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Sum Over Histories Representation of Chemical Kinetics: An Interpretive and Predictive Method
for Modeling Chemical Kinetics Using Time-dependent Pathways

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Chemical kinetics can be viewed as an intricate network of inter-related chemical reactions that work cooperatively to convert reagent species into product species. The network is in general time dependent reflecting the non-steady state nature of the chemistry. When it comes to interpreting and predicting chemical kinetics, the history of chemical moieties can play vital roles. In order to study the histories of chemical substances using time-dependent chemical network, this thesis focuses on developing a Sum Over Histories Representation (SOHR for short) of chemical kinetics. The description of time-dependent chemistry of a reaction network is provided by chemical pathways defined at a molecular level. Using this methodology, the quantitative time evolution of the kinetics is described by enumerating the most important pathways followed by a chemical moiety such as a tagged atom. An explicit formula for the pathway probabilities is derived which takes the form of an integral over a time-ordered product. This expression has a simple and computationally efficient Monte Carlo representation which permits the method to be applied to a wide range of problems.

In SOHR, the history of the chemical moiety can be described by time-dependent pathways. Unlike the static flux methods for path analysis, SOHR includes the explicit time-dependence of pathway probabilities. Using SOHR, the sensitivity of an observable with respect to a kinetic parameter such as a rate coefficient is then analyzed in terms of how that parameter affects the chemical pathway probabilities. This thesis demonstrates that large sensitivities are often associated with rate limiting steps along important chemical pathways or by reactions that control the branching of reactive flux, though they vary with time.

In addition to interpreting chemical kinetics, this thesis studies the practical approach to model-

ing chemical kinetics without solving conventional mass-action ODEs. An iterative framework was introduced that allows the time-dependent pathway probabilities to be generated from a knowledge of elementary rate coefficients. To avoid the pitfall of integrating over the histories of long paths, we proposed a sector-by-sector strategy that shortens the candidate path without losing numerical accuracy. This method was successfully applied to the model Lotka-Volterra system and to a realistic H_2 combustion system.

This thesis culminates with a discussion of the interpretative and predictive applicability of SOHR.