

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

by

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Bai, Shirong (Ph.D., Chemical Physics)

Sum Over Histories Representation of Chemical Kinetics: A Interpretive and Predictive Method  
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Thesis directed by Prof. Rex T. Skodje

Chemical kinetics can be viewed as the cooperative propagation of chemical substances. This idea leads us to use a chemical network to study the cooperative behavior of chemical species. What's more, because of the changing nature of chemical systems, a time-dependent chemical network was adopted in the work of this thesis. 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  $\text{H}_2$  combustion system.

This thesis culminates with another application of SOHR that tackles a problem of time-dependent dimension reduction. Instead of clustering the closest related nodes in a chemical network, we grouped the chattering species based the sum over histories chattering probabilities.

## Dedication

To Zhangying Bai

## **Acknowledgements**

Here's where you acknowledge folks who helped. But keep it short, i.e., no more than one page, as required by the Grad School Specifications.

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## Chapter 1

### Introduction

Many problems of great practical importance are described by large interconnected networks of elementary chemical reactions.[86, 124, 147] In combustion chemistry, for example, numerical simulations combine chemical mechanisms with computational fluid dynamics to describe the consumption of fuels under engine operating conditions.[160, 162, 116, 15, 164] These mechanisms can grow quite large, e.g. n-heptane combustion can be modelled by a network of 7000 elementary gas phase reactions.[30] Likewise, the CAM-chem model of tropospheric chemistry can potentially consist of thousands of elementary chemical reactions.[90] Reactions on surfaces provide another class of problems modelled by large chemical mechanisms.[146, 58] The accurate performance of these models is necessary for important objectives such as engine design[145] and climate prediction.[89] The construction of accurate chemical mechanisms is typically an iterative endeavour where the model is repeatedly improved after comparison to experiment. This process requires insight into the workings of the chemical network. Unfortunately, the behaviour of complex kinetic mechanisms can become quite obscure making the process of validation and improvement difficult. Even the task of numerical simulation can become computationally prohibitive if the mechanism grows too large especially if spatial transport or multi-phase behaviour needs to be included.

We have recently developed a new approach to modeling the kinetics of chemical networks which we term the sum over histories representation, or SOHR for short.[83, 10, 4, 8] This method replaces the usual concentration based kinetics with a representation based on chemical pathways and can lead to new insight and increased computational capability when properly applied. A

chemical pathway is a sequence of elementary reactions where the product of one reaction becomes the reagent for the next reaction. Of course, the notion of the chemical pathway is quite familiar and is ubiquitous in all areas of chemistry. In kinetics, it has been often employed to provide mechanistic insight into complex networks of reactions.[66, 96, 38, 22] In chemical synthesis, for another example, a substrate molecule can be successively functionalized by a sequence of chemical steps. In atmospheric chemistry, a chlorine atom may be followed through a catalytic cycle that leads to the breakdown of ozone. We note that in these cases we are following a chemical moiety as it migrates from species to species due to reactions. In the SOHR, the idea of the chemical pathway becomes the basis of a quantitative representation of the chemical kinetics. The pathways are explicitly defined by following a tagged atom as it migrates through species space. We find that if all the relevant chemical pathways and their associated probabilities are known, then it is possible to directly compute the value of any kinetic observable. The method draws its motivation from Feynmans sum over histories approach to quantum mechanics.[42] As with Feynman path integrals, chemical pathway theory is often more computationally intensive than traditional approaches but it can provide new insight or numerical advantage for select problems.[110, 20, 18] The key mathematical relation in SOHR is an explicit expression for the probability of an arbitrary chemical path in terms of an integral of a time-ordered product. This high-dimensional integral can be evaluated using an efficient Monte Carlo (MC) integration scheme.

We have found it quite useful to visualise the chemical pathways using the methods of graph theory. On a chemical graph, the species are represented by nodes (or vertices) and the chemical reactions that interconvert the species are represented by edges (or lines).[24, 59, 13, 150, 106] As we follow a tagged atom through the chemical network, the pathway is represented by a sequence of vertices and edges. The graph then allows any pathway to be associated with a unique symbol sequence that labels the vertices and edges. Furthermore, all paths of a given length can be automatically generated by expansions in the symbol sequence. The chemical graphs we use here are weighted since the reaction rates can be used to assign a weight to each edge. This identification opens up the possibility of using graphical search algorithms to locate the most important paths

that contribute to a given process.

One aspect of the present method that distinguishes it from previous attempts to quantify chemical pathways[96, 21] is that SOHR fully embraces the dynamical nature of the chemical kinetics graphs. The time-dependence of edge weights (i.e. reactions rates) are accurately included even though this makes the computation of the probabilities much more challenging. Thus, as a molecule moves through the network its path instantaneously responds to the time varying rates. Other methods use static snapshots of the reaction flux or time-averages of the reaction rates to compute quantities such as the branching ratios in the chemical network. Since the rates of reaction can vary dramatically as a function of time, the passage through the network may be badly approximated by the static approximation.

The mathematical underpinning of the SOHR is discussed in Section 2. The computation of pathway probabilities and the methods for pathway enumeration are discussed in detail in this section. In Section 3 we present the results for a chemical network described by linear kinetics which serve to illustrate some of the general characteristics of the method. For a chemical system composed only of first-order reactions, the pathway probabilities can be computed analytically and is found to reduce to a sum of exponentials in time. It is shown that this linear kinetic problem can be solved with many fewer paths than might be expected. In Section 4, we discuss an application of SOHR to the catalytic decomposition of methanol. Under the conditions of low coverage, the system provides a realistic example of first-order kinetics. In Section 5, the  $\text{H}_2$  combustion problem is analysed using the SOHR method. It is shown that the ignition chemistry for this system can be accurately represented using a small number of chemical pathways. The use of the pathway representation also provides new insight into the mechanism and kinetic sensitivities of this problem. Finally, Section 6 presents a short conclusion and some ideas for future research.

## Chapter 2

### Mathematical Development

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#### 2.1 Introduction

The application of the SOHR approach requires a well-defined chemical model, and thus we begin with a review of conventional kinetics. The chemistry of a reaction network is traditionally modeled using mass-action kinetics where the concentrations for  $N$ -species are solved as functions of time, i.e.  $(X_1(t), X_2(t), \dots, X_N(t)) = X(t)$ . We shall assume that the chemical model under consideration consists of  $M$  elementary chemical reactions in a homogeneous well-stirred reactor

$$\sum_i^{\text{reactants}} \bar{v}_{i,j} S_i = \sum_i^{\text{products}} v_{i,j} S_i \quad j = 1, \dots, M \quad (2.1)$$

involving  $N$  distinct chemical species  $S_i$  which have concentration  $X_i$ . The molecularities,  $v_{i,j}$  and  $\bar{v}_{i,j}$ , enforce the elemental mass conservation for each reaction indexed by  $j$ . The rate of each reaction is given by a well-defined rate law,  $R_j(\mathbf{X})$ . [Nothing prevents the SOHR method from being applied to problems with time-dependent rate coefficients although we do not explicitly include a  $t$ -dependence in the formulae.] The continuous concentrations of the distinct species  $S_i$ ,  $X_i(t) \geq 0$ ,

can be expressed as solutions of the differential rate eqn. 2.1. The rate equations are given by

$$\frac{dX_i(t)}{dt} = F_i(\mathbf{X}) \quad (2.2)$$

The net rate for species  $S_i$ ,  $F_i(\mathbf{X})$ , is composed of the source and sink terms from each elementary reaction in the mechanism, i.e.

$$F_i(\mathbf{X}) = \sum_j^{sources} v_{i,j} R_j(\mathbf{X}) - \sum_j^{sinks} \bar{v}_{i,j} R_j(\mathbf{X}) \quad (2.3)$$

The solution to eqn. 2.2 can become difficult if the model grows very large or if multiple time-scales yields a high degree of stiffness in the equations.

We note briefly that another approach to kinetic modeling exists that is based on the methods of stochastic modeling. There, a discrete atomistic representation is adopted in which ensembles of molecules react according to a stochastic model [33]. This viewpoint, pioneered in the early work of McQuarrie[111] and later by Gillespie and coworkers[50, 53, 47], makes use of MC sampling methods to propagate large ensembles of discrete molecules. This method has proved useful in problems, such as those involving biomolecules, where concentrations are very low and hence the fluctuation in the number of molecules can play a role. A mathematical representation for this technique involves the chemical master equation (CME), where one solves for the probability distribution function  $P(\mathbf{x}, t | \mathbf{x}_0, t_0)$ . The variables  $\mathbf{x} = (x_1, x_2, \dots, x_N)$  represent the number of species molecules in a given volume and  $P(\mathbf{x}, t | \mathbf{x}_0, t_0)$  is the probability that the species are populated by  $\mathbf{x}$  at time  $t$  given that they were populated as  $\mathbf{x}_0$  at time  $t_0$ . Obviously, the solution to the CME contains vastly more information than does the mean field eqn. 2.2. It is also much more difficult to solve the CME than the concentration based kinetics equations. The most effective numerical techniques for solving the CME involve averaging many stochastic trajectories which simulate the time evolution of a large ensemble of molecules.

## 2.2 Defining Chemical Pathways

The basic units of description in the SOHR are the chemical pathway themselves. The pathways represent the condition of a chemical moiety as it moves from species to species due to the



action of the elementary chemical reactions. Taken collectively, these pathways describe the entire chemistry of the model. In order to quantitatively apply the SOHR to practical systems, we require an unambiguous procedure to define and enumerate these pathways. One can imagine a reaction pathway as either a sequence of reactions or a sequence of species that propagates the chemical moiety through the chemical network. If the reaction sequence is  $R_1, R_2, \dots, R_n$ , then the product molecule from reaction  $R_i$  should be a reagent molecule for the reaction  $R_{i+1}$ . In terms of species, on the other hand, there will be a sequence of  $n + 1$  moiety-containing molecules  $S_0, S_1, \dots, S_n$  that are connected by  $n$  elementary reactions. For a general non-linear mechanism, it is necessary to specify both the reactions and the species along the reaction pathway in order to achieve uniqueness. Indeed, the same reagents may yield different products or the same products may result from different reagents, depending on which reaction occurs. For example, if we imagine the gas-phase combustion of the methanol molecule,  $\text{CH}_3\text{OH}$ , a hypothetical three-step chemical pathway is  $\text{CH}_3\text{OH}(+\text{OH}) \xrightarrow{R_1} \text{CH}_3\text{O}(+\text{O}) \xrightarrow{R_2} \text{CHO}(+\text{OH}) \xrightarrow{R_3} \text{CO}$  which yields the CO product. Obviously the reagents in first step of this path,  $\text{CH}_3\text{OH} + \text{OH} \xrightarrow{R_1} \text{CH}_3\text{O} + \text{H}_2\text{O}$ , could have equally well yielded the chemically distinct products  $\text{CH}_2\text{OH} + \text{H}_2\text{O}$ , which must be described by a separate reaction  $R'_1$ . Likewise, the distinct reaction  $\text{CH}_3\text{OH} + \text{H} \xrightarrow{R_1} \text{CH}_3\text{O} + \text{H}_2$  is a different reaction route that connects the followed species  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{O}$ .

In most numerical applications of the SOHR methodology, we adopt a followedatom approach for the definition of the chemical pathways. Thus, an atom in a reagent species is tagged at the beginning of the simulation,  $t_0$ , and it is followed as it hops between species due to reaction until the final time  $t_f$ . For example, the carbon atom in the above pathway has a history  $(t_0|S_0R_1S_1R_2S_2R_3S_3|t_f)$  where the C-containing species are  $S_0 = \text{CH}_3\text{OH}$ ,  $S_1 = \text{CH}_3\text{O}$ ,  $S_2 = \text{CHO}$ , and  $S_3 = \text{CO}$ , and the reactions are  $R_1 = \text{CH}_3\text{OH} + \text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O}$ , etc. These histories represent pathways through species space which deliver the chemical moiety (in this case a C-atom) from the reagents to the products. A general pathway that delivers a C-atom from  $\text{CH}_3\text{OH}$  to CO may be arbitrarily long and thus may consist of an arbitrarily long sequence of reactions. The numerical utility of the SOHR method requires that only a finite and manageable number of the pathways are actually

required to converge meaningful results.

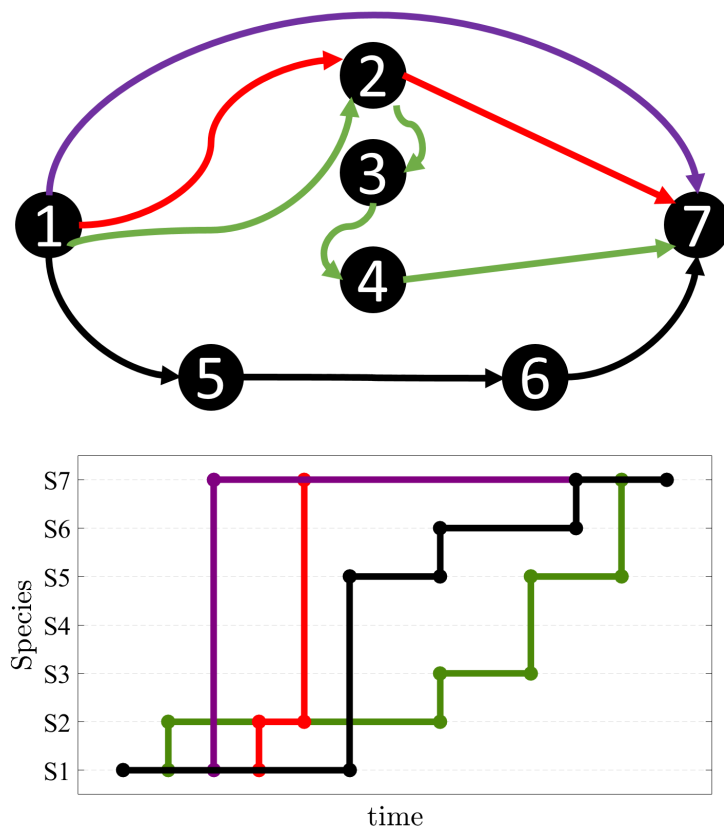
From our atomistic viewpoint, the reactions  $R_1, R_2 \dots R_n$  are a sequence of random events that occur instantaneously at times  $t_1, t_2 \dots, t_n$ . Consistent with the time-ordering along the pathway, the times must satisfy the inequalities  $t_f > t_n > t_{n-1} \dots > t_1 > t_0$ . Hence, we can further specify the path by noting the reaction times along with the initial and final times, i.e.  $(t_0|S_0R_1(t_1)S_1R_2(t_2)S_2R_3(t_3)S_3|t_f)$ . The chemical histories of an atom that goes from an initial to a final species may be, in principle, of any length  $n$  passing through  $n + 1$  species via  $n$  reaction steps occurring at times  $t_f > t_n > t_{n-1} \dots > t_1 > t_0$ . In Fig. 2.1 we show a schematic of several chemical pathways that deliver a tagged atom from species  $S_1$  to species  $S_7$ . In the upper panel, we show these pathways on a chemical graph. In the lower panel, we show trajectories that follow these paths for a particular set of reactions times.

### 2.3 Pathway Probabilities

The essential step that enables the SOHR to be used as a quantitative model of the reaction kinetics is the assignment of a numerical probability for a given chemical pathway. We consider a general pathway consisting of  $n$ -reactions and  $n + 1$ -species, i.e.  $S_0 \xrightarrow[R_1]{t_1} S_1 \xrightarrow[R_2]{t_2} S_2 \dots S_{n-1} \xrightarrow[R_n]{t_n} S_n$  where the followed-atom hops from  $S_i$  to  $S_{i+1}$  at time  $t_{i+1}$  due to elementary reaction  $R_{i+1}$ . We define  $\rho(t_0, t_1, \dots, t_n, t_f)$  as the probability density that, starting at time  $t_0$ ,  $S_0$  undergoes reaction  $R_1$  to form  $S_1$  at time  $t_1$ , then undergoes reaction  $R_2$  at  $t_2$  to form  $S_2$ , and so forth. The final species  $S_n$  that created at  $t_n$  must then survive until the final observation time  $t_f$ . The probability density has units of  $1/\text{time}^n$ . Since the occurrence of reactions  $R_1, \dots, R_n$ , constitute a sequence of independent random events, i.e. a Markov chain, then  $\rho(t_0, t_1, \dots, t_n, t_f)$  is a product of the appropriate decay probability densities for each step along the chain. The total pathway probability,  $P_{path}$ , is obtained by integrating the probability density over all times  $(t_1, \dots, t_n)$  consistent with the time-ordering, i.e.

$$P_{path}(t_0, t_f) = \int_{t_0}^{t_f} dt_n \int_{t_0}^{t_n} dt_{n-1} \dots \int_{t_0}^{t_2} dt_1 \rho(t_0, t_1, \dots, t_n, t_f) \quad (2.4)$$

Figure 2.1: Two representations of chemical histories. In the upper panel, four chemical pathways followed by a tagged atom are displays on a chemical graph. The species are represented as vertices and reactions are lines (or edges). In the lower panel, four analogous stochastic trajectories are plotted as species number vs. time. The time-dependence of the trajectory corresponds to a Markov chain of random reactions.



As a very simple illustration, consider a one-step pathway  $S_0 \rightarrow S_1$  governed by a mechanism consisting of a single first-order reaction with rate law  $k[X_0]$ . The quantity  $\rho(t_0, t_1, t_f)$  is the probability density that a molecule of type  $S_0$ , which was created at time  $t_0$ , decays at time  $t_1$  to form  $S_1$  which then survives until time  $t_f$ . Clearly, in this case  $\rho(t_0, t_1, t_f) = k \times e^{-k(t_1-t_0)}$  since the species  $S_1$  is stable. Integrating over  $t_1$  gives the result  $P_{path} = 1 - e^{-k\Delta t}$ , with  $\Delta t = t_f - t_0$ . Notice for this system there are only two possible paths that can be followed by a tagged atom, viz. the one-step path,  $S_0 \rightarrow S_1$ , and the trivial zero-step path where  $S_0$  does not decay. For the latter path, the pathway probability is the non-decay probability  $e^{-k\Delta t}$  and thus the sum of the pathway probabilities is 1. A slightly less trivial case would be a mechanism with a sequence of two first-order reactions,  $S_0 \rightarrow S_1$  and  $S_1 \rightarrow S_2$ , with rate laws  $k_1[X_0]$  and  $k_2[X_1]$ , respectively. Again  $S_2$  is a stable species. Notice in this case there are three possible paths emanating from  $S_0$ : a two-step path  $S_0 \rightarrow S_1 \rightarrow S_2$ , a one-step path  $S_0 \rightarrow S_1$ , and a zero-step path  $S_0$ . The probability density for the two-step path  $S_0 \rightarrow S_1 \rightarrow S_2$  is

$$P_{path}(t_0, t_1, t_2, t_f) = k_1 e^{-k_1(k_1-k_0)} k_2 e^{-k_2(k_2-k_1)} \quad (2.5)$$

and the total integrated pathway probability is

$$\begin{aligned} P_{path}(2-step) &= \int_{t_0}^{t_f} \int_{t_0}^{t_2} dt_1 \rho(t_0, t_1, t_2, t_f) \\ &= 1 + \frac{k_1 e^{-k_2 \Delta t}}{k_2 - k_1} - \frac{k_2 e^{-k_1 \Delta t}}{k_2 - k_1} \end{aligned} \quad (2.6)$$

where  $\Delta t = t_f - t_0$ . The probability density for the one-step path,  $S_0 \rightarrow S_1$ , is

$$\rho(t_0, t_1, t_2, t_f) = k_1 e^{-k_1(k_1-k_0)} e^{-k_2(k_2-k_1)} \quad (2.7)$$

Note that in eqn. 2.7, we have inserted the non-decay probability of species  $S_1$ , i.e.  $e^{-k_2(t_f-t_1)}$ , which is created at time  $t_1$  and must survive until  $t_f$ . The corresponding pathway probability is

$$\begin{aligned} P_{path}(1-step) &= \int_{t_0}^{t_2} dt_1 \rho(t_0, t_1, t_f) \\ &= -\frac{k_1 e^{-k_2 \Delta t}}{k_2 - k_1} + \frac{k_1 e^{-k_1 \Delta t}}{k_2 - k_1} \end{aligned} \quad (2.8)$$

The zero-step pathway probability is the non-decay probability that  $S_0$  is created at time  $t_0$  and survives until time  $t_f$ , i.e.

$$P_{path}(0 - step) = e^{-k_1 \Delta t} \quad (2.9)$$

It is easily seen that the sum of eqns. 2.6, 2.8, and 2.9 is one.

