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RPPR Final Report

as of 06-Jul-2020

Agency Code:

Proposal Number: 65303EGMUR

Agreement Number: W911NF-14-1-0359

INVESTIGATOR(S):

Name: Donald L. Thompson
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DUNS Number: 153890272

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Report Date: 31-Mar-2020

Date Received: 02-Jul-2020

Final Report for Period Beginning 01-Jul-2014 and Ending 31-Dec-2019

Title: New Theoretical and Experimental Methods for Predicting Fundamental Mechanisms of Complex Chemical Processes

Begin Performance Period: 01-Jul-2014

End Performance Period: 31-Dec-2019

Report Term: 0-Other

Submitted By: Donald Thompson

Email: thompsondon@missouri.edu

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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1

STEM Participants: 10

Major Goals: THOMPSON/MU: The objective was to develop methods to determine the mechanistic details of complex gasphase chemistry from molecular dynamics (MD) simulations. Our focus was to gain reliable, accurate insights into the detailed and the macroscopic behaviors of complex overall reactions such as hydrocarbon combustion.

GREEN/U MASS-BOSTON: For systems away from equilibrium, such as a mixture undergoing combustion, there is not a framework to systematically transform molecular dynamics into macroscopic behaviors—a fact which impacts the predictive power, transferability, and robustness, of available theories—particularly the prediction of chemical signatures at different temperatures and pressures. In this project, we took steps to address this challenge. The objective was to devise theoretical strategies for (1) learning mechanisms from data and (2) predicting the emergent dynamical processes of complex chemistry, namely autoignition. Our theoretical developments are at the intersection of nonequilibrium statistical mechanics, information, and dynamical systems, and directly tested with extensive molecular dynamics and stochastic kinetics simulations of hydrogen combustion.

HEAD-GORDON/BERKELEY: This project is one component of the Don Thompson-led MURI project that aimed to substantially improve our ability to model combustion from first principles. It is the component that sits at the very bottom of the multi-scale and multi-physics modeling challenges associated with combustion simulations over all relevant length and time scales. Electronic structure theory treats all electrons in all molecules from the basic principles of quantum mechanics, and thus is the fundamental basis of atomistic combustion modeling. A truly first principles approach to combustion should begin with the ability to directly simulate reactive molecular dynamics in a high pressure, high temperature gas using electronic structure theory. That is the grand challenge that we have been interested in moving towards, and progress may enable some of the standard compromises of present-day approaches to be avoided. First, it was desirable to avoid the need to extract particular reactive events to treat by electronic structure theory as isolated components of a kinetic network because of the likelihood that not all relevant processes can be reliably identified. Second, it was also desirable to avoid the need to develop economical but potentially inaccurate force field models to perform direct simulations, because of the inherent difficulty of validating such approaches.

MEZIC/UCSB: Thermodynamics and dynamics of complex molecular reactions are governed by highdimensional, complex potential surfaces. Assuming such an ab initio PES is available, several problems still persisted. (1) The complexity of the system leads to numerous, hard to characterize and visualize equilibrium states. (2) The transitions between such equilibrium states are also difficult to characterize, geometrically and rate-wise; as a

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consequence, distinguishing important reactions and their ordering is a complex task. (3) The effect of uncertainties, stemming, e.g., from interpolation (DLT), inherent in the PES calculations on equilibria and dynamics is a challenging high-dimensional problem. To resolve these problems we sought to describe a hierarchy of scales in complex reaction processes, find efficient methods for visualization of phase space structures and develop a Koopman operator-theoretic description of coarse and fine coordinates, including the relaxation coordinates.

MOTTER/NORTHWESTERN: The Northwestern University group has focused on the network analysis and control of combustion reaction systems. The main objectives are to 1) infer the state of the chemical network, 2) determine the impact of unknown intermediate reactions/species, 3) rationally manipulate the behavior of the reaction network, and 4) discover general relations between network structure and dynamics.

VIOLI/U MICHIGAN: The goal of this work was to develop a descriptive abstract model, that can compactly portray a complex network of reactions and that can account for model and experimental uncertainties. This representation is built on a scalable random graphical model for representing chemical reaction mechanisms. This graph representation of the combustion of different fuels can be used to identify the key characteristics of reaction networks, as well as common trends among different reaction networks that can be associated with molecular characteristics (e.g., branching, presence of rings), by employing spectral graph theory and machine learning techniques.

Accomplishments: MU/THOMPSON:

We defined reaction stream for an overall reaction as a pathway leading from the reactants to the products. This pathway is comprised of sequences of isolated reactions of the evolving chemistry. To illustrate the applicability, we identified all sequences of isolated reactions in the overall reaction $10\text{H}_2\text{O}_2 \rightarrow 10\text{H}_2\text{O} + 5\text{O}_2$. We began by defining four sets containing all reaction sequences involving hydrogen atoms: sets containing atomic sequences that transform hydrogen atoms from H_2O_2 to H_2O , from H_2O to H_2O_2 , from H_2O_2 to another H_2O_2 , and from H_2O to another H_2O . We used a reaction identification algorithm to monitor all hydrogen atoms and identify sequences of isolated reactions making up each set. Additionally, we studied the effect of difference in the time scales of different sequences on reaction complexity. Our overall reaction is complex partly because the duration of time for completion of atomic reaction sequence varies significantly from one hydrogen atom to another. We considered two reaction sequences of length two that equally contribute in the set $\text{H}_2\text{O}_2 \rightarrow \dots \rightarrow \text{H}_2\text{O}$ set. While both sequences began with decomposition of a HOOH molecule, one continued by reaction $\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$, and the other continued by reaction $\text{OH} + \text{HO}'\text{H}' \rightarrow \text{O}'\text{H}' + \text{HOH}$. We observed that in presence of equal number of H_2O_2 and H_2O molecules, a nascent OH radical with a lifetime of smaller than 3 ps produced by the decomposition reaction is twice more likely to participate in reaction $\text{OH} + \text{HO}'\text{H}' \rightarrow \text{O}'\text{H}' + \text{HOH}$ than does it in the other reaction.

GREEN/U MASS-BOSTON:

Classical speed limit on stochastic thermodynamic observables (rate of heat release): We have derived an Ehrenfest-like equation of motion for the expectation of stochastic thermodynamic observables and found that the analog of the quantum-mechanical commutator is the covariance between the observable and the rate of change of the information content in the underlying nonequilibrium distribution (Figs. 1 and 2). The energy exchanged as heat between a system and its surroundings, for example, can then be interpreted as a measure of the linear relationship between energy and information. An uncertainty relation follows that bounds the time that elapses before the change in the mean of any observable has the same magnitude as its standard deviation. Analogous to the Mandelstam-Tamm form of the time-energy uncertainty relation in quantum mechanics, this inequality bounds the speed of arbitrary stochastic thermodynamic observables, independent of the dynamics, system size, and nonequilibrium conditions (heat, entropy production/flow, chemical/dissipative work).

