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From electronic structure calculations to temperature and pressure dependent rate constants: a new computational environment.

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Highlights

- Automatic estimation of accurate gas phase rate constants.
- Electronic structure calculations.
- Master equation simulations.
- Multidimensional treatment of anharmonicities.

1. Introduction

The accuracy of electronic structure calculations has progressed dramatically in the last decades, thanks both to increased computational resources and to the development of more accurate theories. Relying on high quality electronic structure data, theoretical kinetics has also progressed greatly, with the accuracy in rate constant predictions for gas phase reactions now approaching that of experiments. In general, the estimation of rate constants involves two steps, the first consisting of a set of electronic structure calculations and the second in the estimation of the rate using a suitable kinetic code, which is often a master equation solver. Here we report the development of a new computational environment, named EStokTP, where electronic structure calculations and rate constant estimation are integrated [1].

2. Methods

EStokTP relies on calls to external codes to perform electronic structure and master equation calculations. Internal torsions can be treated as hindered rotors, in which case they are projected out from the Hessian so that no human manual identification and removal from the frequency list is necessary. Tunneling can be accounted for using both Eckart and multidimensional models, such as small curvature theory. Given a set of input files, the code performs sequentially the series of calculations listed in Figure 1.

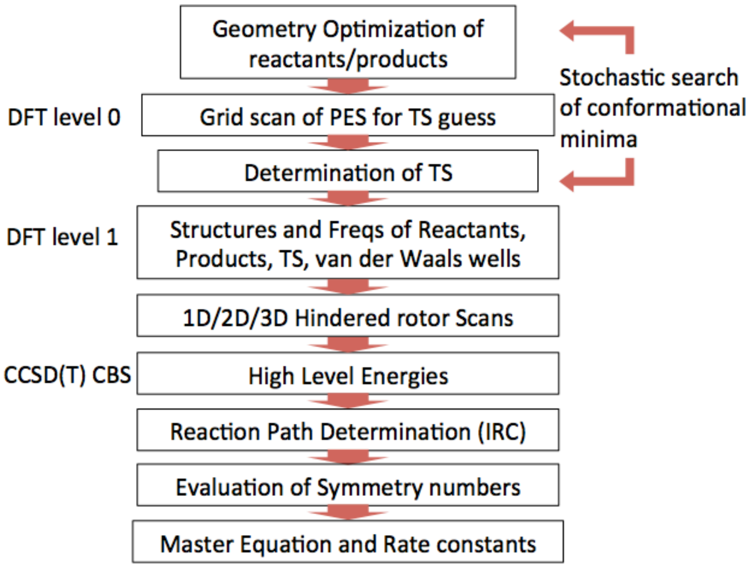

Figure 1. EStokTP program structure.

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The code has been developed along two principles. The first is that it must be able to reliably and automatically determine a large number of rate constants for classes of reactions of a target molecule (e.g. H-abstractions). This requirement is motivated by the perspective of the upcoming availability of exascale computational resources. The code is thus robust, with several automatic fallback options implemented so that human intervention can be limited. The second principle is that EStokTP must be capable of determining highly accurate rate constants, differing by no more than a factor of two from experiments.

3. Results and discussion

An example of results obtained using EStokTP to determine the total H-abstraction rate by OH from methyl acetate are shown in Figure 2a. A good agreement with experiments becomes possible only by performing a two-dimensional analysis of the hindered rotor potential on a 12x12 grid and projecting out the hindered rotor frequencies from the Hessian for each PES point. This rate constant estimation procedure is nowadays implemented only in EStokTP coupled with the MESS master equation solver [2]. A similar accuracy is attainable for addition reactions, as shown in Figure 2b for H radical addition to ethylene. At present, the following reaction classes are implemented: H-abstractions, additions, isomerizations, and beta-decompositions.

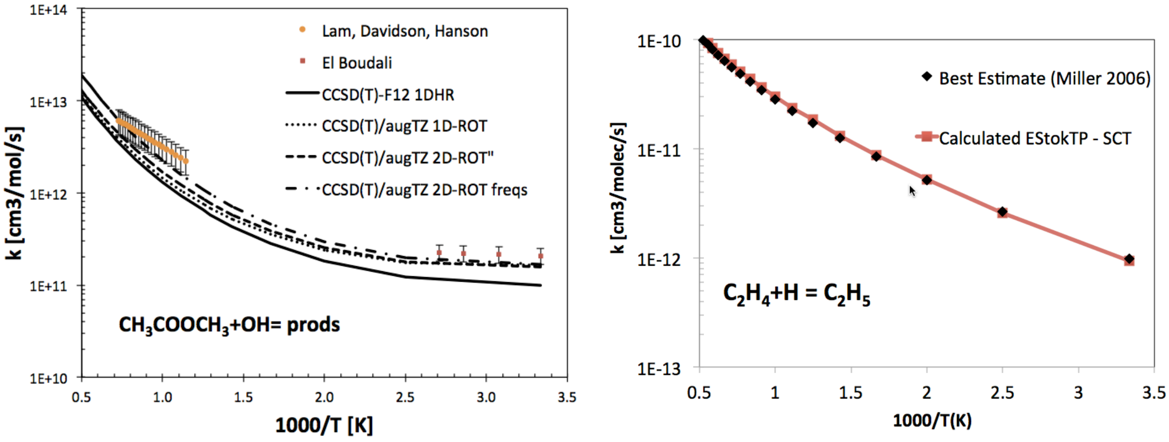

Figure 2. Calculated rate constant for a) the OH + CH_3COOCH_3 H-abstraction reaction and b) H addition to C_2H_4.

4. Conclusions

A new computational environment dedicated to automatic rate constant calculation has been developed. Despite being a software focused on the determination of single rate constants, it is possible to use EStokTP also to investigate complicated potential energy surfaces one elementary step at a time and then automatically combining the results into a single master equation input. At present, EStokTP is actively used in an exascale computing project sponsored by the Department of Energy, part of which is dedicated to the development of a computational environment that is capable of automatically calculating thermodynamic parameters and rate constants for thousands of species and reactions. As a first result, it has recently been shown that thermochemical parameters can be determined for 300 species at a variety of levels in about 1 day of real time [3]. The code is now available upon request from the authors.

References

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Keywords
Rate constant estimation; H-abstraction, addition; electronic structure calculation.