To generalize the probability density for a time-resolved pathway to an arbitrary kinetic mechanism, we find it convenient to define two quantities: the species survival probability and the reaction branching ratio. The species survival probability,  $\mathcal{P}_i(t_a, t_b)$ , is the probability that a molecule of type  $S_i$ , which is created at  $t_a$ , undergoes no reaction in the time interval  $(t_a, t_b)$  where  $\mathcal{P}_i(t, t) = 1$ . Unlike the simple first-order reactions above, where  $P(t_a, t_b) = \exp(-k(t_b - t_a))$ , the survival probability is temporally in-homogeneous for general mechanisms, i.e.  $\mathcal{P}_i(t_a, t_b) \neq \mathcal{P}_i(t_a + \Delta, t_b + \Delta)$ . However it is straightforward to compute the survival probability for any species  $S_i$  by integrating the species decay probability obtained from the sum of sink reactions defined in the rate eqn. 2.2

$$\begin{aligned} \mathcal{P}_i(t_a, t_b) &= \exp \left( - \int_{t_a}^{t_b} \sum_j^{sinks} A_{i,j}(t) dt \right) \\ &\equiv \exp \left( - \int_{t_a}^{t_b} A_i(t) dt \right) \end{aligned} \quad (2.10)$$

The quantities  $A_{i,j}(t)$  are similar to pseudo-first-order rate coefficients (with dimensions of 1/time) and are defined by the time-dependent expressions

$$A_{i,j}(t) \equiv \frac{\bar{v}_{i,j} R_j(\mathbf{X})}{X_i(t)} \quad (2.11)$$

where  $i$  labels the species and  $j$  labels the reactions. The concentrations  $\mathbf{X}(t)$  are evaluated along the solution to eqn. 2.2. The instantaneous decay rate for species  $S_i$  at time  $t_b$ , assuming that  $S_i$  was created at  $t_a$ , is  $-d\mathcal{P}_i(t_a, t_b)/dt_b$ . A second useful quantity is the time-dependent branching ratio,  $\Gamma_i(t)$ , which measures the instantaneous fraction of the reactive flux that follows the correct branch when species  $S_i$  reacts to form products. The branching ratio is simply the reactive flux along the selected  $J$ th-branch divided by the total reactive flux of species  $S_i$ , i.e.

$$\Gamma_i(t) \equiv \frac{A_{i,J}(t)}{A_i(t)} \quad (2.12)$$

In this notation we drop the explicit J-index on  $\Gamma$ . The stoichiometric factors are not included in the numerator of eqn. 2.12 since we are following a single tagged atom. Using these expressions, we have shown that the pathway probability can be written as an integral of a time-ordered product.[10, 4]

$$P_{path}(t_0, t_f) = (-1)^n \int_{t_0}^{t_f} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_2} dt_1 \prod_{i=1}^n \left( \frac{d\mathcal{P}_{i-1}(t_{i-1}, t_i)}{dt_i} \Gamma_{i-1}(t_i) \right) \mathcal{P}_n(t_n, t) \quad (2.13)$$

This expression is similar to Dysons formula for the amplitude in quantum mechanics.[135, 117] Unlike the quantum expression, however, the integrand of eqn. 2.13 is positive definite and thus phase cancellation is not an issue.

The evaluation of the path probability using a numerical quadrature for eqn. 2.13 can become laborious when the dimension,  $n$ , is large. However, this multidimensional integral is well suited for MC evaluation since the integrand is positive. In the numerical implementation of the MC approach, we find that the wide range of time scales present in realistic kinetic problems leads to stiffness and inefficient sampling of the time intervals. This technical difficulty can be overcome by using an importance sampling that employs the integration variables  $P_i$ , rather than  $t_i$ . In this method, a random number  $y_0$  is first chosen for species  $S_0$  in the interval  $(P_{min}^0(t_0), 1)$ ;  $P_{min}^0(t_0) = \mathcal{P}_0(t_0, t_f)$  is the minimum value of the survival probability of  $S_0$  which occurs at  $t = t_f$ . Then, the expression  $y_0 = \mathcal{P}_0(t_0, t_1)$  is inverted to obtain  $t_1$ , the time of the reaction  $R_1$ . This time is used in eqn. 2.6 for  $\Gamma_1$ . Then, for species  $S_1$  a second random number,  $y_1$ , is chosen in the interval  $(P_{min}^1(t_1), 1)$ . As before, the reaction time  $t_2$  is obtained and branching ratio  $\Gamma_2$  is computed. This process is continued for all the species along the pathway, which thus requires a string of  $n$  random numbers. We have for the final MC expression

$$P_{path}(t_0, t_f) = \frac{1}{N} \sum_{q=1}^N \mathcal{P}_n(t_n^q, t_f) \prod_{k=1}^n \left( \Gamma_{k-1}(t_k^q) \left( 1 - P_{min}^{k-1}(t_k^q) \right) \right) \quad (2.14)$$

where the index  $q$  is used to specify each string of  $n$ -random numbers where, in this equation only,  $N$  is the size of the MC sampling. It is important to note that, except for linear or steady state systems, the SOHR apparently requires input from the traditional kinetics representation

since the pseudo-first-order rate coefficients  $A_{i,j}(t)$  are computed using the kinetic solutions  $\mathbf{X}(t)$ . The reference trajectory  $\mathbf{X}(t)$  is an input when treating non-linear kinetic systems. Developing a method to detach the SOHR from traditional kinetics, and from need for a reference trajectory by using an iterative solution technique is an ongoing area of research.[8]

## 2.4 Constructing Observables

The SOHR can be used to compute the values of observables if a sufficient number of chemical pathways are employed. Consider the fundamental task in kinetics of computing the concentration of a species  $S_i$  at time  $t_f$ ,  $[X_i(t_f)]$ , given the values of the initial reagent concentrations  $[X(t_0)]$ . Taking the simplest case first, assume that there is no more than one followed-atom, lets say a carbon atom, that exists in any species. Furthermore, assume that the target species  $S_i$  contains one carbon atom and that only one of the reagent species contains any carbon, say  $S_r$ . This would be the case, e.g. if we were following a carbon atom from  $\text{CH}_4/\text{O}_2$  reagents to the  $\text{CO}_2$  product in a pure  $\text{C}_1$  mechanism. Using the pathway index  $j$ , we enumerate all important paths that deliver the carbon atom from the reagent  $S_r$  at  $t_0$  to the target species  $S_i$  at time  $t_f$ . The pathway probabilities for each path  $j$ , computed using eqn. 2.13 or 2.14, are abbreviated by  $P_j$ . Then, it is clear that the concentration of product is given by

$$[X_i(t_f)] = \sum_j [X_r(t_0)] P_j(t_f) \quad (2.15)$$

Of course this represents only a special case since in general there can be more than one followed-atom in each species and there may be more than one initial reagent species containing followed-atoms. We use the notation  $\mu_i$  to represent the number of chemically equivalent followed-atoms in species  $S_i$ . We generally have that the followed-atom for the target species  $S_i$  lies in a multiplet of  $\mu_i$  chemically equivalent atoms. Likewise, the followed-atom may potentially originate from one of several initial species,  $S_k$ , each of which may contain a multiplet of  $\mu_k$  chemically equivalent followed-atoms. The pathways are labeled by ' $j_k$ ' where  $k$  specifies the species of origin for the path of the followed-atom and the associated probabilities are denoted by  $P_{j_k}$ . Notice that the pathway

probabilities are defined using species to species reaction probabilities and thus the numbers  $\mu_i$  are only required at the beginning and the end of the path. The concentration of  $S_i$  is thus seen to be

$$\mu_i[X_i(t_f)] = \sum_{j_k} \mu_k[X_k(t_0)] P_{j_k}(t_f) \quad (2.16)$$

Most other kinetic observables can be expressed in terms of the species concentrations, and hence the pathway representation can be employed to analyse most kinetic problems.

## 2.5 Graph Theoretic Enumeration of Chemical Pathways

While eqn. 2.16 provides a means to represent kinetic observables given a sufficient number of paths, we must still devise a method to generate those paths. For simple mechanisms that contain a small number of species and reactions, it is possible to construct the chemical pathways by inspection or with chemical insight. When the mechanism is complicated, however, it becomes necessary to employ a more systematic algorithm. A useful approach involves the use of graph theoretic methods.[13] We construct the chemical graph using two sorts of elements: vertices and edges. The vertices, represented by dots on the graph, are species which contain the followed-atom. The edges (or lines) on the graph connect the vertices and correspond to elementary reactions that deliver the followed-atom from one species (vertex) to another. The kinetic graphs employed here have certain specific characteristics which prove useful. First, the graphs are directed since the elementary reactions have a sense of direction. Second, the graphs are weighted since the edges are quantified by the pseudo-first-order rate coefficients,  $A_{i,j}$ . Third, the kinetic graphs are multigraphs since there may be more than one edge connecting two given vertices. Fourth, the graphs are dynamical since the weights are generally time-dependent. A unique chemical pathway of length  $n$  is represented by a specific directed sequence of  $n + 1$ -vertices and  $n$ -edges on the graph.

Elementary graph theory can be used to enumerate those chemical pathways that are sufficiently short. Consider first the case of simple graphs where at most one edge connects any two vertices and no vertex is connected by an edge to itself. This might describe, e.g. the case of a totally linear kinetic network. We define the adjacency matrix,  $\mathbf{M}$ , as an  $N \times N$  matrix (where  $N$  is the order



of graph, i.e. the number of vertices) which has the matrix elements given by

$$M_{i,j} = \begin{cases} 1, & \text{if } i \text{ and } j \text{ are connected by an edge} \\ 0, & \text{if } i \text{ and } j \text{ are not connected by an edge} \end{cases} \quad (2.17)$$

For a simple graph, it is not hard to show that the total number of paths of length  $n$  between species  $i$  and  $j$ ,  $K(n; i, j)$ , is given by

$$K(n; i, j) = (\mathbf{M}^n)_{i,j} \quad (2.18)$$

Furthermore, we can explicitly generate these  $K(n; i, j)$  paths using matrix multiplication. Define the closely related  $\mathbf{S}$ -matrix to be  $S_{i,j} = M_{i,j}s_j$ , where the dummy variable  $s_j$  is the species label (i.e. a symbol). Then the sum of paths of length  $n$  may be obtained by expanding out the  $(i, j)$ th matrix element in the product

$$s_i \times (\mathbf{S}^n)_{i,j} \quad (2.19)$$

These  $K(n; i, j)$  symbol sequences of species labels uniquely define paths on a simple graph since only one possible edge can connect any two vertices.

The situation is more complicated for a general kinetic multigraph where more than one reaction (i.e. edge) can deliver a tagged atom between two species. In this case we need to specify which edge is being followed by the tagged atom. For a multigraph, define the generalized adjacency matrix,  $\mathbf{M}$ , to be

$$M_{i,j} = \begin{cases} m_{i,j}, & \text{if } i \text{ and } j \text{ are connected by } m_{i,j} \text{ edge} \\ 0, & \text{if } i \text{ and } j \text{ are not connected by an edge} \end{cases} \quad (2.20)$$

Then, again, the number of paths of length  $n$  connecting species  $i$  and  $j$  is given by the matrix element of  $\mathbf{M}^n$  specified in eqn. 2.18. To explicitly generate these paths, we generalize the  $\mathbf{S}$ -matrix above to the  $\mathbf{SR}$ -matrix that represents both the species and reactions involved in the path. We

define

$$(SR)_{i,j} = \begin{cases} \sum r(i,j) \times s_j, & \text{if } M_{i,j} \neq 0 \\ 0, & \text{if } M_{i,j} = 0 \end{cases} \quad (2.21)$$

where  $r(i,j)$  are the  $m_{i,j}$  dummy variables (i.e. symbols) labeling the elementary reactions connecting species  $i$  and  $j$ , directed as  $i \rightarrow j$ , and  $s_j$  are again species symbols. The sum of symbol sequences for paths of length  $n$  are obtained expanding the matrix product

$$s_i \times (SR^n)_{i,j} \quad (2.22)$$

The most straightforward approach to the pathway enumeration problem in the SOHR is to use the expansion in eqn. 2.22 to compute all the paths of length up to  $n = n_{max}$ , and then converge the observables by progressively increasing this maximum length.

Obviously the number of potential paths can grow tremendously large as the path length  $n$ , or graph order  $N$ , increases. Even with the efficient MC-algorithm for computing the pathway weights, eqn. 2.14, the SOHR method can bog down if the number of paths required becomes too large. We point out, however, that it is common to find that many of the paths enumerated in eqn. 2.22 have very low probabilities and make a negligible contribution in the expansion of the observables. Hence, it is often advisable to use a method that selects the most important pathways rather than simply employing a full expansion of all paths up to a given length. This brings us to the topic of path search algorithms.

It is a classic problem in computer science to locate optimal paths on a weighted graph.[99] For example, there have been a number of algorithms developed to systematically find the shortest path between two vertices where the edge weight,  $w_i$ , is identified as a length. In that problem, the path length, i.e. the sum of lengths of individual edges  $L = \sum w_i$ , is minimised by varying the path itself. The Dijkstra algorithm[33] is a commonly used procedure to solve this problem. The Bellman-Ford[17] and A\*-search algorithms[63] are also well-known methods and provide somewhat more computationally efficient approaches. The present kinetics system is different from the traditional

shortest path problem in several ways. First, we generally need to find many important paths rather than a single optimal path. This is not a major problem since several of the traditional optimal path methods have been generalised to obtain the 'K-shortest paths' on a weighted graph[35]. Second, the chemical paths we seek will maximise a probability rather than minimising a length. The total probability of a chemical pathway is related to the product of weights for each edge rather than the sum of edge weights used for computing path length. This distinction is easily overcome by taking the logarithm of the pathway weights which converts the product into a sum. Third, and most problematic, as a dynamical graph[61] the weights of the kinetic graph are time-dependent and thus the optimization process is itself time-dependent. This is because the weights of the edges are computed from the time-dependent pseudo-first-order rate coefficients  $A_{i,j}(t)$ . One simple shortcut around this problem would be to hold fixed the values of  $A_{i,j}(t)$  at some particular time value and carry out the optimization for the resulting static graph. Alternatively, one might carry out the search using weights averaged over some time interval. The time-independent weights might also be updated during the run according to some criterion. While the static approximations to the dynamical graph problem may prove useful for some problems, it is easy to imagine scenarios where the true high probability pathways are not correctly identified. Therefore, we have adopted an approach based on stochastic sampling which is discussed in the next section.

## 2.6 Stochastic Pathway Enumeration

We have devised a simple method to enumerate the important chemical pathways on a dynamical graph using a stochastic sampling method closely related to the simulation algorithm developed by Gillespie and coworkers[53] and others[152]. Imagine that we want to identify important paths that carry a tagged atom from an initial species,  $S_0$ , to a final species  $S_f$ . We can locate such pathways by propagating individual molecules through the reaction network using a kinetic MC simulation. An individual molecule of type  $S_i$  carrying the tagged atom has a instantaneous

transition probability (not PDF) for going to species  $S_k$  by reaction  $R_j$  given by

$$TP(S_i \rightarrow S_k; R_j) = A_{i,j}(t) \times \gamma_k^j \quad (2.23)$$

Where  $\gamma_k^j$  indicates the branching ratio the 'tagged' atom flows into species  $S_k$  given reaction  $R_j$  ( $\gamma_k^j$  is typically a constant tensor). Using importance sampling based on the species survival probability, as above, the tagged atom can be propagated efficiently through the network via a random walk. For one step of that walk, a single random number determines the reaction time while a second random number selects the product branching. Those paths that go from  $S_0$  to  $S_j$  are recorded. Using a modest number of such MC trajectories, a list of the important paths along with their approximate ranking is obtained. While this method is not appropriate for locating rare paths, we have found it very useful for many of the kinetic systems we have studied. Since this method involves probabilistic sampling, it is naturally possible that paths can be missed if too few random walks are employed.

## Chapter 3

### Linear Kinetics

Some of the contents of this chapter are reprinted, with permission, from

- [7] Bai, S., & Skodje, R. T. The Sum Over Histories Representation for Chemical Kinetics: A Quantitative Theory Based on Chemical Pathways. *International Reviews in Physical Chemistry*, 35(4), 539-567. **2016**

#### 3.1 Analytical Expression of Linear Kinetics

If the chemistry of a system is accurately described by a purely linear kinetic model, then the implementation of the SOHR becomes especially simple. We use this transparent case to illustrate some of the characteristics of the method. Consider a reaction network consisting of  $N$ -species,  $S_i$  ( $i = 1, \dots, N$ ), which can undergo the first-order reactions  $S_i \rightarrow S_j$  described by the rate laws  $k_{i,j}[X_i]$ . The graph for this linear system is 'simple' since at most one edge (reaction) will connect any two vertices (species) and there are no self reactions,  $S_i \nrightarrow S_i$ . Thus, any  $n$ -step path can be uniquely represented by the corresponding product of species,  $S_0 S_1 \dots S_n$  and it is not necessary to specify the reactions. The quantities  $A_{i,j}(t)$  defined in eqn. 2.11 are constants in time, i.e.  $A_{i,j}(t) = k_{i,j}$ . The species decay rates,  $A_i = \sum A_{i,j} = \sum k_{i,j} \equiv k_i$ , are likewise time-independent and all the species survival probabilities correspond to pure exponential decay, i.e.  $\mathcal{P}_i(t_a, t_b) = \exp(-k_i(k_a - k_b))$ . The reaction branching ratios are given by  $\Gamma_i = k_{i,J}/k_i$  where  $J$  denotes the appropriate channel along the pathway selected. Thus, for linear kinetics the reference trajectory  $\mathbf{X}(t)$  from eqn. 2.2 is not required to implement the SOHR. Given these simplifications,

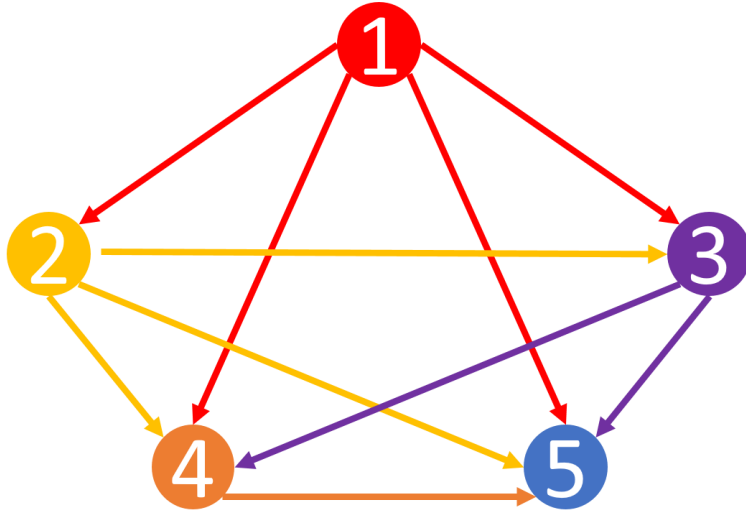
the integral of the time-ordered product, eqn. 2.3, can then be evaluated analytically[10]

$$\begin{cases} P_{path}(t_0, t_f) = \sum_{i=0}^n D_i^n \exp(-k_i(t_f - t_0)), & (a) \\ D_i^n = \frac{\prod_{j=0}^{n-1} k_j \Gamma_j}{\prod_{j=0, j \neq i}^n (k_i - k_j)}, & (b) \end{cases} \quad (3.1)$$

The pathway probability is seen to be related to the integrated rate law for n-sequential first-order reactions.[1] We note that the apparent singularity of this expression, which occurs when two decay rates are equal,  $k_i = k_j$ , can be removed by making a small displacement of one of the  $k_i$ 's.