U CA-BERKELEY/HEAD-GORDON:

- Polarized many-body expansion (PoIBE) for electronic structure of large systems (completed): The use of polarized environment in PoIBE was found to be crucial in providing improved quantitative accuracy at the 2-body level versus the conventional many-body expansion.
- Assessment of REAXFF using electronic structure theory (with Jason Green) (completed) Three variants of ReaxFF were assessed along reaction paths for key elementary reactions in hydrogen combustion, revealing large errors that motivate improved reactive force fields.
- Provision of electronic structure data for development of a reactive force field (with Igor Mezc) (on-going): The aid development of potential stitching tools developed by the Mezc group we provided high quality electronic structure energies along some 20 pathways for hydrogen combustion.

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UCSB/MEZIC:

Developed further a systematic procedure based on programmable potentials for learning coarse-grained reaction EST (A. Avilla, with M. Head-Gordon).

NORTHWESTERN/MOTTER:

The research was oriented by the following questions. What is the relation (if any) between non-normality and non-monotonicity in complex reaction systems? For example, is the transient presence of intermediate species related to the coupling matrix being non-normal? These questions are motivated by practical implications of intermediate species in ignition and other key steps of the reaction process. Here, we used a master equation to model the reaction dynamics to derive a general condition for observing non-monotonic dynamics of individual species, establishing that non-normality promotes non-monotonicity but is not a requirement for it. In contrast, we show that non-normality is a requirement for non-monotonic dynamics to be observed in the Renyi entropy. Using H₂/O₂ combustion as an application, we demonstrate that non-monotonic dynamics under experimental conditions are supported by a linear chain of connected components, in contrast with the dominance of a single giant component observed in typical random reaction networks. This indicates that our approach can also inform dimension reduction in the analysis of very large complex reaction networks. These results were derived in collaboration with Prof. Jason Green's group and are currently under consideration for publication in Physical Review Research.

U MICHIGAN/VIOLI:

1. Combined machine learning and combustion chemistry to analyze reaction networks.
2. Developed a novel computational tool based on sparse learning theory to analyze complex reaction networks
3. Trained and mentored postdoc

Training Opportunities: Nothing to Report

Results Dissemination: U MASS-BOSTON/GREEN:

We are disseminating the final results of this project through the publication of high-quality papers in selective peer-reviewed journals.

UCSB/MEZIC:

- With M. Head-Gordon secured a DARPA project for design of materials using the EST/Programmable Potentials methodology.
- Shared data with AFRL Materials team

Honors and Awards: U CA-BERKELEY/HEAD-GORDON:

- Schrodinger Medal of the World Association of Theoretical and Computational Chemists (WATOC) (2020).
- APS Justin Jankunas Doctoral Dissertation Award in Chemical Physics (to Joonho Lee for the thesis listed above) (American Physical Society, 2020).

U MICHIGAN/VIOLI:

- Angela Violi: Thurnau Professorship U-M
- Angela Violi: 2020 Aspire, Advance and Achieve Mentoring Award from U-M Women in Science and Engineering Program

Protocol Activity Status:

Technology Transfer: U Michigan/Violi:

Products/tools:

1. Mixed integer linear programming (MILP) reduction solver
2. Centrality reduction solver

PARTICIPANTS:

Participant Type: Other (specify)

Participant: Win Grace

Person Months Worked: 3.00

Project Contribution:

Funding Support:

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International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: PD/PI

Participant: Donald L. Thompson

Person Months Worked: 3.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Homayoon Rafatijo

Person Months Worked: 3.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Co PD/PI

Participant: Jason R Green

Person Months Worked: 3.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Schuyler B Nicholson

Person Months Worked: 5.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Rebecca A Bone

Person Months Worked: 5.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Michael E Marucci

Person Months Worked: 1.00

Funding Support:

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as of 06-Jul-2020

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Co PD/PI

Participant: Martin Head-Gordon

Person Months Worked: 1.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: Y
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Luke Bertels

Person Months Worked: 5.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Joonho Lee

Person Months Worked: 3.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Jonathan Wong

Person Months Worked: 5.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Josie Hendricks

Person Months Worked: 5.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Co PD/PI

Participant: Igor Mezic

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as of 06-Jul-2020

Person Months Worked: 1.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Allan Avila

Person Months Worked: 5.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Cory Brown

Person Months Worked: 2.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Co PD/PI

Participant: Adilson E Motter

Person Months Worked: 1.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Faculty

Participant: Takashi Nishikawa

Person Months Worked: 2.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Zachary G Nicolaou

Person Months Worked: 3.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

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Participant: Mayank Baranwal
Person Months Worked: 5.00
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Funding Support:

Participant Type: Co PD/PI
Participant: Angela Violi
Person Months Worked: 2.00
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Funding Support:

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: The Journal of Chemical Physics

Publication Identifier Type: DOI

Publication Identifier: 10.1063/1.4895514

Volume: 1.41E+002 Issue: 1.0E+001 First Page #: 104107

Date Submitted:

Date Published:

Publication Location:

Article Title: Measuring disorder in irreversible decay processes

Authors:

Keywords: Disordered kinetics, irreversibility, statistical length, information-theoretic inequalities

Abstract: Rate coefficients can fluctuate in statically and dynamically disordered kinetics. Here, we relate the rate coefficient for an irreversibly decaying population to the Fisher information. From this relationship we define kinetic versions of statistical-length squared and divergence that measure cumulative fluctuations in the rate coefficient. We show the difference between these kinetic quantities measures the amount of disorder, and is zero when the rate coefficient is temporally and spatially unique.

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Journal: The Journal of Chemical Physics

Publication Identifier Type: DOI

Publication Identifier: 10.1063/1.4907629

Volume: 1.42E+002 Issue: 6.0E+000 First Page #: 64113

Date Submitted:

Date Published:

Publication Location:

Article Title: Order and disorder in irreversible decay processes

Authors:

Keywords: Disordered kinetics, reaction order, reaction mechanisms, irreversibility

Abstract: Dynamical disorder motivates fluctuating rate coefficients in phenomenological, mass-action rate equations. The reaction order in these rate equations is the fixed exponent controlling the dependence of the rate on the number of species. Here, we clarify the relationship between these notions of (dis)order in irreversible decay, $n A \rightarrow B$, $n = 1, 2, 3, \dots$, by extending a theoretical measure of fluctuations in the rate coefficient. The measure, $J_n \geq L_2 n \geq 0$, is the magnitude of the inequality between J_n , the time-integrated square of the rate coefficient multiplied by the time interval of interest, and $L_2 n$, the square of the time-integrated rate coefficient. Applying the inequality to empirical models for non-exponential relaxation, we demonstrate that it quantifies the cumulative deviation in a rate coefficient from a constant, and so the degree of dynamical disorder. The equality is a bound satisfied by traditional kinetics where a single rate constant is sufficient. For these models,

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Date Submitted:

Date Published:

Publication Location:

Article Title: Ergodic theory and visualization. II. Fourier mesochronic plots visualize (quasi)periodic sets

Authors:

Keywords: State Space, Visualization, Dynamical System, Ergodic Theory, Koopman Operator

Abstract: We present an application and analysis of a visualization method for measure-preserving dynamical systems introduced by I. Mezic' and A. Banaszuk [Physica D 197, 101 (2004)], based on frequency analysis and Koopman operator theory. This extends our earlier work on visualization of ergodic partition [Z. Levnajić and I. Mezic', Chaos 20, 033114 (2010)]. Our method employs the concept of Fourier time average [I. Mezic' and A. Banaszuk, Physica D 197, 101 (2004)], and is realized as a computational algorithms for visualization of periodic and quasi-periodic sets in the phase space. The complement of periodic phase space partition contains chaotic zone, and we show how to identify it. The range of method's applicability is illustrated using well-known Chirikov standard map, while its potential in illuminating higher-dimensional dynamics is presented by studying the Froeschl₁e map and the Extended Standard Map.

