mechanical properties of the reactants and the products. They have the same set of keywords. REACT and PROD sections must be built for each reactant and product respectively, and they are named REACT1, REACT2, PROD1, and PROD2. A corresponding number of screens will be provided for the user to fill in the information.

Many keywords in these sections involve more advanced concepts from quantum chemistry than the user is assumed to be familiar with. Therefore, they will be given a detailed treatment in the book which will accompany the software.

STATUS Keyword

This keyword must be the first line of the section. It will always be set to zero (default), indicating that geometry, energy, frequencies, and eigenvectors (in START section) must be calculated.

GEOM Keyword

This keyword is used to describe the geometry of the reactants, products, and, if applicable, saddle point. It is required in all sections. Since STATUS keyword is always set to zero (see above) the geometries will represent a user's guess.

For each reactant, product and saddle point, the user will draw the structural formula with the mouse. The program will then guess the geometry assuming that the molecule is planar and using the covalent radii of the atoms involved. This information will also be used to build the ATOMS keyword in the GENERAL section.

SPECIES Keyword

This keyword is used to specify the linearity and the phase of each species as one of the following:

- Atomic
- Linear reactant or product
- Nonlinear reactant or product (default)
- Solid-state reactant or product
- Linear (generalized) transition state
- Nonlinear (generalized) transition state
- Solid-state (generalized) transition state

In the new product it will be determined automatically whether the species is reactant, product, or transition state, depending on which screen the user is responding to. Other choices will be presented in a form of the pull-down menu, depending on the entry for the GEOM keyword.

If the species is single-atom, the valid choices are atomic and solid-state. If the species is diatom, then the valid choices are linear and solid-state. For all types of species valid choices are linear, nonlinear and solid-state.

CONSTANT Keyword

This keyword is used to indicate coordinates held constant in optimization. It will not be used (current default) in the new product.

ELEC Keyword

This keyword is used to indicate the degeneracy of the electronic states. Current default (all states singly degenerate) will be used in the new product.

ENERGY Keyword

This keyword is used only if STATUS is set to 4 or 6. Since in the new product the status will always be set to zero, this keyword will not be used.

FREQ Keyword

This keyword indicates that normal mode analysis must be performed, which will always be done in the new product.

FREQUNIT Keyword

This keyword specifies user's choice to express frequency in cm^{-1} or in atomic units. This choice will be given to the user via a pull-down menu.

HESSIAN Keyword

This keyword is used only if STATUS=4. Since in the new product STATUS will always be set to zero, this keyword will not be used.

INITGEO Keyword

This keyword will always be set to default value of GEOM indicating that the initial geometries will be taken from the GEOM keyword (See above).

VIB Keyword

This keyword is used only if STATUS=6. Since in the new product STATUS will always be set to zero, this keyword will not be used.

LINAXIS Keyword

This keyword is used to show the orientation of a linear molecule. The default value, *z-axis*, will be used in the new product.

PROJECT Keyword

This keyword is used to indicate that projection operators are applied, which usually leads to better results. Current default, which is to apply projection operators, will be used in the new product.

DIATOM Keyword

This keyword is used to treat diatomic molecules with a Morse function. Current default is to treat diatomic molecules in the same way as all the others. Since there is a separate set of keywords for anharmonicity, it appears to be almost redundant. This keyword will not be used in the new product.

4.1.6 Harmonic/Anharmonicity Sections (Optional)

Several keywords are presently available in POLYRATE to indicate a choice to treat all modes as harmonic oscillators (HARMONIC keyword) or to use one of the following anharmonicity options:

- All modes Morse (MORSE keyword)
- All modes Morse/quadratic-quartic (MORSEQQ keyword)
- All vibrational modes are treated by the WKB method with quadratic-quartic fit (QQWKB keyword)
- All vibrational modes are treated by the semi-classical WKB method with quadratic-quartic fit to potential (QQSEMI keyword)

These options will be available to the user via a pull-down menu. However, the user's choice will be treated as a default, i.e. there will be an option to treat some of the modes differently.

For instance, ground state can be treated by the WKB method with true potential and some modes can be treated using the hindered-rotor approximation. A user can chose one or both these two options with buttons, in which case additional pop-up screens will appear prompting the user to fill in the required information.

The following paragraphs describe specific keywords used with the anharmonicity options.

ANTLR Keyword

This keyword specifies the criterion on the Morse anharmonicity parameter x_e and is used only with Morse/quadratic-quartic calculation. If the user chooses this option, an appropriate box will be activated with the pre-filled default value of 1×10^{-8}. The user may choose to override this default.

DEMIN Keyword

This keyword is needed if any of the Morse anharmonicity options is chosen. It is used to indicate the lowest dissociation energy. Same as for the ANTLR keyword, in such cases an appropriate box will be activated. POLYRATE uses the default value of 0.159 E_h, but it is not recommended. Therefore, a detailed explanation of this concept will be provided in the book that will accompany the new product.

MORMODEL Keyword

This keyword is used to give specifics if the user chooses Morse or Morse/quadratic-quartic model. There are essentially five choices that can be made. They will be provided to the user via a pull-down menu if the choice is made to use Morse or Morse/quadratic-quartic model. Detailed description of these choices will be provided in the accompanying tutorial handbook.

4.2 POLYRATE Tutorial Handbook

Dr. Truhlar of U of Minn detailed the above modifications and GUI into a POLYRATE tutorial handbook, explaining the algorithms in the current version of POLYRATE. This tutorial will be published in Reviews of Computational Chemistry[14]. A copy of this paper, along with all papers being generated using and citing the results of these efforts is being sent to the Government sponsor on CD-ROM. To make POLYRATE portable, it has been modified to run under LINUX, specifically, under g77 compiler, the standard compiler for LINUX platforms.

5 CONCLUSIONS

This Phase I project has developed modifications to POLYRATE capable of being used by a chemist or a chemical engineer who is not an expert in chemical kinetics or quantum chemistry. The new more complex software system design, if implemented, could have an even more broad-based user community. Through the use of interactive GUIs which access the newer higher order functionality of the software, the system could be accessible to any user familiar with the basic concepts and terminology of quantum chemistry, statistical mechanics and chemical kinetics.

For the Phase 2 of this effort, a seamless, integrated computer code can be developed to permit the accurate calculation of rate constants for chemical reactions based on electronic structure calculations. The code would be computationally efficient and would contain a user interface that permits easy use of the program by personnel who are not experts in computational chemistry. By creating an easy to use, rate predictive code that does not rely on information from existing databases, accurate estimates for unknown rates in kinetic models can be obtained. New materials can also be able to be more quickly designed and synthesized in bulk. The approach can be useful for commercial and research applications in materials, chemical vapor deposition (CVD), and combustion chemistry applications including the automotive, aerospace, and electronics industries.

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[14] "Variational Transition State Theory with Multidimensional Tunneling," A. Fernandez-Ramos, B. A. Ellingson, B. C. Garrett, and D. G. Truhlar, in Reviews in Computational Chemistry, Vol. 23, edited by K. B. Lipkowitz and T. R. Cundari (Wiley-VCH, Hoboken, NJ, 2007), pp. 125-232.)