To illustrate the workings of the SOHR for linear kinetics, we consider a simple 20 species system,

Figure 3.1: The chemical graph corresponding to an acyclic linear kinetic model with 5 species. The edges connect only the species  $S_i \rightarrow S_j$  with  $j > i$ .



i.e.  $N = 20$ , where the graph is acyclic. In an acyclic graph, no path can form a closed loop and thus all the paths are of finite length. This condition is enforced here by the condition  $k_{i,j} = 0$  when  $i \geq j$ . In Fig. 3.1 we show the chemical graph restricted to the first 5 species. We allow the lower triangle of the rate constant matrix  $k_{i,j}$  to be fully occupied. The non-zero rate constants are selected with a random number generator over an order of magnitude range, i.e.

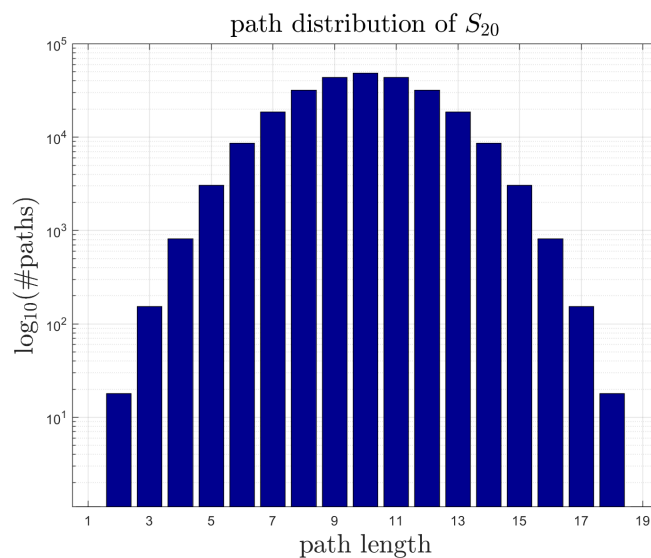
$$k_{i,j} = 1 + (10 - 1) \times \text{random}(0, 1)$$

We find most random sets of rate constants give results that are qualitatively similar.

### 3.2 Number of Pathway vs. Pathway Length

Using the adjacency matrix, eqn. 2.17, we find that the number of potential pathways can grow quite large even for this simple problem. For example, if we follow species  $S_1$  through the network to species  $S_{20}$  there are 262,144 allowed paths that a molecule might take. In Fig. 3.2, we show the distribution of paths vs. path length,  $L$ . There is one path of length  $L = 1$ , viz.  $S_1 \rightarrow S_{20}$ , and one path of length  $L = 19$ , viz.  $S_1 \rightarrow S_2 \cdots S_{19} \rightarrow S_{20}$ . The largest number of paths occur in the middle of the range,  $L = 10$ . Of course the number of paths will depend on the choice of initial and final species.

Figure 3.2: The number of independent chemical pathways connecting species  $S_1$  with  $S_{20}$  in a linear kinetic model with rate coefficients  $k_{i,j} \neq 0$  for  $j > i$  and  $k_{i,j} = 0$  for  $i \geq j$ . The length  $L$  is the number of reactions along the path.



### 3.3 Demonstration of Convergence of SOHR

In order to assess the numerical performance of the SOHR method, we have computed for comparison the 'exact' solution to the linear system using a 4th-order Runge-Kutta integration of the differential kinetics equations

$$\frac{d[X_i]}{dt} = Sources - Sinks = \sum_{j=1}^{i-1} k_{i,j}[X_j] - k_i[X_i] \quad (3.2)$$

We note that species  $S_{20}$  is stable since  $k_{20} = 0$ . Thus, for the initial condition  $[X_i(t=0)] = \delta_{i,1}$  we know that the solution will tend to  $[X_{20}(t)] \rightarrow 1$  as  $t \rightarrow \infty$ . We shall compare the Runge-Kutta solution of the kinetics originating from the  $S_1$  initial condition to the prediction of the SOHR using the pathways originating with  $S_1$ . We note that if all the chemical paths are included in the SOHR expansion we also obtain the exact result.

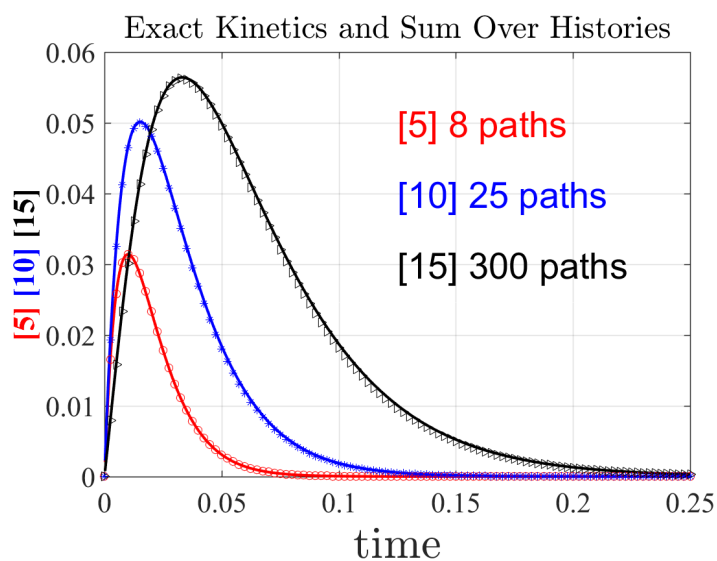
Using the stochastic method described in Section 2.6, we have identified a number of candidate pathways that converts species  $S_1$  to each of the other species,  $S_i$ . Thus, we have run several thousand MC trajectories and produced a rough ranking of the pathways that connect  $S_1$  to the other species. In Fig. 3.3, we show the concentrations of several intermediate species computed using eqn. 3.1 and the pathway expansion  $[X_i(t_f)] = \sum_j P_j [X_1]$ . To achieve better than 1% accuracy, we used 8 paths for  $S_5$ , 25 paths for  $S_{10}$ , and 300 paths for  $S_{15}$ . Clearly, the pathway representation reaches practical convergence for the concentration long before the all of the potential paths are included. Indeed, the rapid convergence of the expansion with respect to the number of paths is a criterion for the practical utility of the SOHR as a computational method.

### 3.4 Pathway Probabilities Changing Over Time

It is instructive to investigate the behaviour of the SOHR in somewhat greater detail for this simple problem. We note that even though the pseudo-first-order rate coefficients are time-independent, the pathway probabilities still possess a strong time-dependence. In Fig. 3.4, we show the pathway probabilities vs. time for the 100 most important paths connecting  $S_1$  to  $S_{15}$ . The paths are colour-coded according to their length. At very early times, the one-step path,



Figure 3.3: The concentration of several chemical intermediates vs. time for the linear kinetic model consisting of 20 species. The solid lines are the result of converged numerical integration of the conventional kinetics equations, eqn. 3.2, for species  $S_5$ ,  $S_{10}$ , and  $S_{15}$ . The symbols are the result of the SOHR using eqn. 3.1 for the pathway probabilities. The pathways were identified using a small stochastic simulation.



i.e.  $S_1 \rightarrow S_{15}$ , dominates the probability. At somewhat later times, the two-step paths, i.e.  $S_1 \rightarrow S_j \rightarrow S_{15}$  begin to play a role. At still later times, the three- and four-step paths begin to contribute. Heuristically, we can understand that a molecule which arrives at species  $S_{15}$  at a later time will tend to take a more circuitous route than one that arrives at an earlier time. In Fig. 3.5, we show the growth of the mean path length as a function of time. Obviously the concentration of a kinetic intermediate is closely connected to the notion of arrival time distributions or first passage time distributions that are often studied in stochastic models.[155] If we consider the full passage through the network to the attracting final state,  $S_{20}$ , the pathway probabilities take a simple form. As  $t \rightarrow \infty$ , the sum of exponentials in eqn. 3.1 contains only the last term with  $k_{20} = 0$ . In this case, the pathway probability becomes the product of the branching ratios along the path and is time-independent. It is interesting to point out that even for a general non-linear mechanism, if the kinetics reaches a steady state condition then the same linear analysis may be invoked to implement the SOHR.

Figure 3.4: Pathway probabilities vs. time for the 100 most probable paths connecting  $S_1$  with  $S_{15}$  in the linear kinetic model. At each time, the sum of probabilities is normalised to unity. The pathway probabilities are colour coded according to their path lengths.

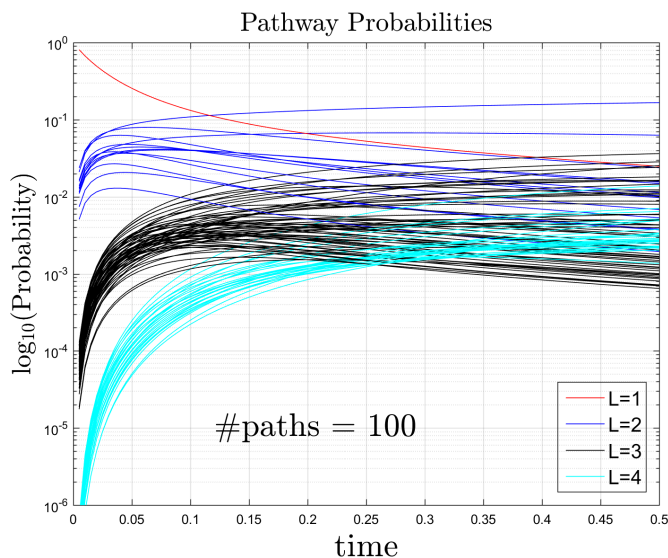
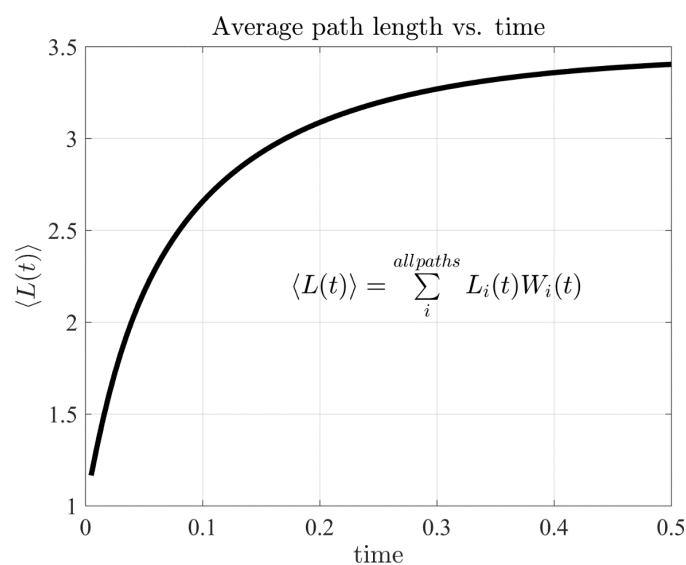


Figure 3.5: The average path length vs. time for chemical paths going from S1 to S15 in the linear kinetic model. The weight of each chemical path is computed using Equation (3.1) where the weights are normalised to unity at each time.



## Chapter 4

### Kinetic Sensitivity Analysis Using Sum Over Histories Representation

Most of the contents of this chapter are reprinted, with permission, from

- [10] Bai, S., Zhou, D., Davis, M. J., & Skodje, R. T. Sum over histories representation for chemical kinetics. *The journal of physical chemistry letters*, 6(1), 183-188. **2014**
- [5] Bai, S., Davis, M. J., & Skodje, R. T. Sum over Histories Representation for Kinetic Sensitivity Analysis: How Chemical Pathways Change When Reaction Rate Coefficients Are Varied. *The Journal of Physical Chemistry A*, 119(45), 11039-11052. **2015**
- [7] Bai, S., & Skodje, R. T. The Sum Over Histories Representation for Chemical Kinetics: A Quantitative Theory Based on Chemical Pathways. *International Reviews in Physical Chemistry*, 35(4), 539-567. **2016**

#### 4.1 Abstract

The sensitivity of kinetic observables is analyzed using a newly developed sum over histories representation of chemical kinetics. In the sum over histories representation, the concentrations of the chemical species are decomposed into the sum of probabilities for chemical pathways that follow molecules from reactants to products or intermediates. Unlike static flux methods for reaction path analysis, the sum over histories approach includes the explicit time dependence of the pathway probabilities. Using the sum over histories representation, 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. The method is illustrated for species concentration target functions in  $\text{H}_2$  combustion where the rate coefficients are allowed to vary over their associated uncertainty ranges. It is found that large sensitivities are often associated with rate limiting steps along important chemical pathways or by reactions that control the branching of reactive flux.

## 4.2 Introduction

Sensitivity analysis provides an important tool for the study of chemical kinetic networks.[87, 130, 153] In chemical kinetic sensitivity analysis the response of a target observable, such as a species concentration at time  $t$ ,  $[\mathbf{X}_i(t)]$ , is probed as a function of variable factors, which are commonly chosen to be the rate coefficients,  $k_j$ . The use of sensitivity measures such as local or global sensitivity indices allows the chemistry described by complex mechanisms to be better understood physically, and in some cases permits the mechanisms to be systematically improved. For example, a large sensitivity index may indicate a key reaction step whose rate coefficient may then be improved upon using better experimental or theoretical methods. Conversely, reactions with very low sensitivity indices may be targeted for removal from the mechanism which will enhance the computational efficiency. Furthermore, if the rate coefficients can be assigned uncertainty ranges, the overall uncertainty of the model predictions can be quantified using the function representation of the target.[121] Although the utility of sensitivity analysis in chemical kinetics is widely appreciated, it is not always possible to identify a specific chemical explanation that rationalizes the observed sensitivities. Thus, it is not uncommon for reaction to be found highly sensitive although it is unclear by what chemical mechanism this sensitivity arises. When the origin of observed kinetic sensitivity is not well understood, the practical utility of the results for model improvement or simplification is a less well motivated endeavor. In this work, we propose the use of our recently developed sum over histories representation as the basis to interpret kinetic sensitivity.[84, 11]

The sum over histories approach to chemical kinetics is based on the idea of expressing the quantitative kinetics of a chemical network using separate numerical contributions (via probabilities)

from distinct chemical pathways. Our method to simulate the time dependence of a chemical network draws its motivation from Feynmans sum over histories approach to quantum mechanics[43] and is closely related to treatments of time-ordered Markov chains[156] discussed by Wiener[46] and Ito.[72] In our method, the paths lie in chemical space unlike Feynmans dynamical paths. The notion of a chemical pathway plays a central role in our understanding of chemical systems and is a quite familiar concept. In synthetic chemistry, for example, one follows a substrate molecule as it undergoes a sequence of alterations en route to a desired product. In general, a pathway is defined as a sequence of species,  $S_0, S_1, \dots, S_N$  connected by elementary reaction  $R_1, R_2, \dots, R_L$  such that the product of one reaction is a reagent for the next reaction along the pathway. Reaction pathways and graphical methods are also well-known in kinetic studies where they are used effectively to interpret and optimize chemical mechanisms.[151, 23, 107, 97, 67, 39, 75] The sum over histories approach is unique, however, in that it provides a fully quantitative and convergent procedure in which the concentration of any target species at time  $t$ ,  $[\mathbf{X}(t)]$  may be computed by a linear combination of chemical pathways that lead from initial reactants to the target

$$[\mathbf{X}(t)] = \sum_i c_i p_i(t) \quad (4.1)$$

where  $p_i(t)$  is the probability for path  $i$  and  $c_i$  are trivial time-dependent coefficients obtained from the stoichiometry. The pathway probabilities are given explicitly by an integral of a time-ordered product that is analogous to the Feynman path integral or the Wiener integral. The advantage of the sum over histories formulation is that the kinetics, and hence the behavior of sensitivity targets, is now represented by complete mechanisms that incorporate complete chemical pathways rather than by individual reaction steps that may participate in many distinct mechanisms. The origin of kinetic sensitivity may then be directly studied in terms of how a kinetic parameter affects the probability for a particular mechanism, i.e., through the pathway probabilities  $p_i(t)$ .

In this work we investigate sensitivity in the kinetics for ignition in the  $H_2$ - $O_2$  system at intermediate temperatures, i.e.,  $T = 1000$  K. We select for sensitivity targets the species concentrations at times before ignition and, thus, we focus on the chemistry underlying the growth of the radical pool,

which determines the ignition induction period. It is well-known that speciation studies provide a particularly effective approach for the improvement and validation of chemical mechanisms.[74] The chemistry of the  $\text{H}_2$  combustion problem is now fairly well understood and the rates of most of the elementary steps are known to good accuracy.[81, 64] Our purpose here, however, is not to improve the combustion model, but rather to investigate a new method to carry out sensitivity analysis. The  $\text{H}_2$  combustion problem is ideal for such a test because it exhibits the generic characteristics of combustion kinetics whereas its mechanism is sufficiently simple to permit a full numerical investigation. We find that although the sum over histories approach is not a panacea, it provides useful insight into the origin of the kinetic sensitivity of speciation targets and it appears to be a useful tool to apply to more complicated problems.

This chapter is organized as follows. In section 4.3, the sum over histories approach to kinetics is reviewed and the use of the high dimension model representation (HDMR) for global sensitivity analysis (GSA) is summarized. In section 4.4, the details of the combustion simulation are discussed and the results of the GSA for speciation in the  $\text{H}_2$  combustion problem are presented. In section 4.5, the chemical pathways that contribute to the various species targets are found and the associated probabilities are computed. It is shown that the species concentrations can be converged by summing a small number of chemical pathways. In section 4.6, the sensitivity of the various target species is discussed using the chemical pathways uncovered in section 4.5. Finally, section 4.7 is a short conclusion.

### 4.3 Methodology

We begin with a brief review of the concepts of sensitivity analysis and of the sum over histories representation that will also serve to define the required mathematical notation. We shall explicitly consider the case of spatially homogeneous kinetics described by the continuous concentrations (number of molecules per unit volume) of the  $N$  distinct species  $S_i$ ,  $X_i(t) \geq 0$ . The

concentrations solve the N-rate equations

$$\frac{dX_i}{dt} = F_i(t) \quad (4.2)$$

Additional differential equations may be required to represent the thermodynamics although we omit those for the present. The rate expression for species  $i$ ,  $F_i$ , is composed of the source and sink terms from each elementary reaction in the mechanism, i.e.

$$\begin{aligned} F_i(\mathbf{X}) &= F_i^{source}(\mathbf{X}) - F_i^{sink} \\ &= \sum_j^{sources} v_{i,j} R_j(\mathbf{X}) - \sum_j^{sinks} \bar{v}_{i,j} R_j(\mathbf{X}) \end{aligned} \quad (4.3)$$

where the elementary rate law for reaction  $j$  is  $R_j(\mathbf{X})$ . The coefficients,  $v_{i,j}$  and  $\bar{v}_{i,j}$ , enforce elemental mass conservation for the balanced chemical equation associated with each reaction, i.e.

$$\sum \bar{v}_{i,j} S_i \rightleftharpoons \sum v_{i,j} S_i \quad \text{reaction } j \quad (4.4)$$

The total reaction mechanism is described by  $L$  elementary reaction steps, of the form (4.4), where the rate laws  $R_j(\mathbf{X})$  are parametrized by the rate coefficients  $k_i$ ,  $i = 1, \dots, L$ . In a typical application of sensitivity analysis, one imagines that these rate coefficients are variable over a range  $\Delta k_i$ . This range of variation may be due to an actual uncertainty in our knowledge of  $k_i$  or may simply be introduced as a formal tool in the analysis of the chemical network.

### 4.3.1 Sum over Histories Representation

In the sum over histories representation, the solution to the kinetics problem is expressed in terms of a sum over chemical pathways that relate an initial condition at  $t = 0$  to some final target observable at time  $t$ . A pathway is specified through a sequence of chemical species  $S_0, S_1, \dots, S_n$  where the product of one reaction is the reagent for the next by means of an elementary reaction,  $R_i$ , i.e.,  $S_{i-1} \xrightarrow{R_i} S_i$ . We have adopted a followed-atom approach in which a given atom (or, more generally, a stable chemical moiety, or even a "hypothesized" atom) is used to specify the paths. Thus, we take a single molecule perspective in which the chemical moiety hops discretely from one



species to the next due to the action of the elementary reactions. The sum over histories method consists of the following practical steps:

- (1) Find the most important chemical pathways for the problem at hand.
- (2) Find the probabilities for each path.
- (3) Combine the probabilities for the pathways to form the observable.