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Journal: arXiv:1506.05333
Publication Identifier Type: **Publication Identifier:**
Volume: 1.0E+000 **Issue:** 1.0E+000 **First Page #:** 1
Date Submitted: **Date Published:**
Publication Location:

Article Title: Mesochronic Classification of Incompressible 3D Finite-Time Vector Fields

Authors:

Keywords: Volume Preserving Dynamical System, Mesohyperbolicity, Finite-Time Dynamics

Abstract: The mesochronic velocity is the average of the velocity field along trajectories generated by the same velocity field over a time interval of finite duration. In this paper we classify initial conditions of trajectories evolving in incompressible vector fields according to the character of motion of material around the trajectory. In particular, we provide calculations that can be used to determine the number of expanding directions and the presence of rotation from the characteristic polynomial of the Jacobian matrix of mesochronic velocity. In doing so, we show that (a) the mesochronic velocity can be used to characterize dynamical deformation of three-dimensional volumes, (b) the resulting mesochronic analysis unifies instantaneous, finite-time, and asymptotic analyses into a single approach, (c) the twodimensional mesochronic analysis¹ extends to three-dimensional state spaces.

Theoretical considerations are further supported by numerical computations performed for a dynamical system

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Journal: Physical Chemistry Chemical Physics

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Volume: 19 **Issue:** 3 **First Page #:** 2175

Date Submitted: 10/26/17 12:00AM **Date Published:** 12/7/16 11:31AM

Publication Location:

Article Title: On the Role of the Termolecular Reactions $2O_2 + H_2 \rightarrow 2HO_2$ and $2O_2 + H_2 \rightarrow H + HO_2 + O_2$ in Formation of the First Radicals in Hydrogen Combustion: Ab Initio Predictions of Energy Barriers

Authors: M. Monge-Palacios, Homayoon Rafati

Keywords: Hydrogen combustion, termolecular reactions, QCT calculations, electronic structure calculations

Abstract: We have investigated the role of termolecular reactions in the early chemistry of hydrogen combustion. We performed molecular chemical dynamics simulations using ReaxFF in LAMMPS to identify potential initial reactions for a 1 : 4 mixture of $H_2:O_2$ in the NVT ensemble at density 276.3 kg m^{-3} and $\sim 3000 \text{ K}$ ($\sim 4000 \text{ atm}$) and $\sim 4000 \text{ K}$ ($\sim 5000 \text{ atm}$), and then characterized the saddle points for those reactions using ab initio methods: CCSD(T) = FC/cc-pVTZ//MP2/6-31G, CCSD(T) = FULL/aug-cc-pVTZ//CCSD = FC/cc-pVTZ and CASSCF MP2/6-31G//MP2/6-31G. The main initial reaction is $H_2+O_2 \rightarrow H+HO_2$, frequently occurring in the presence of a second O_2 as a third body; that is, $2O_2 + H_2 \rightarrow H+HO_2 + O_2$. The second most frequent reaction is $2O_2 + H_2 \rightarrow 2HO_2$. We found three saddle points on the triplet PES of these termolecular reactions: one for $2O_2 + H_2 \rightarrow H + HO_2 + O_2$ and two for $2O_2 + H_2 \rightarrow 2HO_2$. In the latter case, one has a symmetric structure consistent with simultaneous formation of two HO_2 and the other

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Journal: The Journal of Chemical Physics

Publication Identifier Type: DOI

Publication Identifier: 10.1063/1.4961485

Volume: 145

Issue: 8

First Page #: 084112

Date Submitted: 11/2/16 12:00AM

Date Published: 8/1/16 5:00AM

Publication Location:

Article Title: Learning the mechanisms of chemical disequilibria

Authors: Schuyler B. Nicholson, Mohammad Alaghemandi, Jason R. Green

Keywords: Combustion, Classical Statistical Mechanics, Entropy, Hydrogen Reactions

Abstract: When at equilibrium, large-scale systems obey thermodynamics because they have microscopic configurations that are typical. "Typical" states are a fraction of those possible with the majority of the probability. A more precise definition of typical states underlies the transmission, coding, and compression of information. However, this definition does not apply to natural systems that are transiently away from equilibrium. Here, we introduce a variational measure of typicality and apply it to atomistic simulations of a model for hydrogen oxidation. While a gaseous mixture of hydrogen and oxygen combusts, reactant molecules transform through a variety of ephemeral species en route to the product, water. Out of the exponentially growing number of possible sequences of chemical species, we find that greater than 95% of the probability concentrates in less than 1% of the possible sequences. Overall, these results extend the notion of typicality across the nonequilibrium regime and suggest

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Phys. Chem. Chem. Phys.

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Publication Identifier: 10.1039/C5CP05125H

Volume: 18

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First Page #: 2810

Date Submitted: 11/2/16 12:00AM

Date Published:

Publication Location:

Article Title: Reactive symbol sequences for a model of hydrogen combustion

Authors: Mohammad Alaghemandi, Jason R. Green

Keywords: combustion, nonequilibrium, statistical mechanics, molecular dynamics

Abstract: Transient, macroscopic states of chemical disequilibrium are born out of the microscopic dynamics of molecules. As a reaction mixture evolves, the temporal patterns of chemical species encodes some of this dynamical information, while their statistics are a manifestation of the bulk kinetics. Here, we define a chemically-informed symbolic dynamics as a coarse-grained representation of classical molecular dynamics, and analyze the sequences of chemical species for a model of hydrogen combustion. We use reactive molecular dynamics simulations to generate the sequences and derive probability distributions for sequence observables: the reaction time scales and the chain length – the total number of reactions between initiation of a reactant and termination at products. The time scales and likelihood of the sequences depend strongly on the chain length, temperature, and density. Temperature suppresses the uncertainty in chain length for hydrogen sequences, but enhances the uncertainty in ox

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Journal of Chemical Theory and Computation

Publication Identifier Type:

Publication Identifier:

Volume:

Issue:

First Page #:

Date Submitted: 10/26/17 12:00AM

Date Published: 11/3/16 11:19AM

Publication Location:

Article Title: A General Sparse Tensor Framework for Electronic Structure Theory

Authors: S. Manzer, E. Epifanovsky, A.I. Krylov, and Martin Head-Gordon

Keywords: Linear scaling, tensor library, sparsity, electronic structure theory

Abstract: Linear-scaling algorithms must be developed in order to extend the domain of applicability of electronic structure theory to molecules of any desired size. However, the increasing complexity of modern linear-scaling methods makes code development and maintenance a significant challenge. A major contributor to this difficulty is the lack of robust software abstractions for handling block-sparse tensor operations. We therefore report the development of a highly efficient symbolic block-sparse tensor library in order to provide access to high-level software constructs to treat such problems. Our implementation supports arbitrary multi-dimensional sparsity in all input and output tensors. We avoid cumbersome machine-generated code by implementing all functionality as a high-level symbolic C++ language library, and demonstrate that our implementation attains very high performance for linear-scaling sparse tensor contractions.

