

Final Technical Report: Variational Transition State Theory

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This is the final report on a project involving the development and applications of variational transition state theory. This project involved the development of variational transition state theory for gas-phase reactions, including optimized multidimensional tunneling contributions and the application of this theory to gas-phase reactions with a special emphasis on developing reaction rate theory in directions that are important for applications to combustion. The development of variational transition state theory with optimized multidimensional tunneling as a useful computational tool for combustion kinetics involved eight objectives:

- (i) developing and applying new methods of electronic structure calculations (both multi-coefficient wave function theory and density functional theory) for potential energy surfaces underlying dynamics calculations, which are an implicit surfaces defined by electronic structure model chemistries;
- (ii) developing methods to interface reaction-path, reaction-swath, and variable-reaction-coordinate dynamics calculations with electronic structure theory, either by straight direct dynamics or by an interpolation of electronic structure calculations;
- (iii) developing methods to treat vibrational anharmonicity -- both of high-frequency modes and torsions -- and vibration-rotation coupling;
- (iv) developing efficient methods to calculate accurate rate constants from the results of the electronic structure calculations, statistical mechanical treatments of vibrations, rotations, and multiple structures, and semiclassical treatments of tunneling;
- (v) developing multi-structural and multi-path variational transition state theory for extending transition state theory to complex molecules with multiple conformations;
- (vi) developing system-specific quantum Rice-Ramsperger-Kassel theory as a convenient way to treat pressure effects in unimolecular reactions and chemical activation;
- (vii) development and implementation of practical techniques, algorithms, and software for applying the theory to various classes of reactions and transition states, and especially developing and distributing the POLYRATE and GAUSSRATE programs; and
- (viii) applications to specific reactions, with special emphasis on combustion reactions and reactions that provide good test cases for methods needed to study combustion reactions.

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Software

We have developed several software packages for applying variational transition state theory with optimized multidimensional tunneling coefficients to chemical reactions. These packages include reaction-path, reaction-swath, and variable-reaction-coordinate dynamics; they are well documented and distributed with manuals, installation scripts, and test suites. The two most popular packages are POLYRATE and GAUSSRATE; all told, there are nine RATE programs. The latest relevant date for which statistics are available at the present time is the period ending March 17, 2015. As of that date, the total number of requests fulfilled for all RATE programs since we began keeping statistics in 1995 is 3040.

We also distribute the program (*MSTor*) for torsional anharmonicity. Beginning with version 2011, we have distributed *MSTor* through both the *Computer Physics Communications* web site (<http://www.cpc.cs.qub.ac.uk>) and own web site (t1.chem.umn.edu/truhlar/index.htm#software). Approximately 200 copies have been distributed.