The method is quantitative and the chemical kinetics (i.e., concentrations versus time) can be converged by including the contributions from more and more paths. The details of these steps are now briefly reviewed.

The important chemical pathways may be enumerated in one of several ways. In a brute force approach, the chemical pathways can be identified and roughly ranked in importance using a small stochastic simulation using an ensemble of Monte Carlo trajectories in which a sample of molecules are followed through the network. Unlike the more common applications of stochastic simulation methods, the present approach follows a single tagged atom from reactants to the target species.[112, 51, 48, 54] The pathways that are followed by the most molecules are then used for the representation. Alternatively, we may generate the paths using a graph theoretic enumeration procedure. In the language of graph theory, the species are vertices (or nodes) and the reactions connecting them are edges and the chemical pathways are n-step paths on the graph. Because the reactions have a direction the graph is directed and if more than one edge connects two vertices it is a multigraph. The edges of the graph are weighted by the kinetic flux for the product formation due to the edge reaction. Search algorithms may be employed to identify the most probable pathways on the weighted graph.

The next task is to compute the probability for a general pathway consisting of n-reactions and n + 1 species, i.e.,  $S_0 \xrightarrow[R_1]{t_1} S_1 \xrightarrow[R_2]{t_2} S_2 \cdots S_{n-1} \xrightarrow[R_n]{t_n} S_n$ , where the reactions obey the time ordering  $t_f > t_n > \cdots t_1 > t_0$ . Because the occurrence of each reaction constitutes a random event, we must integrate the probability density over all allowed times consistent with the time ordering. To find the probability for a given pathway, it is convenient to define the species survival probability,

$\mathcal{P}_{S_i}(t_a, t_b)$ , which is the probability that species  $S_i$  undergoes no reaction in the general time interval  $(t_a, t_b)$  where  $\mathcal{P}_{S_i}(t, t) = 1$ . Using the rate equations, the survival probability for any species  $S_i$  is obtained by integrating the species decay probability computed from the totality of sink reactions, defined in eqn. 4.4

$$\begin{aligned}\mathcal{P}_i(t_a, t_b) &= \exp\left(-\int_{t_a}^{t_b} \sum_j^{sinks} A_{i,j}(t) dt\right) \\ &\equiv \exp\left(-\int_{t_a}^{t_b} A_i(t) dt\right)\end{aligned}\tag{4.5}$$

where we abbreviate the subscript of P as i instead of  $S_i$  for brevity. The quantities  $A_{i,j}(t)$  are similar to a pseudo-first-order rate coefficients (with dimension 1/time) and are defined by the time-dependent expression

$$A_{i,j}(t) \equiv \frac{\bar{v}_{i,j} R_j(\mathbf{X})}{X_i(t)}\tag{4.6}$$

where i labels the species and j labels the reaction. The concentrations  $\mathbf{X}(t)$  are evaluated along the solution to eqn. 4.2. A second useful quantity is the time-dependent branching ratio,  $\Gamma_i(t)$ , which measures the fraction of the reactive flux that follows the correct pathway branch when species  $S_i$  reacts to form products. The branching ratio is simply the reactive flux along the correct Jth branch divided by the total reactive flux of species  $S_i$ , i.e.

$$\Gamma_i(t) \equiv \frac{A_{i,J}(t)}{A_i(t)}\tag{4.7}$$

In this notation we drop the explicit J-index on  $\Gamma$ . Given these expressions, we have shown that the pathway probability can be written as an integral of a time ordered product[11, 118]

$$\begin{aligned}P_{path}(t_0, t) &= (-1)^n \int_{t_0}^{t_f} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_2} dt_1 \\ &\quad \prod_{i=1}^n \left( \frac{d\mathcal{P}_{i-1}(t_{i-1}, t_i)}{dt_i} \Gamma_{i-1}(t_i) \right) \mathcal{P}_n(t_n, t)\end{aligned}\tag{4.8}$$

This multidimensional integral can be numerically evaluated using a Monte Carlo integration scheme that is particularly efficient for long paths. In this method, a random number  $y_0$  is first chosen for species  $S_0$  in the interval  $(P_{min}^0(t_0), 1)$  where  $P_{min}^0(t_0) = \mathcal{P}_0(t_0, t)$  is the minimum of the survival probability of  $S_0$  that occurs at  $t$ . Then,  $y_0 = \mathcal{P}_0(t_0, t_1)$  is inverted to obtain  $t_1$ , the time

of the reaction  $R_1$ , which is used in eqn. 4.7. Then, for species  $S_1$  a second random number,  $y_1$ , is chosen in the interval  $P_{min}^1(t_1)$ ; as before, the reaction time  $t_2$  is obtained and branching ratio  $\Gamma_2$  is computed. This process is continued for all the followed-atom containing species along the pathway, which thus requires a string of  $n$  random numbers. We have for the final MC expression

$$P_{path}(t_0, t) = \frac{1}{N} \sum_{q=1}^N \mathcal{P}_n(t_n^q, t) \prod_{k=1}^n \left( \Gamma_{k-1}(t_k^q) \left( 1 - P_{min}^{k-1}(t_k^q) \right) \right) \quad (4.9)$$

where the index  $q$  is used to specify each string of  $n$ -random numbers.

The final step in the method is to combine the pathway probabilities to obtain the desired observable. Most observables of interest can be expressed in terms of the chemical concentrations. Thus, we describe how to compute the concentration of some species  $S_i$  at a time  $t_f$ ,  $X_i(t_f)$ , given the initial conditions  $\mathbf{X}(t)$  at time  $t_0$ . We follow a specific atom found in  $X_i(t_f)$  that may potentially originate from one of several initial species,  $S_k$ , each of which may contain more than one chemically equivalent followed atom, viz.  $\mu_k$ . The pathways are labeled by  $m_k$  where  $k$  specifies the species of origin for the path of the followed atom. The probability of the atom following pathway  $m_k$  from initial species  $S_k$  arriving at the target species  $S_i$  at time  $t_f$  is given by  $P_{m_k}(t_f)$ . Then the concentration of  $S_i$  is given by

$$X_i(t_f) \cdot \mu_i = \sum_{m_k} X_k(t_0) P_{m_k}(t_f) \cdot \mu_k \quad (4.10)$$

where we define  $X_i$  to be the concentration of species  $S_i$ . Each chemically equivalent followed atom in a reagent species is sampled equally and the sum of all probabilities for a given followed atom is 1, and thus,  $\sum_{m_k} P_{m_k}(t) = 1$ , at any time  $t > t_0$ .

#### 4.3.2 Sensitivity Analysis

In sensitivity analysis, we define a target observable,  $\tau$ , that is computed using solutions to the kinetics equation eqn. 4.2 and is a function of the variable factors. Examples of  $\tau$  might be the concentration of a species  $S_i$  at a specific time or the ignition delay time in a combustion problem. To be explicit, we shall consider the variable factors to be the L rate coefficients,  $k_i$ , and we assume

the initial conditions of the reaction are fixed. Thus, we have a well defined target function

$$\tau = \tau(k_1, \dots, k_L) \quad (4.11)$$

The local variation of  $\tau$  with respect to  $k_i$  in the vicinity of the nominal mechanism,  $\mathbf{k}_0$ , is measured by the derivative  $\partial\tau/\partial k_i$ . A dimensionless local sensitivity index may be defined using the form

$$s_i = \left. \frac{\partial \ln(\tau)}{\partial \ln(k_i)} \right|_{\mathbf{k}=\mathbf{k}_0} \quad (4.12)$$

or through the normalized expression

$$w_i = \left. \frac{\left| \frac{\partial \tau}{\partial k_i} \right|}{\sqrt{\sum_j \left( \frac{\partial \tau}{\partial k_j} \right)^2}} \right|_{\mathbf{k}=\mathbf{k}_0} \quad (4.13)$$

If the factors  $k_i$  enter eqn. 4.11 in a highly nonlinear fashion, or if ranges  $\delta k_i$  are large, then it is advisable to analyze the kinetics using Global Sensitivity Analysis.[121, 28, 29, 114, 165, 166, 158, 132, 136] The global sensitivity analysis is carried out using the analysis of variance (ANOVA)[144] strategy with the aid of the high dimensional model representation (HDMR).[126, 100, 102, 175, 174, 172, 141, 80, 31, 169] The global sensitivity index for rate coefficient  $k_i$  is then given by the ratio of the partial variance to the total variance of the target function, i.e., the main effect

$$W_i = \frac{\sigma_i^2}{\sigma_T^2} \quad (4.14)$$

The total variance is given by  $\sigma_T^2 = \langle \tau^2 \rangle - \langle \tau \rangle^2$  where the bracket indicates an average over the uncertainty hypercube in the L-dimension rate coefficient space. The partial variance is obtained using the HDMR expansion

$$\tau(k_1, k_2, \dots, k_N) = \tau_0 + \sum_{i=1}^L F_i(k_i) + \sum_{i>j}^L G_{i,j}(k_i, k_j) + \dots \quad (4.15)$$

where  $\tau_0 = \langle \tau \rangle$ . Because it can be shown that  $\langle F_i \rangle = \langle F_i F_j \rangle_{i \neq j} = \langle G_{i,j} \rangle = \langle F_i G_{n,m} \rangle = \dots = 0$  if the component functions are expanded using orthogonal polynomials, then the partial variance at first-order is given by

$$\sigma_i^2 = \langle F_i^2 \rangle \quad (4.16)$$

The L component functions,  $F_i(k_i)$ , are obtained using a least-squares fitting of a Legendre expansion,  $F_i(k_i) = \sum_{j=1}^n c_j P_j(k_i)$ . Similarly, the higher order component functions are obtained using the product form, e.g.,  $G_{i,j}(k_i, k_j) = \sum_{i',j'}^n c_{i',j'} P_{i'}(k_i) P_{j'}(k_j)$ . Thus, the uncertainty hypercube is randomly sampled using a large number M of Monte Carlo values,  $(k_1, \dots, k_L)_l$ ,  $l = 1, \dots, M$ , for which  $\tau$  is computed, and this sample is used to determine all of the component functions. The HDMR expansion is carried out to higher and higher order until the predicted variance is sufficiently close to the exact variance obtained from the data set. Thus, if the expansion in first-order component functions  $F_i$  proves inadequate, then some or all the second-order terms,  $G_{i,j}$ , are included, which then incorporates part of the interaction between the factors  $k_i$ . An advantage of global sensitivity analysis over local sensitivity analysis is that the global index not only reflects the response of the target to variation of the factors but also accounts for the size of the uncertainty range of the factors. Thus, a large global sensitivity coefficient suggest that an improved measurement of  $k_i$  could lead to a large reduction in the overall uncertainty of the model.

In the present work, we shall focus on the most basic set of target functions of the rate coefficients, viz. the  $S_i$  species concentration at time t, i.e.,  $\tau = X_i(t)$ . The sensitivity indices are obtained by simply solving the differential eqn. 4.2 from fixed initial conditions,  $\mathbf{X}(t = 0)$  while varying  $k_j$ 's. These quantities are a probe of the speciation of the reaction network which may, under some circumstances, be directly measured in experiments.

The target functions  $X_i(t)$  are among many examples of kinetic observables that can be written as linear combinations of the contributions of separate chemical pathways via

$$\tau = \sum_i c_i p_i \quad (4.17)$$

In eqn. 4.17,  $p_i$  are the pathway probabilities and the constants  $c_i$  do not depend explicitly on  $p_i$ . From eqn. 4.10 we see that for speciation the  $c_i$ 's are given by the initial concentrations and the stoichiometric coefficients and do not depend on the rate coefficients. Hence the sensitivity of this target to the  $k$ 's is carried totally by the pathway probabilities themselves.

#### 4.4 Sensitivity Analysis of Hydrogen Combustion Chemistry

The combustion of hydrogen is often chosen as a model system to investigate the performance of new chemical kinetic techniques. Though the chemistry of this problem is fairly simple by the standards of combustion kinetics, it exhibits most of the generic features seen in the burning of more complicated fuels while at the same time being describable by a manageable small mechanism. The  $\text{H}_2\text{-O}_2$  system is described here by a model consisting of 19 reversible reactions (plus two duplicate reactions) and 8 distinct chemical species. The reactions and species are labeled using a numbering scheme defined in Table 4.1 and Table 4.2. The corresponding rate coefficients and uncertainty ranges are provided in the Appendix C. The simulations were carried out using a stoichiometric mixture of pure  $\text{H}_2\text{-O}_2$  at an initial temperature of  $T = 1000$  K and an initial pressure of  $p = 5.62$  bar. The calculations were carried out while the volume and total energy were kept fixed. Under these conditions, the mixture exhibits ignition at  $\tau_{ign} = 3.4$  ms. To illustrate the general behavior

Table 4.1: Species Labeling of  $\text{H}_2\text{-O}_2$  system.

Species Index	Species Name
0	$\text{O}_2$
1	$\text{H}_2\text{O}$
2	$\text{H}_2$
3	$\text{H}_2\text{O}_2$
4	$\text{H}$
5	$\text{OH}$
6	$\text{HO}_2$
7	$\text{O}$

<sup>†</sup>Indices start at 0.

of the kinetics, the concentrations versus time are plotted on a logarithmic scale in Fig. 4.1. It is seen that the radical pool shows a steady increase until it spikes upward at the ignition time,  $\tau_{ign}$ . For the present work, we shall consider the sensitivity exhibited by the chemistry for times before  $\tau_{ign}$ . The highly reactive radicals  $\text{O}$ ,  $\text{H}$ , and  $\text{OH}$  are seen to be roughly in steady state for a significant fraction of the time shown. The concentration of the hydroperoxy radical,  $\text{HO}_2$ , is seen

Table 4.2: Reaction Labeling of  $\text{H}_2\text{-O}_2$  system. The backward reactions, where the right-hand side is the reagent, are denoted with an \* in the text; i.e., R17\* denotes  $\text{HO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}$  and R17 denotes  $\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{HO}_2 + \text{H}_2$ .

Species Index	Species Name
0	$\text{H} + \text{O}_2 = \text{O} + \text{OH}$
1	$\text{O} + \text{H}_2 = \text{H} + \text{OH}$
2	$\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$
3	$\text{O} + \text{H}_2\text{O} = \text{OH} + \text{OH}$
4	$\text{H}_2 + \text{M} = \text{H} + \text{H} + \text{M}$
5	$\text{O} + \text{O} + \text{M} = \text{O}_2 + \text{M}$
6	$\text{O} + \text{H} + \text{M} = \text{OH} + \text{M}$
7	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$
8	$\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$
9	$\text{HO}_2 + \text{H} = \text{H}_2 + \text{O}_2$
10	$\text{HO}_2 + \text{H} = \text{OH} + \text{OH}$
11	$\text{HO}_2 + \text{O} = \text{O}_2 + \text{OH}$
12	$\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$
13	$\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$
14	uplicated reaction
15	$\text{H}_2\text{O}_2 (+\text{M}) = \text{OH} + \text{OH} (+\text{M})$
16	$\text{H}_2\text{O}_2 + \text{H} = \text{H}_2\text{O} + \text{OH}$
17	$\text{H}_2\text{O}_2 + \text{H} = \text{HO}_2 + \text{H}_2$
18	$\text{H}_2\text{O}_2 + \text{O} = \text{OH} + \text{HO}_2$
19	$\text{H}_2\text{O}_2 + \text{OH} = \text{HO}_2 + \text{H}_2\text{O}$
20	uplicated reaction

<sup>†</sup>Indices start at 0.

to exhibit substantially more time variation than the other radicals. In this preignition phase of the reaction, the contributions from some of the more important elementary reaction steps are shown in Fig. 4.2 where we plot the logarithm of the instantaneous rates versus time. We note in particular the behavior of reactions R13 ( $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ ) and R17\* ( $\text{HO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}$ ), which are both sink reactions for  $\text{HO}_2$  and source reactions for  $\text{H}_2\text{O}_2$ . (The asterisk indicates the backward reaction in Table 4.2.) There is clearly a crossover behavior where the abstraction path (R17\*) is largest at short times and the radicalradical disproportionation reaction (R13) becomes larger at longer times. We also notice that the rate for R15 ( $\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{OH} + \text{M}$ ), which is an important sink for  $\text{H}_2\text{O}_2$ , crosses that for both R13 and R17\*. We also show, in Fig. 4.3, the behavior of the species decay rate (defined as  $A_i(t)$  in eqn. 4.5) for all eight species versus time. It is seen that the chemical lifetimes of the key species  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$  are on the order of  $10^{-3}$  s, which is comparable to the ignition time itself.

The global sensitivity indices for the speciation targets  $\tau = X_i(t)$  for  $i = 18$  were computed at

Figure 4.1: Concentrations versus time obtained from the combustion simulation. The simulation was carried out at  $T=1000$  K,  $p=5.62$  bar, and  $\Phi=1$ . No buffer was present and the reaction occurred in a constant volume and constant energy. We set  $\tau$  to be the ignition delay time.

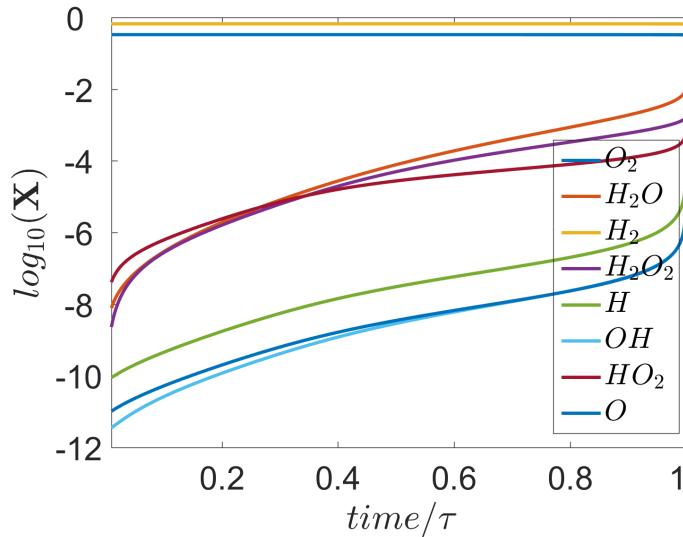




Figure 4.2: Rates of the most important reactions versus time in units of the ignition time. The reaction index is defined in Table 4.1 and the \* notation indicates a backward reaction.