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Date Submitted: 11/2/16 12:00AM

Date Published: 9/1/16 5:00AM

Publication Location:

Article Title: Programmable Potentials: Approximate N-body potentials from coarse-level logic

Authors: Gunjan S. Thakur, Ryan Mohr, Igor Mezic

Keywords: d. Applied Mathematics, Atomic and molecular physics, Chemical physics

Abstract: This paper gives a systematic method for constructing an N-body potential, approximating the true potential, that accurately captures meso-scale behavior of the chemical or biological system using pairwise potentials coming from experimental data or ab initio methods. The meso-scale behavior is translated into logic rules for the dynamics. Each pairwise potential has an associated logic function that is constructed using the logic rules, a class of elementary logic functions, and AND, OR, and NOT gates. The effect of each logic function is to turn its associated potential on and off. The N-body potential is constructed as linear combination of the pairwise potentials, where the "coefficients" of the potentials are smoothed versions of the associated logic functions. These potentials allow a potentially low-dimensional description of complex processes while still accurately capturing the relevant physics at the meso-scale. We present the proposed formalism to construct coarse-grained potentials.

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Volume: 9

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Date Submitted: 10/26/17 12:00AM

Date Published: 8/1/16 10:00AM

Publication Location:

Article Title: Mesochronic classification of trajectories in incompressible 3D vector fields over finite times

Authors: Marko Budisic, Stefan Siegmund, Doan Thai Son, Igor Mezic

Keywords: Nonautonomous dynamical systems, finite-time dynamics, time averaging, hyperbolicity, volume-preserving flows

Abstract: The mesochronic velocity is the average of the velocity field along trajectories generated by the same velocity field over a time interval of finite duration. In this paper we classify initial conditions of trajectories evolving in incompressible vector fields according to the character of motion of material around the trajectory. In particular, we provide calculations that can be used to determine the number of expanding directions and the presence of rotation from the characteristic polynomial of the Jacobian matrix of mesochronic velocity. In doing so, we show that (a) the mesochronic velocity can be used to characterize dynamical deformation of three-dimensional volumes, (b) the resulting mesochronic analysis is a finite-time extension of the Okubo–Weiss–Chong analysis of incompressible velocity fields, (c) the two-dimensional mesochronic analysis from Mezic et al. “A New Mixing Diagnostic and Gulf Oil Spill Movement”, *Science* 330, (2010), 486–489, extends to three-dimensional st

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Journal: Measurement Science and Technology

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Publication Identifier: 10.1088/0957-0233/27/9/094010

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Publication Location:

Article Title: A hybrid experimental-numerical technique for determining 3D velocity fields from planar 2D PIV data

Authors: A Eden, M Sigurdson, I Mezic, C D Meinhart

Keywords: microfluidics, electrothermal flow, optimization, PIV

Abstract: Knowledge of 3D, three component velocity fields is central to the understanding and development of effective microfluidic devices for lab-on-chip mixing applications. In this paper we present a hybrid experimental-numerical method for the generation of 3D flow information from 2D particle image velocimetry (PIV) experimental data and finite element simulations of an alternating current electrothermal (ACET) micromixer. A numerical leastsquares optimization alg PIV data to generate an improved estimation of the steady state velocity field. This 3D velocity field can be used to assess mixing phenomena more accurately than would be possible through simulation alone. Our technique can also be used to estimate uncertain quantities in experimental situations by fitting the gathered field data to a simulated physical model. The optimization algorithm reduced the root-mean-squared difference between the experimental and simulated velocity fields in the target region by more than a factor of 4

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Publication Location:

Article Title: Using invariant manifolds to construct symbolic dynamics for three-dimensional volume-preserving maps

Authors: Bryan Maelfeyt, Spencer A. Smith, and Kevin A. Mitchell,

Keywords: volume-preserving maps, heteroclinic tangles, invariant manifolds, topological dynamics, symbolic dynamics, homotopy theory

Abstract: Topological techniques are powerful tools for characterizing the complexity of many dynamical systems, including the commonly studied area-preserving maps of the plane. However, the extension of many topological techniques to higher dimensions is filled with roadblocks preventing their application. This article shows how to extend the homotopic lobe dynamics (HLD) technique, previously developed for 2D maps, to volume-preserving maps of a three-dimensional phase space. Such maps are physically relevant to particle transport by incompressible fluid flows or by magnetic field lines. Specifically, this manuscript shows how to utilize two-dimensional stable and unstable invariant manifolds, intersecting in a heteroclinic tangle, to construct a symbolic representation of the topological dynamics of the map. This symbolic representation can be used to classify system trajectories and to compute topological entropy. We illustrate the salient ideas through a series of examples with incr

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Journal: Chaos: An Interdisciplinary Journal of Nonlinear Science

Publication Identifier Type: DOI Publication Identifier: 10.1063/1.4931570

Volume: 25 Issue: 9 First Page #: 097621

Date Submitted: 10/26/17 12:00AM Date Published: 9/1/15 3:00PM

Publication Location:

Article Title: Networkcontrolology

Authors: Adilson E. Motter

Keywords: networkcontrolology nonlinearity high-dimensionality

Abstract: An increasing number of complex systems are now modeled as networks of coupled dynamical entities. Nonlinearity and high-dimensionality are hallmarks of the dynamics of such networks but have generally been regarded as obstacles to control. Here, I discuss recent advances on mathematical and computational approaches to control high-dimensional nonlinear network dynamics under general constraints on the admissible interventions. I also discuss the potential of network control to address pressing scientific problems in various disciplines.

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Journal: Physical Review Letters
Publication Identifier Type: **Publication Identifier:**
Volume: **Issue:** **First Page #:**
Date Submitted: 11/16/17 12:00AM **Date Published:** 11/4/16 2:53AM
Publication Location:

Article Title: Global network control from local information

Authors: Aleksandar Haber, Ferenc Molnar, and Adilson E. Motter

Keywords: Complex networks, control, sparsification

Abstract: In the classical control of network systems, the control actions on a node are determined as a function of the states of all nodes in the network. Motivated by applications where the global state cannot be determined in real time due to limitations in the collection, communication, and processing of data, here we introduce a control approach in which the control actions can be computed as a function of the states of nodes within a limited state information neighborhood. The trade-off between the control performance and the size of this neighborhood is primarily determined by the condition number of the controllability Gramian. Our theoretical results are supported by simulations on regular and random networks and are further illustrated by an application to the control of power-grid synchronization. We demonstrate that for well-conditioned Gramians, there is no significant loss of control performance as the size of the state information neighborhood is reduced, allowing efficient contr

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Journal: The Journal of Physical Chemistry A

Publication Identifier Type: DOI **Publication Identifier:** 10.1021/acs.jpca.7b00249