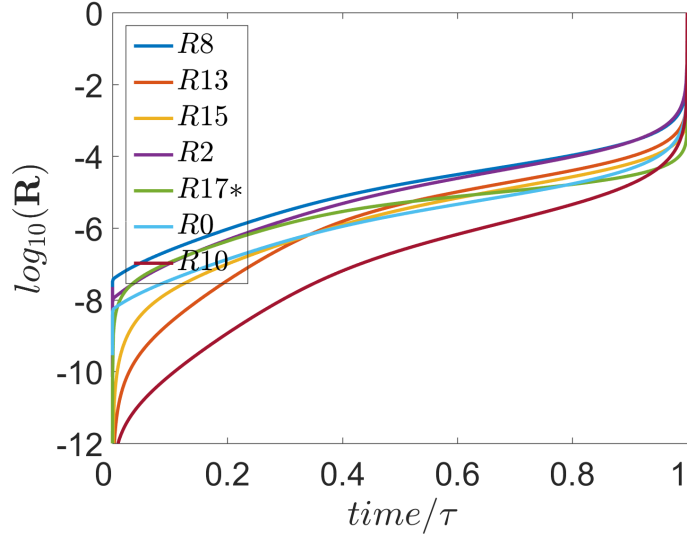
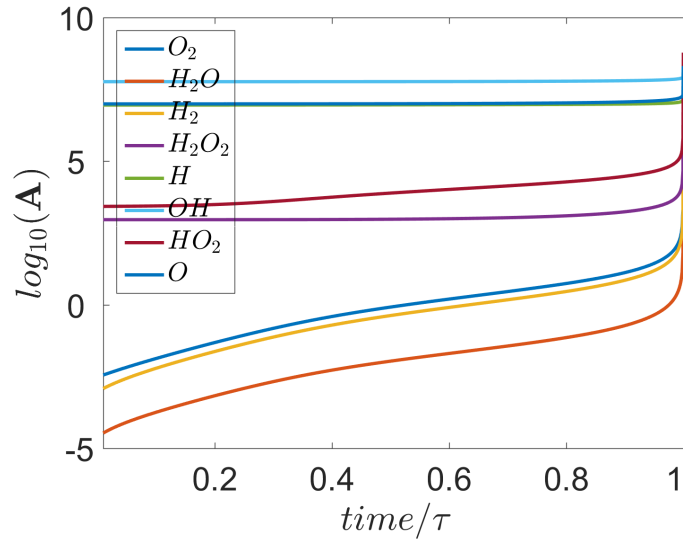


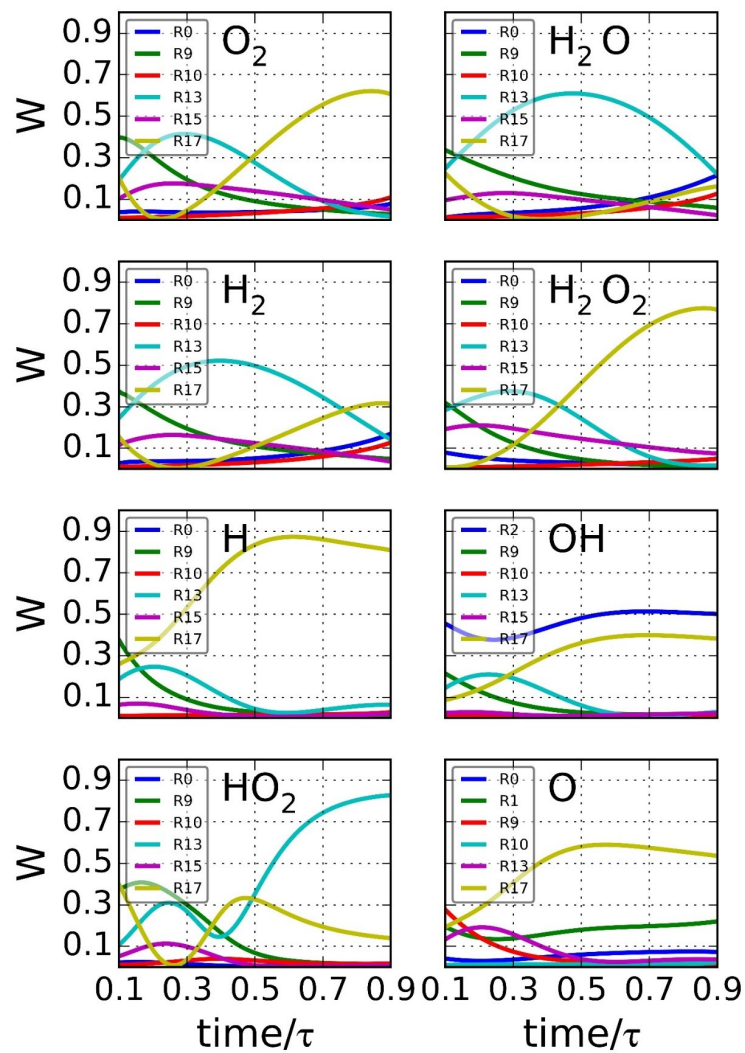
Figure 4.3: Species decay rate, i.e., the sum of the rates of all the sink reactions, plotted versus time for all eight species.



a grid of times between  $t = 0$  and the ignition time,  $\tau_{ign}$ . These computations employed numerical solutions of the kinetic rate equations, eqn. 4.2, with rate coefficients randomly selected from within their uncertainty ranges. For rate coefficients of the form  $k(T) = AT^\delta \exp(-E_a/(RT))$ , this sampling is accomplished by varying the value of the pre-exponential factor  $A$ . The rate coefficients reverse reactions are set by detailed balance and thus are not independent from the forward rates. We note that the sensitivity index for a forward reaction, such as R17, is thus exactly equal to that for the backward reaction, R17\*, regardless of the value of the reactive flux in the forward and backward directions. Using 5000 sets of random rate coefficients, the HDMR component functions  $F_i(k_i)$  from eqn. 4.15 were fit by regression to fifth-order expansions in Legendre polynomials in a single fitting procedure consisting of  $19 \times 6 = 114$  parameters. As in our previous work, the sensitivity indices were then obtained by integration using eqn. 4.10.[141, 80, 31, 169] In Fig. 4.4 we show the sensitivity indices  $W_i$  versus time for all 8 species. For clarity, we have included in the plot only the most important reactions. It is seen that reactions R17, R15, R13, R9, and R0 have consistently the highest values of  $W_i$ . We note that reactions R17, R13, and R9 involve the production and destruction of the  $\text{HO}_2$  radical, which is known to play an important role in determining the ignition properties of  $\text{H}_2$  and other fuels.[163, 78, 77] Reactions R17, R15, and R13 also involve the  $\text{H}_2\text{O}_2$  species, which is also important in the generation of the radical  $\text{OH}$ . [95, 171] Reaction R0,  $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ , is well-known to be a critical chain branching step in all combustion reactions. Here, R0 is seen to be particularly important for the formation of  $\text{OH}$  radicals. The species  $\text{O}$  is unique in being the only target that is significantly sensitive to the reaction R1,  $\text{O} + \text{H}_2 = \text{OH} + \text{H}$ .

Despite differences in the shape of the sensitivity curves for the various species, there is actually a significant amount of similarity in overall behavior of the results. All the species exhibit large values at early times for the initiation reaction  $\text{H}_2 + \text{O}_2 = \text{HO}_2 + \text{H}$  (R9), which then falls off sharply at later times. This is understandable because reaction R9 is the main initiator for autoignition but is not important for chain propagation and chain branching. During the later stages of the reaction,  $t \geq 0.4\tau_{ign}$ , reactions R17 ( $\text{HO}_2 + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$ ) and R13 ( $\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 +$

Figure 4.4: Global sensitivity index  $W$  for the speciation targets  $[X_i(t)]$  versus time. The results shown are restricted to the most sensitive reactions for each case.



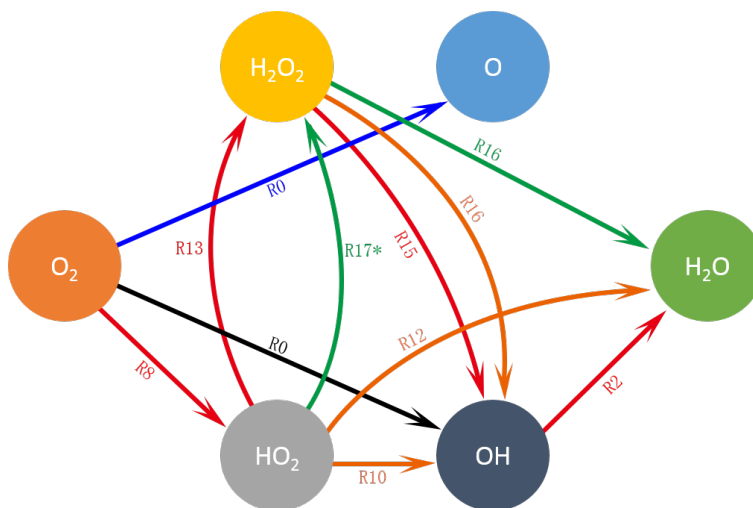
O<sub>2</sub>) usually carry the largest sensitivities, as occasionally does R15 ( $\text{H}_2\text{O}_2 + \text{M} = \text{M} + 2\text{OH}$ ). It is interesting to note for many targets we see a trend where  $W_{17}$  is more sensitive at earlier times but then is surpassed by  $W_{13}$ , which grows larger at later times. For all species except H and O, there is a crossover where  $W_{17} > W_{13}$  at short times but then  $W_{13} > W_{17}$  at longer times. That the sensitivity coefficients of the different species in a large model behave similarly has been noted previously by Skodje and Davis<sup>51</sup> and Turanyi et al;<sup>[176]</sup> this behavior is related to the fact that the kinetics tends to rapidly approach a low-dimensional manifold in which the species concentrations are slaved to one another. The equivalence between the different sensitivity plots is only qualitative in the present case because for global analysis the different values of the uncertainty ranges,  $\Delta k_i$ , introduces quantitative differences between the various  $W_i$ . This can be appreciated by noting that global sensitivity index can be crudely approximated by  $W_i \approx \left| \frac{d[X(t)]}{dk_i} \times \Delta k_i \right|$ , where  $\mathbf{X}(t)$  is the species concentration computed using the nominal (unperturbed) rate coefficients. Thus, clearly, the relative values of  $W_i$  can be adjusted using the externally provided uncertainty ranges.

#### 4.5 Description of Chemical Pathways for H<sub>2</sub>-O<sub>2</sub> Combustion

When the species target functions are expressed as linear combinations  $\tau = \sum_i c_i p_i$ , the sensitivity of  $\tau$  to  $\mathbf{k}$  can be understood in terms of the behavior of the pathway probabilities. Hence, we must first determine a sufficient number of chemical pathways and their probabilities to converge the speciation targets of interest,  $X_i(t)$ . Then, we investigate the  $\mathbf{k}$  dependence of the probabilities. In our previous work, we studied the early stage combustion of hydrogen using an H atom following scheme. It was found that convergence of the concentrations to within several percent was obtained using about a dozen chemical pathways. Here, we reexamine the pathway representation using, instead, O atom following pathways. Although convergence to the exact result may be obtained by following any moiety present in the target species, the choice of followed atom may affect the efficiency of the algorithm. In the present case, we find that O atom following converges significantly faster than H atom following. For reference, in Fig. 4.5 we show the full graph that shows all species (nodes) and the most important reactions (lines) that contribute to

the present mechanism. The O atom following pathways lie on the subgraph containing only the oxygen possessing species.

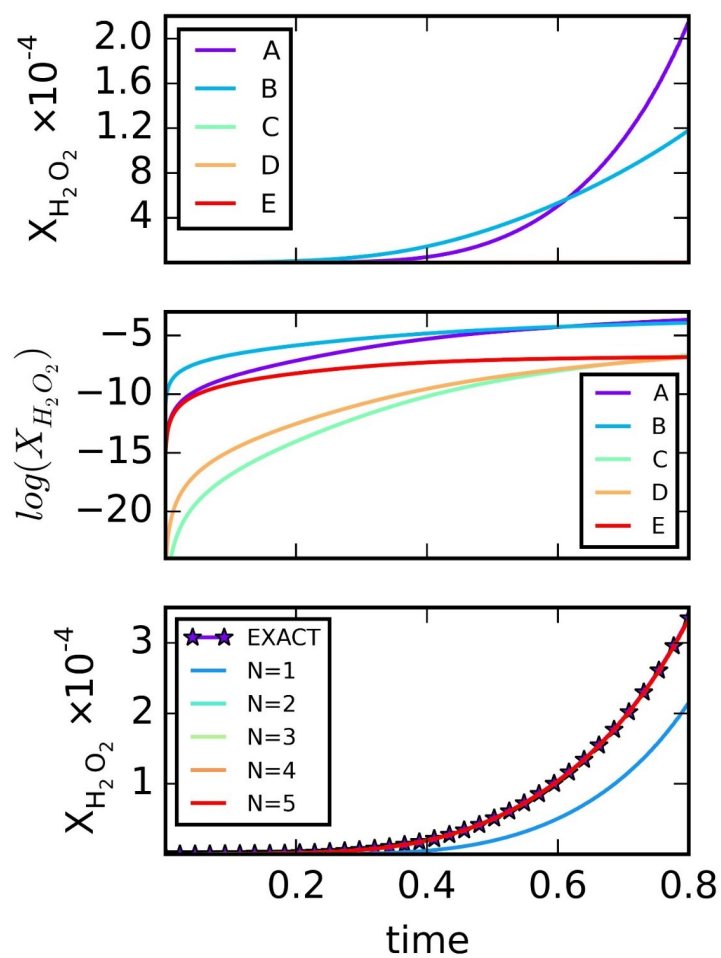
Figure 4.5: Graph representing all species and the most important reactions for the  $\text{H}_2\text{-O}_2$  system by following Oxygen atom.



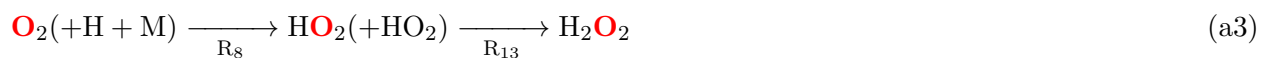
To identify a set of candidate pathways for study, we first use a small size stochastic simulation, i.e.,  $10^5 - 10^6$  simulated paths, computed at the nominal value of  $\mathbf{k}$ . Thus, during a time interval  $\Delta t$ , a given molecule of  $S_i$  has a decay probability of  $A_i(t)\Delta t$ . Using one random number to sample this decay, and a second random number to select a product branch  $j$ ,  $\Gamma_j(t)$ , a given O atom is then followed through the network one node (species) at a time. Recording each pathway that occurs, an approximately ordered set of candidates is produced that describes the passage of a followed atom to a given target. For the present problem, typically about 100 pathways were identified in this way, although many fewer were needed to converge the targets. Although this calculation is not efficient enough to compute accurate pathway probabilities, it does yield the important pathways for high level computation using eqn. 4.8 or 4.9. Because the ordering of the pathway probabilities will be a function of  $\mathbf{k}$ , we retain some of the smaller probability pathways because they may become larger in certain regions of  $\mathbf{k}$ -space.

We begin by showing the most probable pathways for the creation of several important target

Figure 4.6: Pathway probabilities for  $\text{H}_2\text{O}_2$ . In the upper panel, the probabilities for the five most important pathways, ranked at time  $t = 0.8\tau_{ign}$ , are shown versus time in units of  $\tau$ . In the middle panel, the same probabilities are reproduced on a logarithmic scale. In the lower panel, the convergence of the concentration to the exact simulation result is shown; it is seen that probability converges to good accuracy with just two paths.



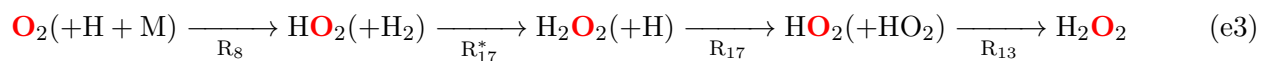
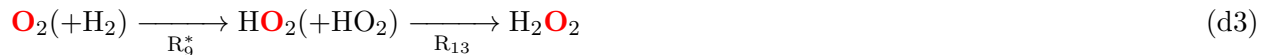
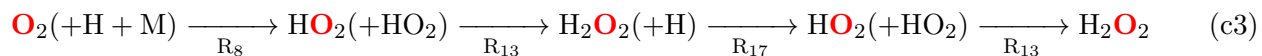
species. Consider first the formation of the transient intermediate  $\text{H}_2\text{O}_2$  which was used as a test case in our previous work. Although we see from Table 4.2 that there are six elementary reactions that generate  $\text{H}_2\text{O}_2$ , we find that just two chemical pathways are sufficient to converge  $[\text{H}_2\text{O}_2]$  to within 1% at times in the range  $0 < t < 0.9\tau_{ign}$ . In Fig. 4.6 we show the pathway probabilities for these paths, along with the prediction for  $[\text{H}_2\text{O}_2(t)]$ . Many more paths were required to converge the results using the H atom following algorithm. The two dominate chemical pathways for the formation of this species are path a3 (where a means the most probable pathway and 3 indicates that  $\text{H}_2\text{O}_2$  is species 3 in Table 4.1)



and path b3 (b for the second most probable pathway, etc.)



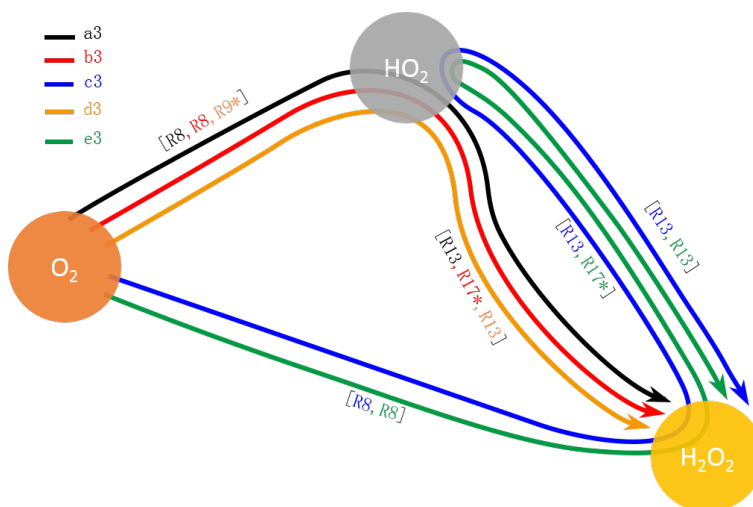
In the chemical pathway formulas, we indicated the followed atom in red, the nonfollowed reagents are in parentheses, and the nonfollowed products are dropped from the equation. We can see by the figure that the pathway probabilities for  $\text{H}_2\text{O}_2$  formation show a crossover behavior where the path involving  $\text{R}_{17}^*$  is largest at short times whereas the path containing  $\text{R}_{13}$  is larger at long times. The remaining pathways we computed were lower in probability by factors of 100 or more. The next three pathways are



It is interesting to note that pathways c3 and e3 are quite closely related to the main pathways a3 and b3. We see that in mechanism c3, the  $\text{H}_2\text{O}_2$  is formed along pathway a3 but then is recycled

back to  $\text{HO}_2$  by H atom attack, , only then to regenerate  $\text{H}_2\text{O}_2$  by radicalradical recombination, R13. In mechanism e3, we see the same scenario except the initial  $\text{H}_2\text{O}_2$  molecule is generated by path b3. In mechanism d3, the  $\text{H}_2\text{O}_2$  is formed by radical recombination R13 but the followed species  $\text{HO}_2$  is generated by the initiation reaction R9, i.e.,  $\text{H}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{H}$  rather the higher flux reaction R6. For reference, we indicate the contributing pathways on the O atom subgraph in Fig. 4.7.

Figure 4.7: Graph for the oxygen following paths, a3 - e3, leading to the  $\text{H}_2\text{O}_2$  product.



For the  $\text{H}_2\text{O}$  product species (species 1 in Table 4.1), we find that there are more contributing pathways than for  $\text{H}_2\text{O}_2$ . We find that five paths account for about 98% formation under the present conditions. The convergence of the target  $[\text{H}_2\text{O}(t)]$  versus time is shown in Fig. 4.8. The most important O atom following pathways that connect the  $\text{O}_2$  reagent to the  $\text{H}_2\text{O}$  product are

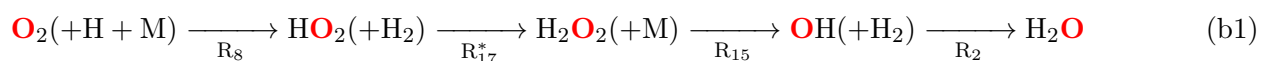
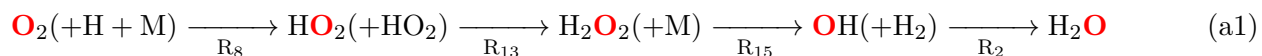
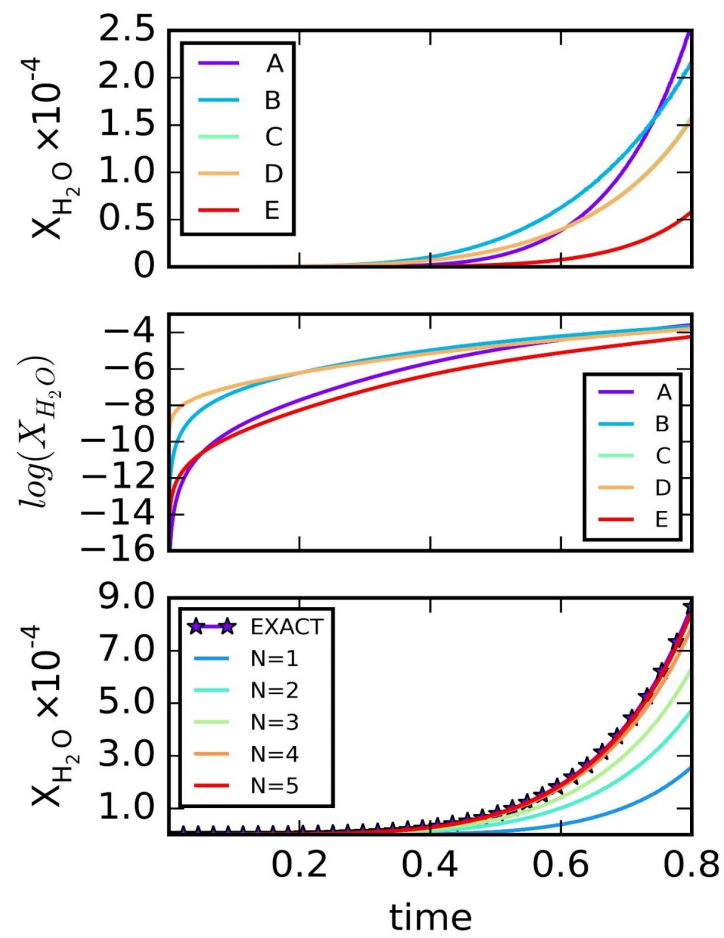
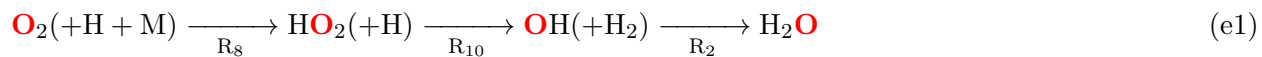
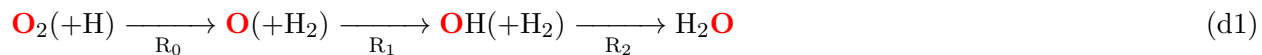




Figure 4.8: Same as Fig. 4.6 except for the target function  $[H_2O(t)]$ .