Volume: 121 **Issue:** 8 **First Page #:** 1686

Date Submitted: 10/26/17 12:00AM **Date Published:** 2/1/17 6:00AM

Publication Location:

Article Title: Ignition in an Atomistic Model of Hydrogen Oxidation

Authors: Mohammad Alaghemandi, Lucas B. Newcomb, Jason R. Green

Keywords: Combustion Ignition Molecular dynamics

Abstract: Hydrogen is a potential substitute for fossil fuels that would reduce the combustive emission of carbon dioxide. However, the low ignition energy needed to initiate oxidation imposes constraints on the efficiency and safety of hydrogen-based technologies. Microscopic details of the combustion processes, ephemeral transient species, and complex reaction networks are necessary to control and optimize the use of hydrogen as a commercial fuel. Here, we report estimates of the ignition time of hydrogen-oxygen mixtures over a wide range of equivalence ratios from extensive reactive molecular dynamics simulations. These data show that the shortest ignition time corresponds to a fuel-lean mixture with an equivalence ratio of 0.5, where the number of hydrogen and oxygen molecules in the initial mixture are identical, in good agreement with a recent chemical kinetic model. We find two signatures in the simulation data precede ignition at pressures above 200 MPa. First, there is a peak in hydrogen

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Journal: The Journal of Chemical Physics

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Date Submitted: 10/26/17 12:00AM

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Publication Location:

Article Title: Nonequilibrium phase coexistence and criticality near the second explosion limit of hydrogen combustion

Authors: Lucas B. Newcomb, Mohammad Alaghemandi, Jason R. Green

Keywords: d. Combustion, Ignition, Phase transitions, Nonequilibrium statistical mechanics

Abstract: While hydrogen is a promising source of clean energy, the safety and optimization of hydrogen technologies rely on controlling ignition through explosion limits: pressure-temperature boundaries separating explosive behavior from comparatively slow burning. Here, we show that the emergent nonequilibrium chemistry of combustible mixtures can exhibit the quantitative features of a phase transition. With stochastic simulations of the chemical kinetics for a model mechanism of hydrogen combustion, we show that the boundaries marking explosive domains of kinetic behavior are nonequilibrium critical points. Near the pressure of the second explosion limit, these critical points terminate the transient coexistence of dynamical phases—one that autoignites and another that progresses slowly. Below the critical point temperature, the chemistry of these phases is indistinguishable. In the large system limit, the pseudo-critical temperature converges to the temperature of the second explosion limit

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Journal of Chemical Theory and Computation

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Volume: 13

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Date Submitted: 10/26/17 12:00AM

Date Published: 1/1/17 12:00PM

Publication Location:

Article Title: Coupled-Cluster Valence-Bond Singles and Doubles for Strongly Correlated Systems: Block-Tensor Based Implementation and Application to Oligoacenes

Authors: Joonho Lee, David W. Small, Evgeny Epifanovsky, Martin Head-Gordon

Keywords: coupled cluster theory, valence bond, strong correlation

Abstract: We demonstrate a block-tensor based implementation of coupled-cluster valence-bond singles and doubles (CCVB-SD) [Small, D. W.; Head-Gordon M. J. Chem. Phys. 2012, 137, 114103] which is a simple modification to restricted CCSD (RCCSD) that provides a qualitatively correct description of valence correlations even in strongly correlated systems. We derive the τ -equation of CCVB-SD and the corresponding unrelaxed density matrices. The resulting production-level implementation is applied to oligoacenes, correlating up to 318 electrons in 318 orbitals. CCVB-SD shows a qualitative agreement with exact methods for short acenes and reaches the bulk limit of oligoacenes in terms of natural orbital occupation numbers, whereas RCCSD shows nonvariational behavior even for relatively short acenes. A significant reduction in polyradicaloid character is found when correlating all valence electrons instead of only the τ -electrons.

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Volume: 13

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Date Submitted: 10/26/17 12:00AM

Date Published: 4/1/17 10:00AM

Publication Location:

Article Title: Assessing DFT-D3 Damping Functions Across Widely Used Density Functionals: Can We Do Better?

Authors: Jonathon Witte, Narbe Mardirossian, Jeffrey B. Neaton, Martin Head-Gordon

Keywords: dispersion corrections, density functional theory, damping functions

Abstract: With the aim of improving the utility of the DFT-D3 empirical dispersion correction, we herein generalize the DFT-D3 damping function by optimizing an additional parameter, an exponent, which controls the rate at which the dispersion tail is activated. This method, DFT-D3(op), shorthand for “optimized power,” where power refers to the newly introduced exponent, is then parametrized for use with ten popular density functional approximations across a small set of noncovalent interactions and isomerization energies; the resulting methods are then evaluated across a large independent test set of 2475 noncovalent binding energies and isomerization energies. We find that the DFTD3(op) tail represents a substantial improvement over existing damping functions, as it affords significant reductions in errors associated with noncovalent interaction energies and geometries. The revPBE0-D3(op) and MS2-D3(op) methods in particular stand out, and our extensive testing indicates they are competitive

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Volume: 146

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Date Submitted: 10/26/17 12:00AM

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Publication Location:

Article Title: Effective empirical corrections for basis set superposition error in the def2-SVPD basis: gCP and DFT-C

Authors: Jonathon Witte, Jeffrey B. Neaton, Martin Head-Gordon

Keywords: basis set superposition error, counterpoise correction, geometric counterpoise correction

Abstract: With the aim of mitigating the basis set error in density functional theory (DFT) calculations employing local basis sets, we herein develop two empirical corrections for basis set superposition error (BSSE) in the def2-SVPD basis, a basis which—when stripped of BSSE—is capable of providing near complete-basis DFT results for non-covalent interactions. Specifically, we adapt the existing pairwise geometrical counterpoise (gCP) approach to the def2-SVPD basis, and we develop a beyond-pairwise approach, DFT-C, which we parameterize across a small set of intermolecular interactions. Both gCP and DFT-C are evaluated against the traditional Boys-Bernardi counterpoise correction across a set of 3402 non-covalent binding energies and isomerization energies. We find that the DFT-C method represents a significant improvement over gCP, particularly for non-covalently-interacting molecular clusters. Moreover, DFT-C is transferable among density functionals and can be combined with existing functionals

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Publication Location:

Article Title: A General Sparse Tensor Framework for Electronic Structure Theory

Authors: Samuel Manzer, Evgeny Epifanovsky, Anna I. Krylov, Martin Head-Gordon

Keywords: sparse tensors, electronic structure theory

Abstract: Linear-scaling algorithms must be developed in order to extend the domain of applicability of electronic structure theory to molecules of any desired size. However, the increasing complexity of modern linear-scaling methods makes code development and maintenance a significant challenge. A major contributor to this difficulty is the lack of robust software abstractions for handling block-sparse tensor operations. We therefore report the development of a highly efficient symbolic block-sparse tensor library in order to provide access to high-level software constructs to treat such problems. Our implementation supports arbitrary multidimensional sparsity in all input and output tensors. We avoid cumbersome machine-generated code by implementing all functionality as a high-level symbolic C++ language library and demonstrate that our implementation attains very high performance for linear-scaling sparse tensor contractions.

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Journal: Molecular Physics

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Publication Location:

Article Title: Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals

Authors: Narbe Mardirossian, Martin Head-Gordon

Keywords: density functionals, density functional theory, computational chemistry

Abstract: In the past 30 years, Kohn–Sham density functional theory has emerged as the most popular electronic structure method in computational chemistry. To assess the ever-increasing number of approximate exchange–correlation functionals, this review benchmarks a total of 200 density functionals on a molecular database (MGCDB84) of nearly 5000 data points. The database employed, provided as Supplemental Data, is comprised of 84 data-sets and contains non-covalent interactions, isomerisation energies, thermochemistry, and barrier heights. In addition, the evolution of non-empirical and semi-empirical density functional design is reviewed, and guidelines are provided for the proper and effective use of density functionals. The most promising functional considered is B97M-V, a range-separated hybrid meta-GGA with VV10 nonlocal correlation, designed using a combinatorial approach. From the local GGAs, B97-D3, revPBE-D3, and BLYP-D3 are recommended, while from the local meta-GGAs, B97M-rV is the

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Volume: Issue: First Page #: 1
Date Submitted: 10/26/17 12:00AM Date Published: 7/17/17 5:00AM
Publication Location:

Article Title: State observation and sensor selection for nonlinear networks

Authors: Aleksandar Haber, Ferenc Molnar, Adilson E. Motter

Keywords: Complex networks, observability, sensor selection, state and parameter estimation

Abstract: A large variety of dynamical systems, such as chemical and biomolecular systems, can be seen as networks of nonlinear entities. Prediction, control, and identification of such nonlinear networks require knowledge of the state of the system. However, network states are usually unknown, and only a fraction of the state variables are directly measurable. The observability problem concerns reconstructing the network state from this limited information. Here, we propose a general optimization-based approach for observing the states of nonlinear networks and for optimally selecting the observed variables. Our results reveal several fundamental limitations in network observability, such as the trade-off between the fraction of observed variables and the observation length on one side, and the estimation error on the other side. We also show that, owing to the crucial role played by the dynamics, purely graph-theoretic observability approaches cannot provide conclusions about one's practical a

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Volume: 147 Issue: First Page #:
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Article Title: General Application of Tolman's Concept of Activation Energy

Authors: Homayoon Rafatijo, Donald L. Thompson

Keywords: Activation Energies, Tolman, activation energy concept, Hydrogen Combustion Reaction kinetics
Classical Molecular Dynamics

Abstract: We present a generalization of Tolman's concept of activation energy applicable to thermal and non-thermal reactions in molecular dynamics simulations of reactions in bulk gases. To illustrate the applicability of the method molecular dynamics calculations were carried out for the NVT ensemble to determine the activation energies of $O_2 + H_2 \rightarrow H + HO_2$ and $2O_2 + H_2 \rightarrow 2HO_2$ from MD simulation results for $[H_2]/[O_2] = 1$ at 3,000 K using the reactive force field ReaxFF. Assuming local thermodynamic equilibrium we define the reaction cluster local energy (RCLE), the energy of the atoms participating in an individual reaction, which is conserved. The generalized Tolman activation energy (GTEa) approach is applicable to reactions of any molecularity. Although we have applied GTEa for thermal conditions, it is applicable to chemistry occurring under non-thermal conditions because it rests upon local rather than global equilibrium. We have defined the transition configuration (TC), unique point

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Publication Location:

Article Title: Explosion limits of hydrogen–oxygen mixtures from nonequilibrium critical points

Authors: Lucas B. Newcomb, Michael E. Marucci, Jason R. Green

Keywords: Explosion limits, stochastic kinetics, phase transitions

Abstract: The explosion limits of hydrogen–oxygen mixtures are macroscopic, temperature–pressure boundaries that divide the overall chemistry of hydrogen oxidation into slow-burning and explosive regimes. Here, we demonstrate that it is possible to recover the three chemical explosion limits of H₂/O₂ mixtures from nonequilibrium stochastic trajectories. This demonstration relies on the finding that, in explosive regimes, these trajectories have the quantitative features of a dynamical phase transition. Through computer simulations for both a generic and a reduced model for hydrogen oxidation, we find only one dominant reactive phase at temperatures below the explosion limits. At temperatures above the limits, however, a second phase transiently emerges from the chemistry. By locating the pseudo-critical temperature where two reactive phases are distinguishable, we construct all three explosion-limit boundaries for model hydrogen–oxygen mixtures of finite size.

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Publication Location:

Article Title: Entrance and escape dynamics for the typical set

Authors: Schuyler B. Nicholson, Jonah S. Greenberg, Jason R. Green

Keywords: d. Nonequilibrium statistical mechanics, information theory, Markov processes

Abstract: According to the asymptotic equipartition property, sufficiently long sequences of random variables converge to a set that is typical. While the size and probability of this set are central to information theory and statistical mechanics, they can often only be estimated accurately in the asymptotic limit due to the exponential growth in possible sequences. Here we derive a time-inhomogeneous dynamics that constructs the properties of the typical set for all finite length sequences of independent and identically distributed random variables. These dynamics link the finite properties of the typical set to asymptotic results and allow the typical set to be applied to small and transient systems. The main result is a geometric mapping—the triangle map—relating sequences of random variables of length n to those of length $n + 1$. We show that the number of points in this map needed to quantify the properties of the typical set grows linearly with sequence length, despite the exponential

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Date Submitted: 8/23/18 12:00AM

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Publication Location:

Article Title: Effects of temperature and mass conservation on the typical chemical sequences of hydrogen oxidation

Authors: Schuyler B. Nicholson, Mohammad Alaghemandi, Jason R. Green

Keywords: d. Nonequilibrium statistical mechanics, information theory, hydrogen combustion

Abstract: Macroscopic properties of reacting mixtures are necessary to design synthetic strategies, determine yield, and improve the energy and atom efficiency of many chemical processes. The set of time-ordered sequences of chemical species are one representation of the evolution from reactants to products. However, only a fraction of the possible sequences is typical, having the majority of the joint probability and characterizing the succession of chemical nonequilibrium states. Here, we extend a variational measure of typicality and apply it to atomistic simulations of a model for hydrogen oxidation over a range of temperatures. We demonstrate an information-theoretic methodology to identify typical sequences under the constraints of mass conservation. Including these constraints leads to an improved ability to learn the chemical sequence mechanism from experimentally accessible data. From these typical sequences, we show that two quantities defining the variational typical features of ...