The two most probable pathways, a1 and b1, again generate an  $\text{H}_2\text{O}_2$  intermediate from  $\text{HO}_2$  radicals, which indicates that a large fraction of the  $\text{H}_2\text{O}$  product passes through this intermediate species. Indeed, the first three steps for a1 and b1 are seen to be identical to the dominate pathways for  $\text{H}_2\text{O}_2$  formation, i.e., a3 and b3. In both a1 and b1, the  $\text{H}_2\text{O}_2$  breaks down via the unimolecular dissociation reaction R15 with the resulting OH radical converted to water through the reaction R2, i.e.,  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ . From the figure, we again note a crossover behavior where path a1 (containing R13) is more probable at long times whereas path b1 (contain R17\*) is more probable at shorter times. The three next most probable pathways are mechanistically distinct from the  $\text{H}_2\text{O}_2$  forming pathways a1 and b1. It is seen in Fig. 4.8 that the contributions from c1 and d1 are nearly identical because it is clear that these paths are closely related. In these two pathways, we are tracking the separate progress of the two oxygen atoms of  $\text{O}_2$  following the initiation reaction R0, i.e.,  $\text{O}_2 + \text{H} \rightarrow \text{OH} + \text{O}$ . In the first case, c1, the OH radical from R0 reacts quickly with  $\text{H}_2$  to produce the water product in a single step, R2. Along the other path, d1, the O atom product of R0 first abstracts an H atom via R1 to form OH and then the OH reacts with  $\text{H}_2$  to form water. Because nearly all the OH is consumed to form  $\text{H}_2\text{O}$  and nearly all the O reacts with  $\text{H}_2$  to form OH, it is not surprising that the probabilities for c3 and d3 are very close. In both cases, the species containing the followed O atom quickly forms water upon reaction with  $\text{H}_2$ . Finally, pathway e5 again is initiated by formation of  $\text{HO}_2$  through the recombination reaction R8. However, in e5 the  $\text{HO}_2$  radical reacts with H via R10 to form the OH radical, which then quickly converts to  $\text{H}_2\text{O}$  by R10. The five pathways are depicted graphically in Fig. 4.9.

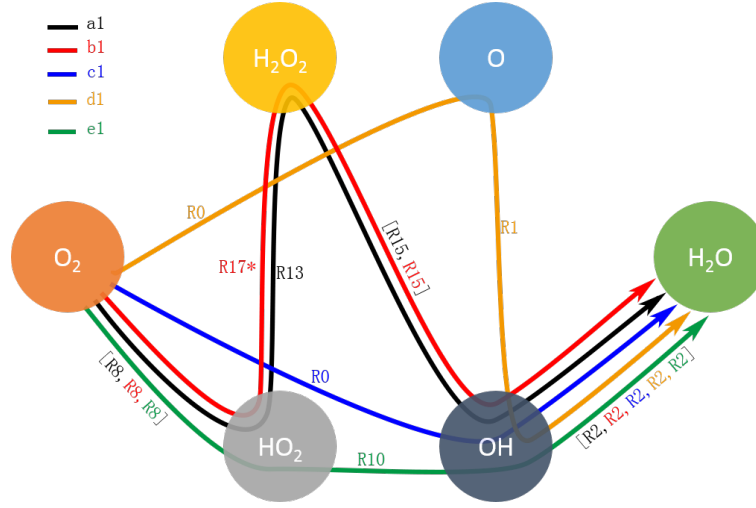
Finally, we consider the speciation of the critical  $\text{HO}_2$  radical. In Fig. 4.10, we show the relevant pathway probabilities for of the  $[\text{HO}_2(t)]$ . It is very interesting to note that one pathway carries the vast majority of the probability. Specifically, almost all of the  $\text{HO}_2$  species is generated by the

recombination mechanism

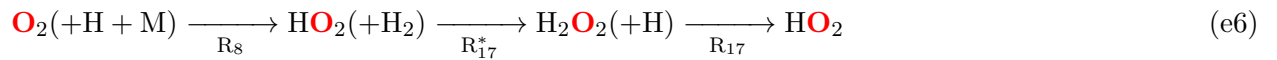
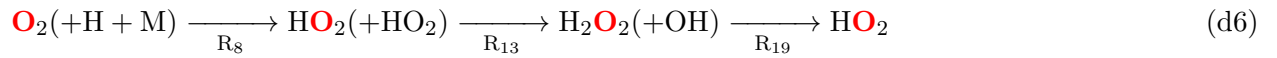
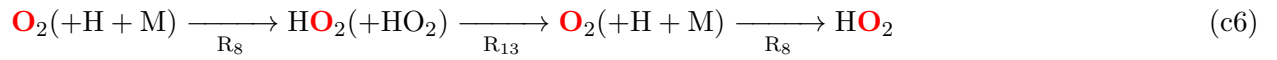
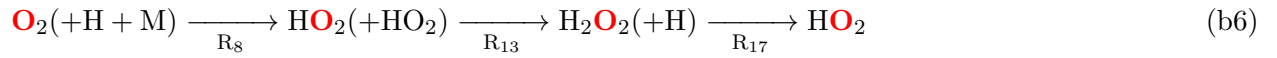


As seen in the figure, the probabilities for other production pathways are lower by at least a factor

Figure 4.9: Oxygen atom following pathways leading to the formation of the  $\text{H}_2\text{O}$  product.



of 1000. For completeness, however, we note that the algorithm does quantify the probabilities for the other minor pathways



It is seen that b6–e6 are cyclic paths. For all these pathways, the  $\text{HO}_2$  radical is first generated

Figure 4.10: Same as Fig. 4.6 except for the  $\text{HO}_2$  product.

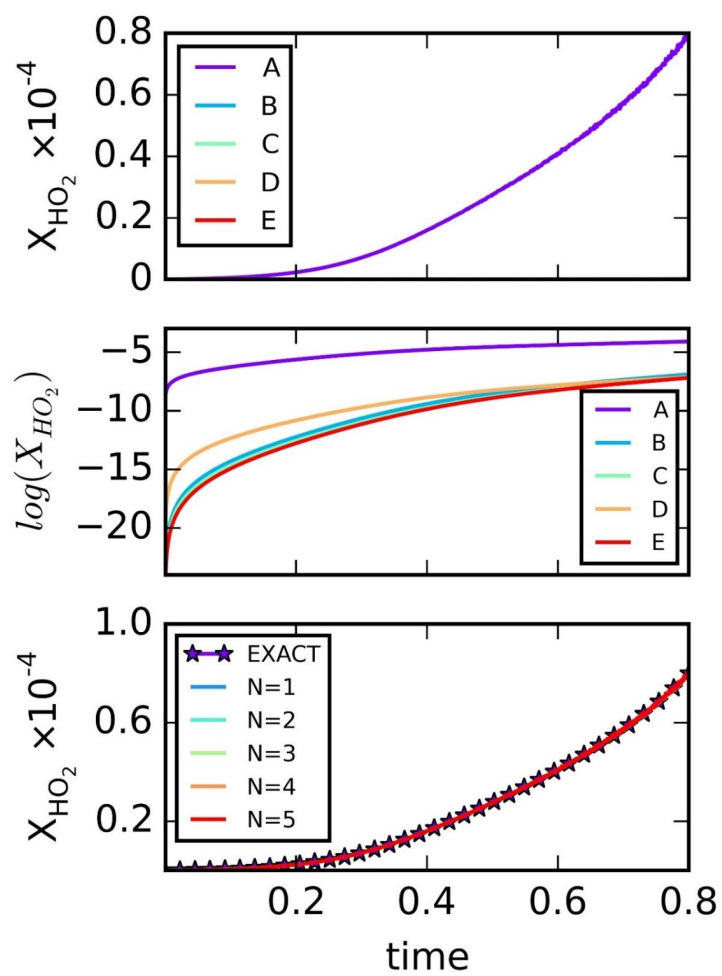
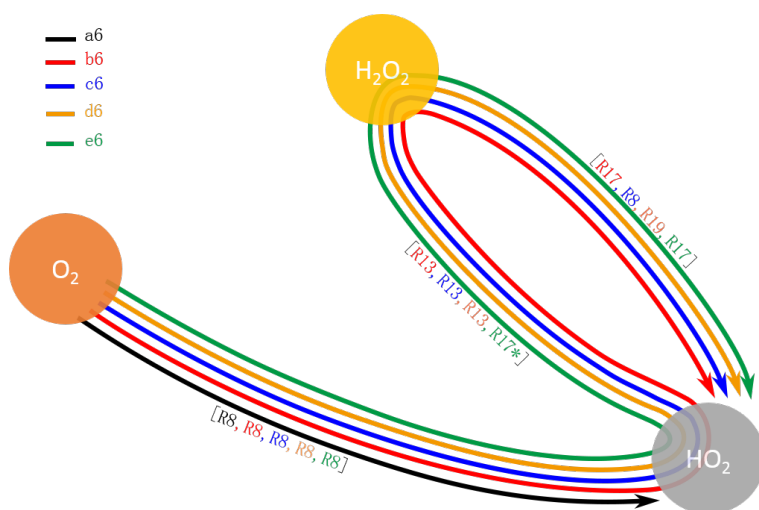


Figure 4.11: Oxygen atom following pathways leading to the formation of the HO<sub>2</sub> product.



by recombination but then reacts to form other species, such as  $\text{H}_2\text{O}_2$ , only then to regenerate the  $\text{HO}_2$  radical. These pathways are depicted in graphical form in Fig. 4.11. Because we are using O atom following, the origin of the H atom in these pathways is not specified. Obviously, the formation of H radicals does involve important rate limiting behavior for the formation of  $\text{HO}_2$ .

## 4.6 Pathway Interpretation of Sensitivity

Now that the dominant pathways that lead to various species targets have been uncovered, we can interpret the sensitivity results presented in Fig. 4.4 using the sum over histories approach via  $\tau = \sum_i c_i p_i$ . Thus, each probability  $p_i$  is a function of  $\mathbf{k}$  and has a total variance over the uncertainty range of  $\sigma_T^{i,2}$ . To quantify the global sensitivity of the pathway probabilities with respect to the individual rate coefficient  $k_j$ , we express each  $p_i$  as a first-order HDMR expansion, i.e.

$$p_i(k_1, k_2, \dots, k_L) = p_0^i + \sum_{j=1}^L F_j^i(k_j) \quad (4.18)$$

The component functions for pathway  $i$ ,  $F_j^i(k_j)$ , were expressed as fifth-order expansions in Legendre polynomials fit using linear regression from 2000 sets of rate coefficients that were randomly selected from the uncertainty range. We have verified by direct computation that the totality of the second order terms of the HDMR were small, typically on the scale of  $\sim 5\%$  of the first-order terms, although they are occasionally larger. We have also verified that there was not over-fitting of the first-order component functions. We determine the first order global sensitive coefficient for the pathway probability  $p_i$  with respect to rate coefficient  $k_j$  using the normalized partial variance

$$\begin{aligned} \widehat{W}_j^i &\equiv \frac{\sigma_j^{i,2}}{\sigma_T^{i,2}} \\ &= \frac{\langle F_j^{i,2} \rangle}{\sigma_T^{i,2}} \end{aligned} \quad (4.19)$$

which is completely analogous to eqs 4.14 and 4.16. Correlations between pathways may be gauged using the coefficients

$$\text{Corr}(i, i') = \frac{\langle p_i p_{i'} \rangle - \langle p_i \rangle \langle p_{i'} \rangle}{\sqrt{\sigma_T^{i,2} \sigma_T^{i',2}}} \quad (4.20)$$

If the first-order HDRM expansion, eqn. 4.18, is inserted into eqn. 4.20, it is seen that expressions of the following form appears.

$$W_j^{i,i'} = \frac{\langle F_j^i F_j^{i'} \rangle}{\sigma_T^{i,2} \sigma_T^{i',2}} \quad (4.21)$$

The total correlation between paths  $i$  and  $i'$  may thus be decomposed into contributions from the individual rate coefficients as

$$Corr(i, i') = \sum_{j=1}^L \widehat{W}_j^{i,i'} \quad (4.22)$$

We should note that this pathway correlation,  $Corr(i, i')$ , reflects how the change in flux along path  $i$  affects the flux along path  $i'$ ; it is not a correlation between individual reaction steps which would require a higher order HDMR expansion to model.

Although the general chemical flux in the reaction network may depend on the rate coefficients in a complicated manner, there are two scenarios that are particularly simple for interpretation. In the first, a single chemical pathway dominates the flux to the target function  $X_n(t)$ . Under these circumstances, the rate limiting step (i.e., the slowest step) to the target, and the fastest step away from the target may prove the most sensitive. For simplicity of illustration, assume that reactions along the path are described by pseudo-first-order kinetics with constant decay rates and branching ratios. The rate limiting step to the target  $X_n(t)$  is modeled by a pseudo-first-order rate law  $K_J X_J$  and the fastest decay channel for  $S_n$  is described by  $K_n X_n$ . We therefore expect the speciation target function to behave as

$$X_n(t) \approx X_0 \cdot \frac{K_J}{K_n - K_J} [e^{-K_n t} - e^{-K_J t}] \quad (4.23)$$

where  $X_0$  is a constant. This approximate expression applies at times that are long compared to the transient rates along the pathway. Clearly, the target will show strong sensitivity to the rate limiting formation step and/or the dominate decay step and only weak sensitivity to the other steps. Although this result is not surprising, it does serve to emphasize the connection between pathways and sensitivity. A different scenario occurs for pathway switching in which a sensitive rate coefficient causes the reactive flux to change paths. Consider the case where the largest flux

pathway splits into two branches (labeled a and b) that subsequently flow to the target  $X_n(t)$ . If we again assume pseudo-first-order kinetics, we have the branching ratios

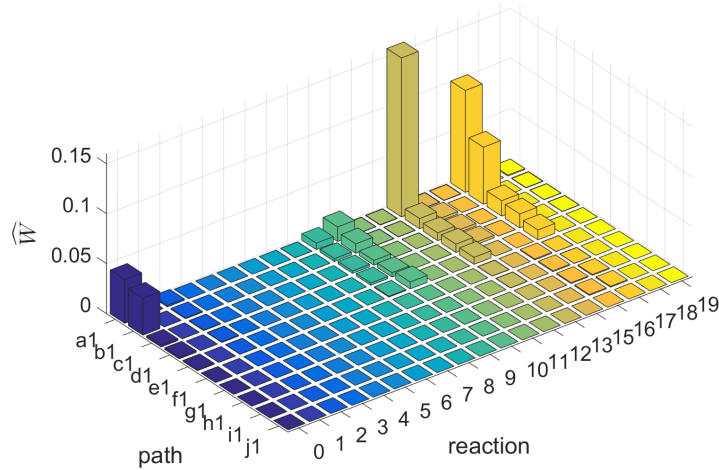
$$\begin{aligned}\Gamma_a &= \frac{k_a}{k_a + k_b} \\ \Gamma_b &= \frac{k_b}{k_a + k_b}\end{aligned}\tag{4.24}$$

where  $k_a$  and  $k_b$  are the conventional rate coefficients at the branching step. Then the contribution to the target will be roughly given by

$$X_n(t) \approx c(\Gamma_a p_a + \Gamma_b p_b)\tag{4.25}$$

where  $c$  is a constant and  $p_a$  and  $p_b$  are the probabilities for paths a and b. Thus, we expect there to be a large sensitivity of the target to  $k_a$  and  $k_b$  provided that  $p_a$  and  $p_b$  are significantly different numerically. We also predict a high level of correlation between the factors  $k_a$  and  $k_b$ .

Figure 4.12: Sensitivity indices of the pathways leading to the  $\text{H}_2\text{O}$  target concentration evaluated at  $t = 0.8\tau_{ign}$ . In this figure we plot  $F_j^{i,2}/\sigma_T^{i,2}$ , where each path has a common normalizing factor so that less probable pathway show smaller indices.



As an application, consider the  $[\text{H}_2\text{O}]$  target, which possesses the most interesting and complicated pathway representation. We focus first on a single time,  $t = 0.8\tau_{ign}$ . From the global



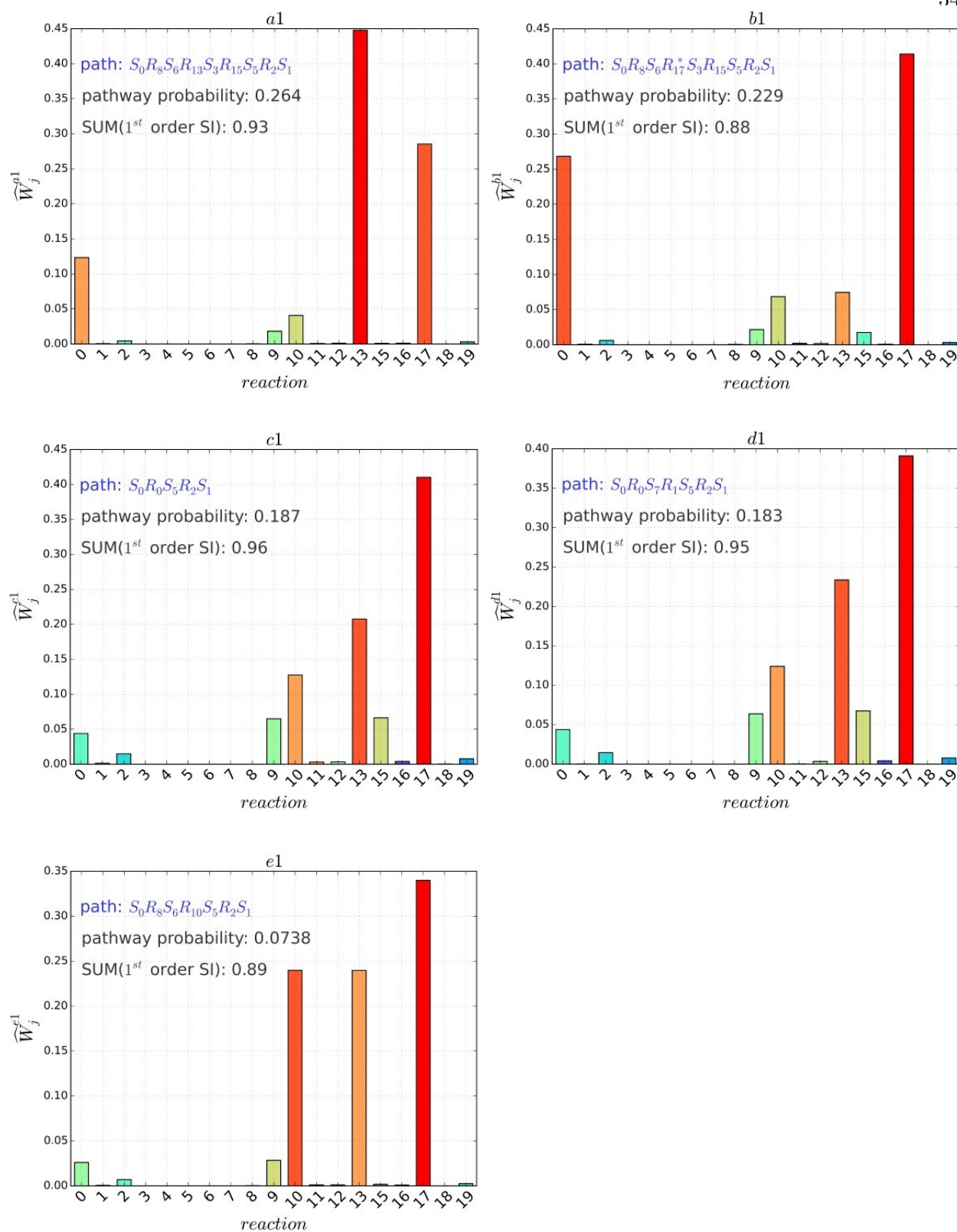


Figure 4.13: Sensitivity indices versus reaction index for the five most important paths leading to the  $H_2O$  target evaluated at time  $0.8\tau_{ign}$ . The relevant reactions for each path are reproduced on the figure panels. Also shown in each panel is the pathway probability and the sum of first-order indices obtained by the HDMR expansion of  $p_i$ .