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Article Title: Ab initio and transition state theory study of the OH + HO₂ → H₂O + O₂(³S_g)/O₂(¹g) reactions: yield and role of O₂(¹g) in H₂O₂ decomposition and in combustion of H₂

Authors: M. Monge-Palacios, S. Mani Sarathy

Keywords: variational transition state theory (VTST), ab initio, kinetics, kinetic models, hydrogen combustion, radicals, and singlet excited molecular oxygen

Abstract: Reactions of hydroxyl (OH) and hydroperoxyl (HO₂) are important for governing the reactivity of combustion systems. We performed post-CCSD(T) ab initio calculations at the W3X-L//CCSD = FC/cc-pVTZ level to explore the triplet ground-state and singlet excited-state potential energy surfaces of the OH + HO₂ → H₂O + O₂(³S_g)/O₂(¹D_g) reactions. Using microcanonical and multistructural canonical transition state theories, we calculated the rate constant for the triplet and singlet channels over the temperature range 200–2500 K, represented by $k(T) = 3.08 \times 10^{12} T^{0.07} \exp(1151/RT) + 8.00 \times 10^{12} T^{0.32} \exp(-6896/RT)$ and $k(T) = 2.14 \times 10^6 T^{1.65} \exp(-2180/RT)$ in cm³ mol⁻¹ s⁻¹, respectively. The branching ratios show that the yield of singlet excited oxygen is small (0.5% below 1000 K). To ascertain the importance of singlet oxygen channel, our new kinetic information was implemented into the kinetic model for hydrogen combustion recently updated by Konnov (Combust. Flame, 2015, 162, 3755–3772). The

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Publication Location:

Article Title: Regularized Orbital-Optimized Second-Order Møller–Plesset Perturbation Theory: A Reliable Fifth-Order-Scaling Electron Correlation Model with Orbital Energy Dependent Regularizers

Authors: Joonho Lee, Martin Head-Gordon

Keywords: electron correlation, quantum chemistry, perturbation theory, bond-breaking, regularization

Abstract: We derive and assess two new classes of regularizers that cope with oscillating denominators in the single-reference second-order Møller-Plesset perturbation theory (MP2). In particular, we discuss the use of two types of orbital energy dependent regularizers, η and ϵ , in conjunction with orbital-optimized MP2 (OOMP2). The resulting fifth-order scaling methods, η -OOMP2 and ϵ -OOMP2, have been examined for bond-breaking, thermochemistry, non-bonded interactions and biradical problems. Both methods with strong enough regularization restore restricted to unrestricted instability (i.e. Coulson-Fischer points) that unregularized OOMP2 lacks when breaking bonds in H₂, C₂H₆, C₂H₄, and C₂H₂. The training of the η and ϵ regularization parameters was performed with the W4-11 set. We further developed scaled correlation energy variants, η -S-OOMP2 and ϵ -S-OOMP2, by training on the TAE140 subset of the W4-11 set. Those new OOMP2 methods were tested on the RSE43 set and the [prev: TA14]TA13 set where unmo

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Title: EXPLORING CHEMICAL REACTION COMPLEXITY: APPLICATION TO HYDROGEN COMBUSTION

Authors: Homayoon Rafatijo

Acknowledged Federal Support: Y

Publication Type: Thesis or Dissertation

Institution: University of California-Berkeley

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Title: Fast Algorithms for Exact Exchange

Authors: Samuel Fenton Manzer

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Title: DESIGNING AND ASSESSING DENSITY FUNCTIONALS

Authors: NARBE MARDIROSSIAN

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Project Summary - Grant # W911NF-14-1-0359
Reporting Period: September 1, 2019 – December 31, 2019
Effort Title: *New Theoretical and Experimental Methods for Predicting Fundamental Mechanisms of Complex Chemical Processes*

Donald L. Thompson, PI
Chemistry Department
University of Missouri * Columbia, Missouri 65211

Objective

The objective was to develop methods for determining the mechanistic details of complex gas-phase chemistry from molecular dynamics (MD) simulations, and to gain reliable, accurate insights into the detailed and the macroscopic behaviors of complex overall reactions such as hydrocarbon combustion.

Approach

We carried out molecular dynamics (MD) simulations to develop methods for making better predictions of the behaviors of combustion chemistry under conditions of practical interest. To this end we used the approximate force field ReaxFF to characterize the progress of overall chemistry towards the final equilibrium in hydrogen combustion and the thermal dissociation of HOOH. We have developed theoretical methods based on Bodenstein's theory of collisions to identify sequences of reactions that transform the reactants into the products from MD simulation results. We have developed software for monitoring the evolution of total number of species, which are present in the system, during the course of an overall reaction. This provides a means of determining how the chemistry evolves from reactants to final products.

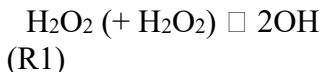
Relevance to Army

This project provides DoD researchers with practical modeling capability and computational tools to guide the development of new fuels and more efficient use of existing fuels. This work could facilitate the design of more efficient and powerful engines. Furthermore, it educated students and postdoctoral fellows in research relevant to DoD missions and thus could have decades-long ramifications for DoD research capabilities.

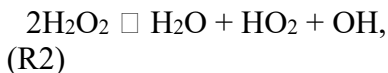
Accomplishments for Reporting Period

Proposed the concept of reaction stream for overall reactions. We have attempted to define the reaction stream for an overall reaction as a pathway leading from the reactants to the products in order to illustrate the concept. The stream is comprised of all sequences of individual reactions of the evolving chemistry. We illustrated the applicability of the concept by identifying all the reaction sequences in the overall reaction $10\text{H}_2\text{O}_2 \rightarrow 10\text{H}_2\text{O} + 5\text{O}_2$. We began by defining four sets containing all reaction sequences involving hydrogen atoms: sets containing atomic sequences that transform hydrogen atoms from H_2O_2 to H_2O , from H_2O to H_2O_2 , from H_2O_2 to another H_2O_2 ($\text{HO}'\text{O}'\text{H}' \rightarrow \dots \rightarrow \text{HOOH}$), and from H_2O to another H_2O ($\text{HO}'\text{H}' \rightarrow \dots \rightarrow \text{HOH}$). Then, we used a reaction identification algorithm to monitor all hydrogen atoms and identify all sequences of isolated reactions making up each set. We used arborescence graphs to depict these sets; see Figure 1.

ReaxFF-based NVE simulations of ten H₂O₂ molecules at 2,100 K predicted two initial reactions:



and



with contributions of 62% and 38% to the initial radical production, respectively. The most frequent subsequent reactions were



We examined how the differences in the time scales of different sequences of reactions affect chemical reaction complexity. The overall reaction $10\text{H}_2\text{O}_2 \rightarrow 10\text{H}_2\text{O} + 5\text{O}_2$ is complex partly because the times required for completion of atomic reaction sequences varies significantly. We considered two reaction sequences of length two that equally contribute in the set $\text{H}_2\text{O}_2 \rightarrow \dots \rightarrow \text{H}_2\text{O}$ set. The first sequence (R1-R3) began with the decomposition of a HOOH molecule and proceeded by reaction $\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$, and the second sequence (R1-R7) began with decomposition of a HOOH molecule and proceeded by reaction $\text{OH} + \text{HO}'\text{H}' \rightarrow \text{O}'\text{H}' + \text{HOH}$. We observed that in presence of equal number of H₂O₂ and H₂O molecules, a nascent OH radical with a lifetime smaller than 3 ps produced by the decomposition reaction is twice as likely to participate in the reaction $\text{OH} + \text{HO}'\text{H}' \rightarrow \text{O}'\text{H}' + \text{HOH}$ than in $\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$; see Figure 2.