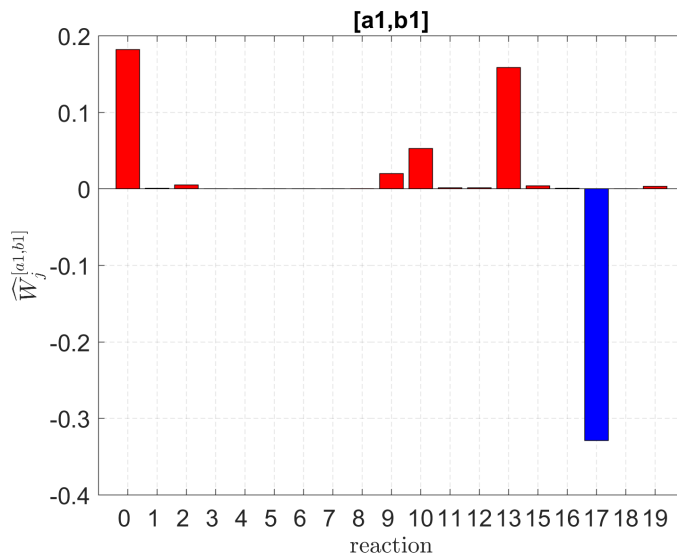
sensitivity results of Fig. 4.4, we see that the most important reactions for the H<sub>2</sub>O formation at this time are, in descending order, R13, R0, R17, R9, and R10. We can understand this pattern from the behavior of the paths. At  $t = 0.8\tau_{ign}$ , the pathway probabilities are 0.264 (a1), 0.229 (b1), 0.187 (c1), 0.184 (d1), and 0.074 (e1). In Fig. 4.12 we show the spectrum of sensitivity indices, i.e.,  $\widehat{W}_j^1$  versus  $j$ , obtained for the largest pathways ranked by order of probability. In this figure, we have plotted sensitivity indices using a common normalization factor, i.e.,  $\langle F_j^{i,2} \rangle / \sigma_T^2$  where  $\sigma_T^2$  is the total variance for all paths, so that that the less important pathways show lower indices. In Fig. 4.13 we show the sensitivity spectrum for the five most probable paths, a1e1, using the conventional normalization, eqn. 4.19. First, we note that the reactions that have the largest value of H<sub>2</sub>O target sensitivity,  $W_j$ , in Fig. 4.4 are also, on average, the most sensitive reactions for the paths leading to the target. However, we notice that the detailed distributions of  $\widehat{W}_j^1$  values differ significantly from pathway to pathway. For brevity we use the pathway superscript  $i$  going from 1–5 for pathways a1–e1. The most probable path, a1, shows strongest sensitivity to R13 and R17 with a modest contribution from R0, i.e.,  $\widehat{W}_{13}^1 > \widehat{W}_{17}^1 > \widehat{W}_0^1$ . For the second most important path, b1, the contribution from R17 is now clearly the largest, with R2 second and R13 and R10 also present, i.e.,  $\widehat{W}_{17}^2 > \widehat{W}_2^2 > \widehat{W}_{13}^2 \approx \widehat{W}_{10}^2$ . Paths c1 and d1 give a nearly identical spectrum because, as discussed in section 4.5, they are closely related physically. For those two paths, we see that  $\widehat{W}_{17}^3 > \widehat{W}_{13}^3 > \widehat{W}_{10}^3$ . For e1, we have  $\widehat{W}_{17}^5 > \widehat{W}_{13}^5 \approx \widehat{W}_{10}^5$ . We can understand the results of Fig. 4.13 from the detailed character of the chemical pathways. The pathway a1 is most sensitive to R13, which is rate limiting along this pathway. For b1, on the contrary, the reaction R17\* is most sensitive because it is rate limiting for this pathway. We note that both  $\widehat{W}_{17}^3$  and  $\widehat{W}_{13}^3$  are appreciable in both the a1 and b1 spectra due to the pathway switching mechanism. Clearly, by changing the ratio  $k_{13}/k_{17}^*$ , we will alter whether the O atom follows the a1 path or the b1 path. Indeed, inspection of the graph in Fig. 4.8 shows that a1 and b1 are identical except for the step where the HO<sub>2</sub> radical decays via  $\text{H}\text{O}_2(+\text{HO}_2) \xrightarrow{\text{R}_{13}} \text{H}_2\text{O}_2$  for a1 and via  $\text{H}\text{O}_2(+\text{H}_2) \xrightarrow{\text{R}_{17}^*} \text{H}_2\text{O}_2$  for b1. It is interesting to notice that R0,  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ , is quite important for a1 and b1 even though this step does not enter into either path. More understandably, this reaction is also

sensitive in c1 and d1, where it is the initial step. For a1 and b1, the graphs in Figs. 4.5 and 4.9 make it is easy to see that R0 is in competition with R8,  $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ , which is the initial step for a1 and b1. Thus, again the sensitivity to R0 is a case of pathway switching between (c1, d1) and (a1, b1). The pathway e1 is interesting in that the reaction R10,  $\text{HO}_2 + \text{H} \rightarrow \text{OH} + \text{OH}$ , emerged as the key step. This is consistent with the observation that the sensitivity index  $\widehat{W}_{10}^5$  for this reaction is seen to be quite large. That R13 and R17\* are also sensitive reactions again reflects the competition from those reactions for the  $\text{HO}_2$  radical and thus pathway switching.

In addition to the sensitivity indices of the pathway probabilities, we have also computed the correlations between the pathways that lead to the  $\text{H}_2\text{O}$  target. In the interest of brevity, we focus on the correlation that develops within just two pairs of pathways, (a1, b1) and (a1, c1). Using eqn. (4.21), we see in Fig. 4.14 that the largest interactions for the (a1, b1) pair,  $\widehat{W}_j^{a1,b1}$ , are due to reaction R17\*, a negative correlation, and reactions R0 and R13, positive correlations. For the (a1, c1) pair,  $\widehat{W}_{17}^{a1,c1}$ , is again the largest, with a positive  $\widehat{W}_{13}^{a1,c1}$ , the next largest but  $\widehat{W}_0^{a1,c1}$  now yielding a negative correlation. The explanation for these results can be provided by examining the first-order component functions,  $F_j^i(k_j)$ , for paths  $i = \text{a1, b1, c1}$ . In Fig. 4.15 we plot  $F_j^i(k_j)$  for a1, b1, and c1 over the uncertainty range for each rate coefficient. Note that  $F_j^i(k_j) = 0$  because the mean probability is already taken out. The negative correlation for reaction R17\* arises because  $F_{17}^{a1}(k_{17}^*)$  decreases with increasing  $k_{17}^*$  whereas  $F_{17}^{b1}(k_{17}^*)$  and  $F_{17}^{c1}(k_{17}^*)$  both increase. This is quite understandable because for path a1 reactions R13 and R17\* are in competition to consume the  $\text{HO}_2$  radical; thus an increase in  $k_{17}^*$  decreases the flux along path a1 for which the R13 step is rate limiting. On the contrary, pathway b1 includes the rate limiting R17\* step and so increasing  $k_{17}^*$  promotes this pathway. The pathway probability for c1 ( $i = 2$ ) increases with  $k_{17}^*$  because reaction R17\* produces an H-radical which then promotes reaction R0,  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ . Because reaction R13 leads to the formation of  $\text{H}_2\text{O}_2$ , which almost always decays to  $\text{OH} + \text{OH}$ , increasing  $k_{13}$  also increases the probability for c1 by promoting reaction R2,  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ . Finally,  $F_0^2(k_0)$  increases with increasing  $k_0$  because R0 is the initiation step of this pathway; on the contrary,  $F_0^0(k_0)$  and  $F_0^1(k_0)$  both decrease with increasing  $k_0$  because R0 is in competition

with R8, which initiates pathways a1 and b1. In a similar fashion we could also understand the correlations that develop between other pathways in the model.

Figure 4.14: Correlation between pathways (a1, b1) in the upper panel and (a1, c1) in the lower panel for the H<sub>2</sub>O target evaluated at  $t = 0.8\tau_{ign}$ . The correlation has been decomposed into the contributions from specific reactions via eqn. 4.21.



One of the most interesting aspects of the H<sub>2</sub>–O<sub>2</sub> system is the crossover behavior where the R17\* is the main source of H<sub>2</sub>O<sub>2</sub> at early times whereas R13 becomes largest at long times. This mechanistic crossover is apparent in the overall reaction rates, Fig. 4.2, which shows that the rate for R13 crosses and then exceeds that for R17\* at about  $t = 0.5\tau_{ign}$ . In terms of pathways, H<sub>2</sub>O<sub>2</sub> production is dominated by just two, a3 and b3, which account for over 99% of the total. These two paths differ only in the step that produces H<sub>2</sub>O<sub>2</sub> from HO<sub>2</sub>, reactions R13 and R17\*, respectively. Thus, in Fig. 4.6, we saw that the pathway probability for a3 likewise crosses and exceeds that for b3 at roughly the same point in time as the rates. It is instructive to study the pathway sensitivities versus time for this crossover regime. In Fig. 4.16 we see the sensitivities for paths a3 and b3 are dominated by R13 and R17\*, respectively, but in a quite asymmetrical way. As we might expect, pathway a3 is more sensitive to R13 than to R17\* and b3 is more sensitive to R17\* than R13.

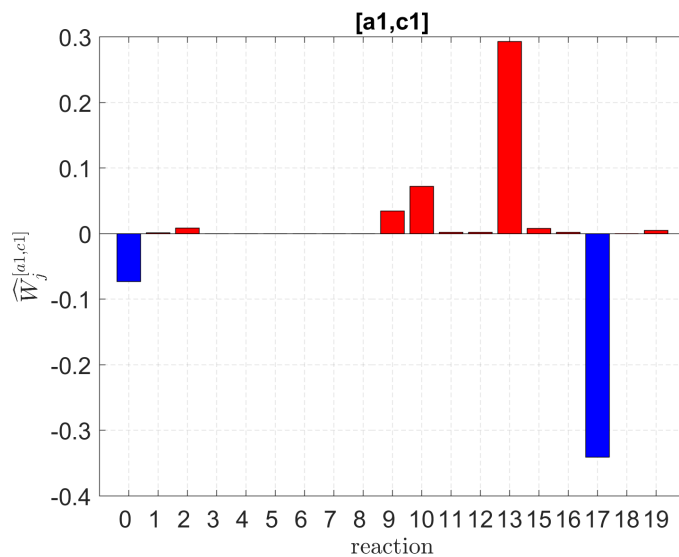
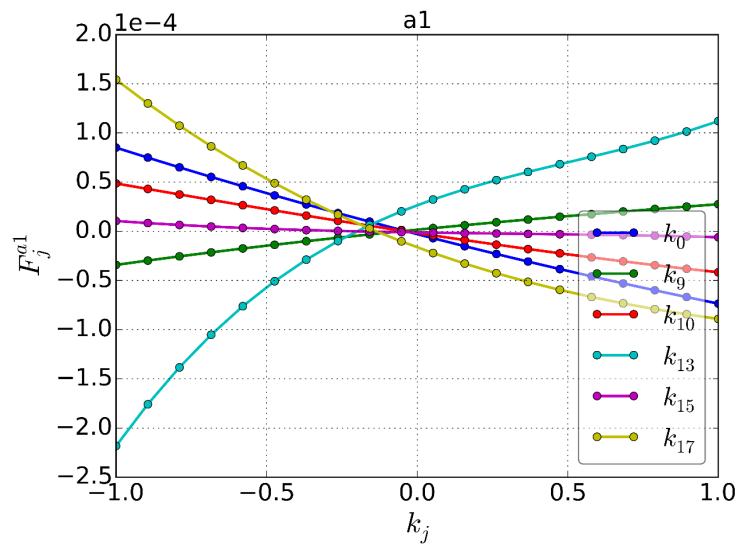
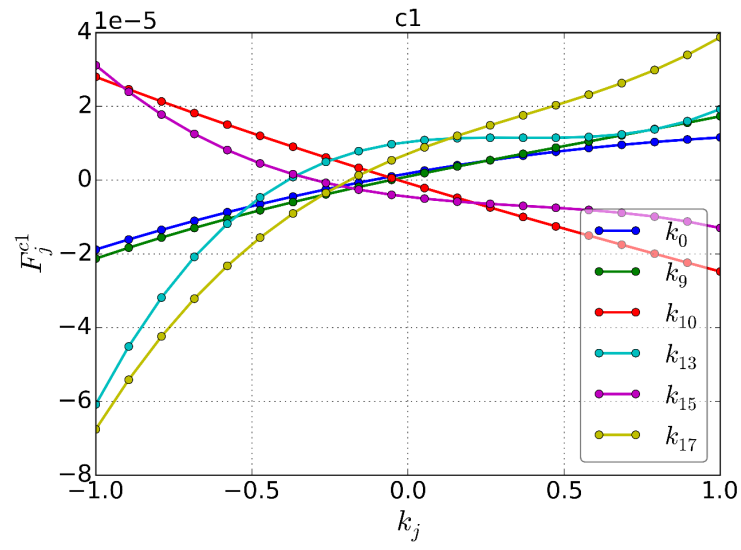
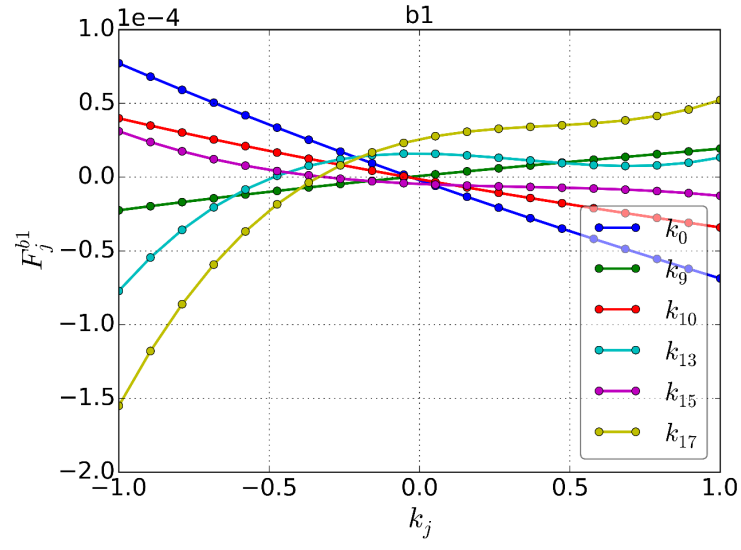


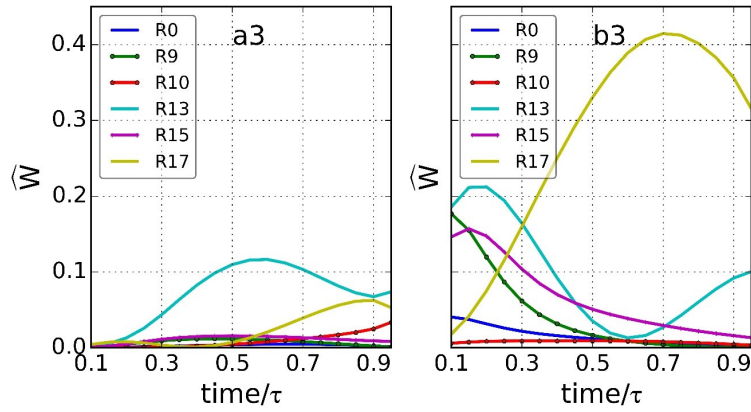
Figure 4.15: First-order component function for the HDMR expansion of the pathway probabilities a1, b1, and c1 for the H<sub>2</sub>O target evaluated at  $t = 0.8\tau_{ign}$ .





However, the degree of sensitivity and the shapes of the profiles versus time are dissimilar, which reflects the differing functional dependence of  $p_{a3}$  and  $p_{b3}$  on the rate coefficients. The a3 pathway shows a growth in both the R13 and R17\* sensitivity near the  $t = 0.5\tau_{ign}$  crossover point. The b3 pathway shows a significant growth in R17\* sensitivity early in the ignition process and a more complicated oscillating sensitivity to R13 versus time.

Figure 4.16: Sensitivity indices for the two dominant paths leading to  $\text{H}_2\text{O}_2$  as a function of time.



Finally, we note the unexpected results obtained for the  $\text{HO}_2$  target. The sensitivity indices for this target shown in Fig. 4.4 are generally similar to that for other species, viz. strong contributions from the R13, R17\*, R15, and R9. Unlike the other species, however,  $\text{HO}_2$  formation is dominated by a single one-step chemical pathway,  $\text{O}_2 + \text{H} + \text{M} \rightarrow \text{HO}_2 + \text{M}$ , described by R8. Hence, it is at first surprising that R8 does not significantly contribute to the sensitivity spectrum at any time. Instead, the  $W_j$  are largest for reactions involved in the decay of the  $\text{HO}_2$  species, R13 and R17\*, and the secondary decay of  $\text{H}_2\text{O}_2$ , i.e., R15. The lack of R8 dependence is partly due to use of O atom following. Clearly,  $\text{HO}_2$  formation is limited not by oxygen but instead by the formation of H-radicals. Indeed, R8 is found to be much faster than R17\* ( $\text{HO}_2 + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}_2$ ) and R9 ( $\text{H}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{H}$ ), which are both sources of H atoms and both appear in the sensitivity spectrum.

## 4.7 Conclusions

The sum over histories approach offers a uniquely quantitative method for investigating the contribution of distinct and competing chemical pathways to the behavior of large mechanisms. The sum over histories method allows the concentration of species to be represented in terms of a sum over the probabilities for chemical pathways that generate that species. This method differs from other techniques for reaction path analysis that represent the pathways at an instant of time using a flux snapshot. Instead, our method permits the time evolving chemistry of the system to be quantitatively incorporated into the probability for the chemical pathways. Hence, the dominant chemical pathways followed by chemical moieties are allowed to change as time progresses. In the present work we have used the sum over histories approach to analyze the sensitivity of speciation in the  $\text{H}_2\text{--O}_2$  combustion system. Thus, the formation of any target species is described in terms of a sequence of reactions that carry a tagged atom from reactants to the target. Using O atom following, it was found that a small number of chemical pathways could account for the formation of the products and intermediates prior to the ignition time. The observed sensitivities for species targets to the values of the rate coefficients could, for the most part, be traced to key steps along the chemical pathways. In particular, it was observed that the chemistry of  $\text{HO}_2$  radicals and the subsequent formation of  $\text{H}_2\text{O}_2$  were essential steps along many dominate chemical pathways. It was found that high sensitivity was often associated with rate limiting steps or pathway switching phenomena involving  $\text{HO}_2$  self-reaction, R13, and  $\text{HO}_2 + \text{H}_2$ , R17\*.

As a final point, we note that there remains an element of choice when applying the sum over histories representation, specifically in the selection of the chemical moiety to be followed. In principle, we may select any atom in the target molecule as our followed atom to implement the algorithm. However, the efficiency of the method, and the insight it affords, does depend on this choice. For the present  $\text{H}_2\text{--O}_2$  combustion problem, e.g., we found that O atom following procedure was more rapidly convergent and more useful for interpretation than the H atom following approach. However, the sensitivity of  $\text{HO}_2$  species formation to the rate coefficients could not be well explained



in this representation. Instead, the formation of  $\text{HO}_2$  is largely controlled by H atom production required for the association reaction  $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ . Hence, for this species it is advisable to switch to the H atom following scheme to understand the results of the sensitivity analysis.

## Chapter 5

### Simulating Chemical Kinetics Without Differential Equations

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- [7] Bai, S., & Skodje, R. T. The Sum Over Histories Representation for Chemical Kinetics: A Quantitative Theory Based on Chemical Pathways. *International Reviews in Physical Chemistry*, 35(4), 539-567. **2016**
- [9] Bai, S., & Skodje, R. T. Simulating Chemical Kinetics Without Differential Equations: A Quantitative Theory Based on Chemical Pathways. *The Journal of Physical Chemistry Letters*, 8(16), 3826-3833. **2017**

#### 5.1 Abstract

A new approach is presented for simulating the time-evolution of chemically reactive systems. This method provides an alternative to conventional modeling of mass-action kinetics that involves solving differential equations for the species concentrations. The method presented here avoids the need to solve the rate equations by switching to a representation based on chemical pathways. In the Sum Over Histories Representation (or SOHR) method, any time-dependent kinetic observable, such as concentration, is written as a linear combination of probabilities for chemical pathways leading to a desired outcome. In this work, an iterative method is introduced that allows the time-dependent pathway probabilities to be generated from a knowledge of the elementary rate coefficients thus avoiding the pitfalls involved in solving the differential equations of kinetics.

The method is successfully applied to the model Lotka-Volterra system and to a realistic  $\text{H}_2\text{--O}_2$  combustion model.

## 5.2 Introduction

Simulation of chemical reaction networks using mass-action chemical kinetics provides an invaluable tool for uncovering chemical mechanisms and predicting time-dependent chemical behavior as functions of controllable parameters such as temperature, pressure, and initial concentrations. As chemical mechanisms grow large, such as for hydrocarbon combustion, the resulting kinetic behavior can become quite difficult to physically decipher and, in some cases, the simulations themselves can bog down due to the proliferation of species and the need for small time steps owing to the existence of multiple time scales. Thus, considerable effort has been devoted in the disciplines of chemistry, biochemistry, physics and engineering to interpreting and simplifying kinetic behavior in complex networks.

The usual computational approach to mass-action kinetics involves constructing and solving a set of differential equations in the continuous concentration variables  $X_i(t)$  that model the local rates of formation and destruction of each of the  $N$  chemical species,  $S_i$ , [88, 148, 125] i.e.

$$\frac{dX_i}{dt} = \sum_j^{\text{sources}} v_{i,j} R_j - \sum_j^{\text{sinks}} \tilde{v}_{i,j} R_j \quad i = 1, \dots, N \quad (5.1)$$

For the  $M$  elementary reaction steps, defined by

$$\sum_i^{\text{reactants}} \tilde{v}_{i,j} R_j = \sum_i^{\text{products}} v_{i,j} R_j \quad j = 1, \dots, M \quad (5.2)$$

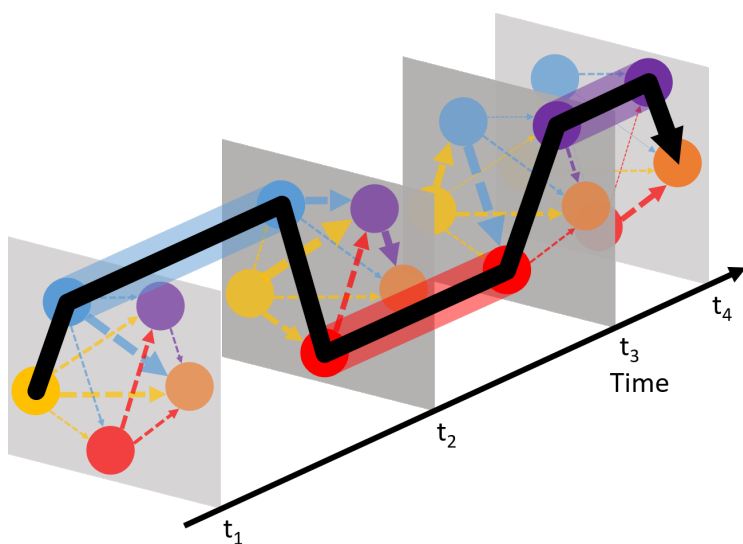
the explicit rate laws  $R_j(\mathbf{X})$  are provided by an external experimental or theoretical determination and  $v_{i,j}$  are known constants. This representation is properly regarded as a mean field theory that becomes valid in the thermodynamic limit. For systems involving very low concentrations or strong local environment effects, more intensive simulations may be used that employ stochastic or Monte Carlo algorithms that may account for the influence of fluctuations. [113, 52, 73]

In this paper, we propose a new method to simulate the kinetics of general nonlinear mechanisms

that builds on, and fundamentally extends, our earlier work.[85, 12, 6, 7] In contrast to the local rate equation approach to kinetics, we propose a self-contained global method based on chemical pathways that tracks molecules and fragments as they move throughout the network. A pathway follows a chemical moiety, at a molecular level, as it hops from species to species under the influence of elementary chemical steps. A convenient approach to the unique specification of a chemical pathway utilizes an atom-following algorithm. If, e.g., the carbon-atom in a  $\text{CH}_4$  reagent is initially tagged,  $\text{CH}_4(+\text{OH}) \xrightarrow{\text{R}_1} \text{CH}_3(+\text{OH}) \xrightarrow{\text{R}_2} \text{CH}_2(+\text{O}) \xrightarrow{\text{R}_3} \text{CH}_2\text{O}$  defines a three-step pathway leading from  $\text{CH}_4$  to the product  $\text{CH}_2\text{O}$ . Each reaction is modeled as a random event governed by transition probabilities obtained from the elementary rate laws. By constructing paths for a complete set of atoms in the initial state at a time  $t_0$ , it is possible to predict the subsequent values of any kinetic observable given the pathway probabilities (see below). Hence, the method is global in the sense that it replaces local rate equations based on instantaneous rates for individual species with expressions that span the entire network over finite times using multistep chemical pathways.

The use of chemical paths to analyze the behavior of chemical networks has a long history. A most convenient way to visualize and enumerate chemical paths involves the use of graph theory.[115, 14, 45] Graph theoretic analysis of chemical mechanisms was initiated by the early work of Christiansen[25] and also King and Altman[79] who exploited the analogy between chemical and electrical circuit theory. Since then, there have been numerous treatments of chemical networks, especially for biochemical systems, that have demonstrated the utility of graph theory.[123, 70, 44, 68, 98, 40, 108] Closely related work on the solution of master equations via network analysis has also been explored using graph theory.[134, 2] Much of work on kinetic graphs has focused on the developing expressions for the steady state rates for first-order or pseudo-first-order chemical mechanisms. Typically, the vertices of those graphs comprise a subset of the species, such as biochemical intermediates, and the edges are reaction steps. Quantitative treatment of the kinetics are possible using edge weights obtained from the steady state fluxes. In our work, we have developed a quantitative pathway analysis, called the Sum Over Histories Representation or SOHR, which goes beyond steady state conditions and fully embraces the time-dependent and nonlinear

Figure 5.1: A schematic representation of a time-dependent pathway followed by a tagged atom through a chemical network of five species. The reactions occur instantaneously at times  $t_1$ ,  $t_2$ ,  $t_3$ , and  $t_4$ , which are randomly selected and averaged to obtain the pathway probability.



behavior of general mechanisms. As emphasized in the schematic diagram of Fig. 5.1, the SOHR method employs time-resolved chemical pathways in which reaction occur at specific randomly selected times. This treatment employs dynamical graph theory[62] in which the edge weights are time-dependent. This is quite important for quantitative modeling since static snapshots of the reactive flow can be very deceptive for interpreting and modeling time-dependent chemical flux. Our approach draws inspiration from Feynmans path integral representation of quantum mechanics.[41] We have previously used the SOHR method to interpret the workings of several kinetic networks, including those involved with surface catalysis and combustion. While we could readily identify and quantify the important chemical paths that guided the kinetics, the results were interpretative rather than predictive. That is, for general nonlinear problems, the determination of the pathway probabilities requires a knowledge of the time-dependence of the pseudo-first order rate coefficients which, in turn, requires an a priori knowledge of the concentrations versus time. For interpretive analysis, the nonlinear kinetics was first solved using conventional kinetics to obtain a reference trajectory,  $\mathbf{X}(t)$ , and then the kinetics was decomposed into contributing pathways. In this work, we overcome this limitation and formulate the SOHR as a predictive theory that does not require a solution to eqn. 5.1. In this way, the need to solve the usual differential equations of mass action kinetics is avoided, and the pathway probabilities can be solved in a self-consistent manner.

The key to our formulation is the use of an iterative solution technique to obtain the pathway probabilities. After a brief review of the interpretive SOHR method, the iterative SOHR method is presented. Given a set of chemical pathways, the pathway probabilities and the species concentrations are obtained simultaneously by the iteration. A strategy to identify the most important chemical pathways is given. The new predictive SOHR method is numerically tested on the Lotka Volterra model and  $\text{H}_2\text{--O}_2$  combustion system. The results presented demonstrate that the method is accurate and quickly convergent. We conclude with a discussion of the possible advantages of the new method.

### 5.3 The Predictive SOHR Method

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## Appendix A

### Weird Exam Answers

**About appendices:** Each appendix follow the same page-numbering rules as a regular chapter; the first page of a (multi-page) appendix is not numbered. By the way, the following are supposedly authentic answers to English GCSE exams!

- (1) The Greeks were a highly sculptured people, and without them we wouldnt have history.  
The Greeks also had myths. A myth is a female moth.
- (2) Actually, Homer was not written by Homer but by another man of that name.
- (3) Socrates was a famous Greek teacher who went around giving people advice. They killed him. Socrates died from an overdose of wedlock. After his death, his career suffered a dramatic decline.
- (4) Julius Caesar extinguished himself on the battlefields of Gaul. The Ides of March murdered him because they thought he was going to be made king. Dying, he gasped out: Tee hee, Brutus.
- (5) Nero was a cruel tyranny who would torture his subjects by playing the fiddle to them.
- (6) In midevil times most people were alliterate. The greatest writer of the futile ages was Chaucer, who wrote many poems and verses and also wrote literature.
- (7) Another story was William Tell, who shot an arrow through an apple while standing on his sons head.

- (8) Writing at the same time as Shakespeare was Miguel Cervantes. He wrote Donkey Hote. The next great author was John Milton. Milton wrote Paradise Lost. Then his wife died and he wrote Paradise Regained.
- (9) During the Renaissance America began. Christopher Columbus was a great navigator who discovered America while cursing about the Atlantic. His ships were called the Nina, the Pinta, and the Santa Fe.
- (10) Gravity was invented by Issac Walton. It is chiefly noticeable in the autumn when the apples are falling off the trees.
- (11) Johann Bach wrote a great many musical compositions and had a large number of children. In between he practiced on an old spinster which he kept up in his attic. Bach died from 1750 to the present. Bach was the most famous composer in the world and so was Handel. Handel was half German half Italian and half English. He was very large.
- (12) Soon the Constitution of the United States was adopted to secure domestic hostility. Under the constitution the people enjoyed the right to keep bare arms.
- (13) The sun never set on the British Empire because the British Empire is In the East and the sun sets in the West.
- (14) Louis Pasteur discovered a cure for rabbis. Charles Darwin was a naturalist who wrote the Organ of the Species. Madman Curie discovered radio. And Karl Marx became one of the Marx brothers.

## Appendix B

### Ode to Spot

**(Data, Stardate 1403827)** (A one-page chapter — page must be numbered!) Throughout the ages, from Keats to Giorchamo, poets have composed “odes” to individuals who have had a profound effect upon their lives. In keeping with that tradition I have written my next poem . . . in honor of my cat. I call it . . . Ode . . . to Spot. (Shot of Geordi and Worf in audience, looking mystified at each other.)

Felus cattus, is your taxonomic nomenclature  
 an endothermic quadruped, carnivorous by nature?  
 Your visual, olfactory, and auditory senses  
 contribute to your hunting skills, and natural defenses.  
 I find myself intrigued by your sub-vocal oscillations,  
 a singular development of cat communications  
 that obviates your basic hedonistic predilection  
 for a rhythmic stroking of your fur to demonstrate affection.  
 A tail is quite essential for your acrobatic talents;  
 you would not be so agile if you lacked its counterbalance.  
 And when not being utilized to aid in locomotion,  
 It often serves to illustrate the state of your emotion.

(Commander Riker begins to applaud, until a glance from Counselor Troi brings him to a halt.)

Commander Riker, you have anticipated my denouement. However, the sentiment is appreciated.

I will continue.

O Spot, the complex levels of behavior you display  
 connote a fairly well-developed cognitive array.  
 And though you are not sentient, Spot, and do not comprehend  
 I nonetheless consider you a true and valued friend.

## Appendix C

### The Hydrogen Combustion Model

The combustion of  $H_2$  is modeled using a detailed mechanism that consists of 21 individual steps and 8 distinct chemical species. The specific mechanism employed here is a sub-mechanism of a larger model for methanol combustion used by Li et al.[104] The reactions and species used are listed in the tables below. The temperature dependence of the rate coefficients is given by the three parameter fit

$$k(T) = AT^\delta E^{-E_a/k_B T} \quad (C.1)$$

where the values of  $A$ ,  $\delta$ , and  $E_a$  for each reaction are listed in Table C.1. The pressure-dependent reactions rate are calculated using the Troe centering expression

$$k = k_\infty \left( \frac{P_r}{1+P_r} F \right) \quad (C.2)$$

where

$$P_r = \frac{k_0 [M]}{k_\infty} \quad (C.3)$$

and the high pressure limit ( $k_\infty$ ) and low pressure limit ( $k_0$ ) rate coefficients are parameterized by the three parameter expression in eqn. C.1. The function  $F$ <sup>1</sup> is given by Troe and coworkers.[49] The reverse reaction rates are defined consistently with micro-reversibility using the equilibrium constant

$$k_r = \frac{k_f}{k_{eq}^c} \quad (C.4)$$

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<sup>1</sup> The function  $F$  is defined as  $\log F = \left[ 1 + \left[ \frac{\log P_r + c}{n - d(\log P_r + c)} \right] \right]^{-1} \log F_{cent}$  where  $F_{cent} = (1 - \alpha) \exp(-T/T^{***}) + \alpha \exp(T/T^*) + \exp(-T^{**}/T)$  and centering parameters  $T^*$ ,  $T^{**}$ , and  $T^{***}$  are provided in the table.

In the mechanism, there are two pairs of duplicated reactions; i.e., they have the same reactants and products but different rate coefficients. This allows a much more flexible representation of the overall temperature dependence of the rate coefficients. The combustion kinetics is simulated using the constraints of constant volume and constant energy. The time development of each species is modeled by the following set of equations:

$$\begin{aligned}\frac{dY_k}{dt} &= \frac{W_k \dot{\omega}_k}{\rho}, \quad k = 1, \dots, 8 \\ \frac{dT}{dt} &= -\frac{1}{\rho C_v} \sum_k W_k \dot{\omega}_k e_k\end{aligned}\tag{C.5}$$

where  $Y_k$  represents the mass fraction of species  $k$  (which is proportional to its concentration  $[X_k]$ ),  $W_k$  is its molecular weight,  $\dot{\omega}_k$  refers to the production rate of the  $k$ th species obtained from the mechanism,  $\rho$  is the bulk density,  $C_v$  is the constant volume heat capacity and  $e_k$  is the internal energy of the  $k$ th species.

Table C.1: Rate coefficients and uncertainty ranges of H<sub>2</sub>-O<sub>2</sub> system.

Index	Reaction	A(cm <sup>3</sup> /mol-s) or s <sup>-1</sup>	$\delta$	E <sub>a</sub> (kcal/mol)	Uncertainty
0	H+O <sub>2</sub> =O+OH	3.55E+15	-0.4	16599.0	1.26
1	O+H <sub>2</sub> =H+OH	5.08E+04	2.7	6290.0	1.58
2	H <sub>2</sub> +OH=H <sub>2</sub> O+H	2.16E+08	1.5	3430.0	2.00
3	O+H <sub>2</sub> O=OH+OH	2.97E+06	2.0	13400.0	2.50
4	H <sub>2</sub> +M=H+H+M	4.58E+19	-1.4	104380.0	3.00
H <sub>2</sub>			Enhanced by 2.500E+00		
H <sub>2</sub> O			Enhanced by 1.200E+01		
5	O+O+M=O <sub>2</sub> +M	6.16E+15	-0.5	0.0	2.00
H <sub>2</sub>			Enhanced by 2.500E+00		
H <sub>2</sub> O			Enhanced by 1.200E+01		
6	O+H+M=OH+M	4.71E+18	-1.0	0.0	5.00
H <sub>2</sub>			Enhanced by 2.500E+00		
H <sub>2</sub> O			Enhanced by 1.200E+01		
7	H+OH+M=H <sub>2</sub> O+M	3.80E+22	-2.0	0.0	2.00
H <sub>2</sub>			Enhanced by 2.500E+00		
H <sub>2</sub> O			Enhanced by 1.200E+01		
8	H+O <sub>2</sub> (+M)=HO <sub>2</sub> (+M)	1.48E+12	0.6	0.0	3.16
Low pressure limit			0.63660E+21	-0.17200E+01	0.52480E+03
TROE centering			0.80000E+00	0.10000E-29	0.10000E+31
H <sub>2</sub>			Enhanced by 2.000E+00		
H <sub>2</sub> O			Enhanced by 1.100E+01		
O <sub>2</sub>			Enhanced by 7.800E-01		
9	HO <sub>2</sub> +H=H <sub>2</sub> +O <sub>2</sub>	1.66E+13	0.0	823.0	2.00
10	HO <sub>2</sub> +H=OH+OH	7.08E+13	0.0	295.0	2.00
11	HO <sub>2</sub> +O=O <sub>2</sub> +OH	3.25E+13	0.0	0.0	3.16
12	HO <sub>2</sub> +OH=H <sub>2</sub> O+O <sub>2</sub>	2.89E+13	0.0	-497.0	3.16
13	HO <sub>2</sub> +HO <sub>2</sub> =H <sub>2</sub> O <sub>2</sub> +O <sub>2</sub>	4.20E+14	0.0	11982.0	5.00
Declared duplicate reaction...					
14	HO <sub>2</sub> +HO <sub>2</sub> =H <sub>2</sub> O <sub>2</sub> +O <sub>2</sub>	1.30E+11	0.0	-1629.3	5.00
Declared duplicate reaction...					
15	H <sub>2</sub> O <sub>2</sub> (+M)=OH+OH(+M)	2.95E+14	0.0	48430.0	3.16
Low pressure limit			0.12020E+18	0.00000E+00	0.45500E+05
TROE centering			0.50000E+00	0.10000E-29	0.10000E+31
H <sub>2</sub>			Enhanced by 2.500E+00		
H <sub>2</sub> O			Enhanced by 1.200E+01		
16	H <sub>2</sub> O <sub>2</sub> +H=H <sub>2</sub> O+OH	2.41E+13	0.0	3970.0	5.00
17	H <sub>2</sub> O <sub>2</sub> +H=HO <sub>2</sub> +H <sub>2</sub>	4.82E+13	0.0	7950.0	5.00
18	H <sub>2</sub> O <sub>2</sub> +O=OH+HO <sub>2</sub>	9.55E+06	2.0	3970.0	3.00
19	H <sub>2</sub> O <sub>2</sub> +OH=HO <sub>2</sub> +H <sub>2</sub> O	1.00E+12	0.0	0.0	5.00
Declared duplicate reaction...					
20	H <sub>2</sub> O <sub>2</sub> +OH=HO <sub>2</sub> +H <sub>2</sub> O	5.80E+14	0.0	9557.0	5.00
Declared duplicate reaction...					

†Indices start at 0.