Collaborations and Technology Transfer

N/A

Research plans for next reporting period

N/A

Resulting Journal Publications During Reporting Period

- Homayoon Rafatijo, *Computing Activation Energies of Non-Thermal Reactions*, Molecular Physics, doi: 10.1080/00268976.2020.1749952.

Graduate Students Involved During Reporting Period

- None

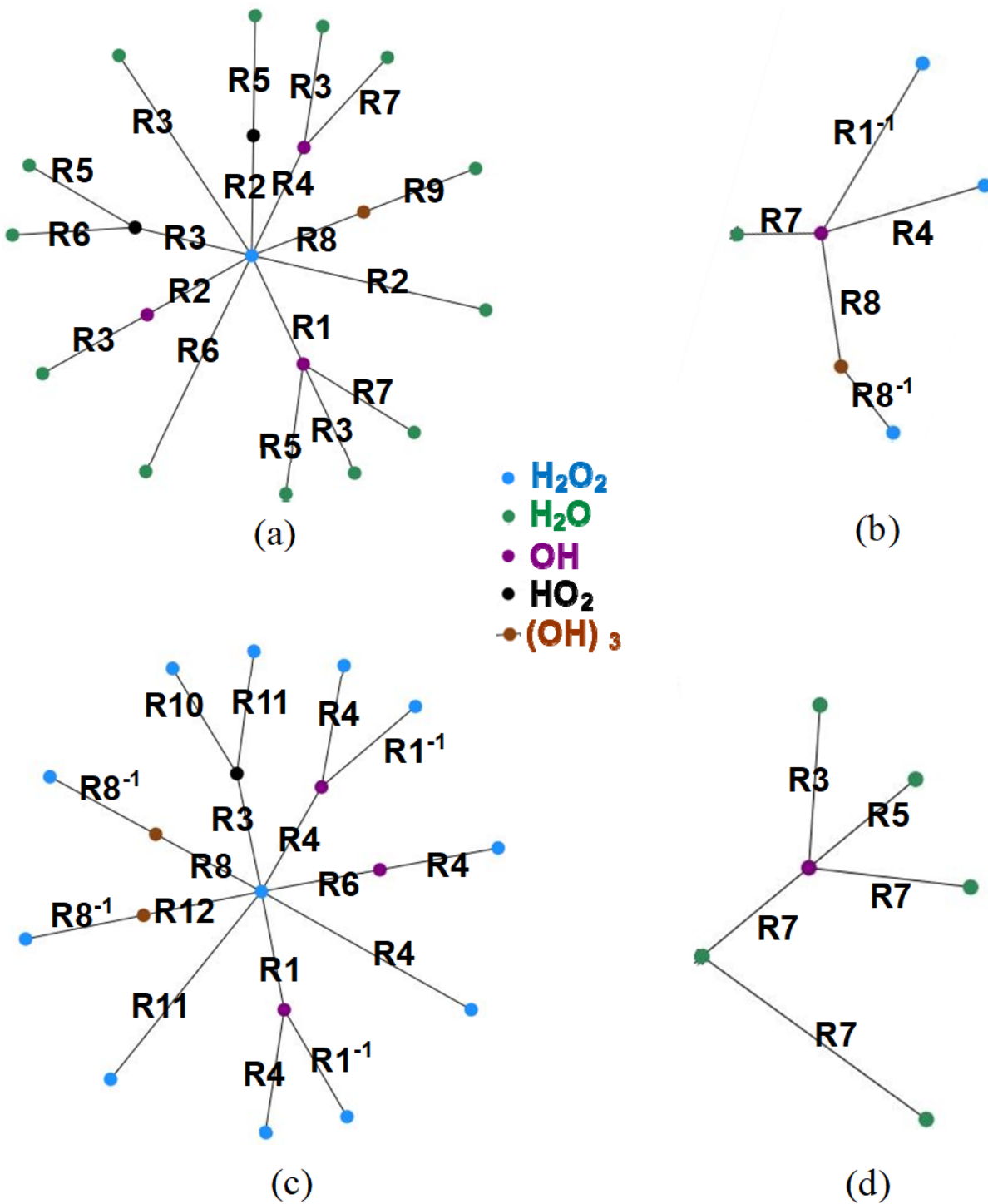


Figure 1. We used arborescence graphs to depict the four sets of reaction sequences making up the reaction stream. Vertices represent different species distinguished by different colors, and the line between two vertices represents a reaction transmitting hydrogen atoms between the two

vertices. Depending on the sequence set the root vertex is either H_2O_2 or H_2O . Atomic reaction sequences for each set are ranked based on their frequency in Table I. Dominant atomic reaction sequences for hydrogen atoms in the overall reaction $10\text{H}_2\text{O}_2 \rightarrow 10\text{H}_2\text{O} + 5\text{O}_2$ that connect (a) a H_2O_2 molecule to a water molecule, (b) a water molecule to a H_2O_2 molecule, (c) a H_2O_2 molecule to another H_2O_2 molecule, and (d) a H_2O molecule to another H_2O molecule.

Table I: Frequencies for the atomic reaction sequences illustrated in Figure 1.

| Reaction Stream | | | | | | | |
|---|------------------------|--|------------------------|--|------------------------|--|------------------------|
| $\text{H}_2\text{O}_2 \rightarrow \dots \rightarrow \text{H}_2\text{O}$ (63%) ^a | | $\text{H}_2\text{O} \rightarrow \dots \rightarrow \text{H}_2\text{O}_2$ (3%) ^a | | $\text{HO}'\text{O}'\text{H}' \rightarrow \dots \rightarrow \text{HOOH}$ (23%) ^a | | $\text{HO}'\text{H}' \rightarrow \dots \rightarrow \text{HOH}$ (11%) ^a | |
| ARS ^c | Frequency ^b | ARS | Frequency ^b | ARS | Frequency ^b | ARS | Frequency ^b |
| R3 | 27% | R7-R1 ⁻¹ | 54% | R4 | 33% | R7 | 54% |
| R1-R7 | 13% | R7-R4 | 29% | R3-R10 | 13% | R7-R7 | 27% |
| R1-R3 | 11% | R7-R8-R8 ⁻ | 14% | R1-R4 | 9% | R7-R5 | 8% |
| R6 | 6% | | | R8-R8 ⁻¹ | 7% | R7-R3 | 5% |
| R3-R5 | 5% | | | R11 | 6% | | |
| R2 | 4% | | | R6-R4 | 5% | | |
| R4-R3 | 3% | | | R4-R4 | 4% | | |
| R3-R6 | 3% | | | R12-R8 ⁻¹ | 3% | | |
| R1-R5 | 2% | | | R3-R11 | 2% | | |
| R4-R7 | 2% | | | R1-R1 ⁻¹ | 2% | | |
| R8-R9 | 2% | | | R4-R1 ⁻¹ | 2% | | |
| R2-R3 | 1% | | | | | | |
| R2-R5 | 1% | | | | | | |

^a This is the percentage contribution of the set to the reaction stream.

^b The frequency in each case was calculated as the ratio of number of times the sequence was detected and the total number of atomic reaction sequences in that set multiplied by 100.

^c ARS stands for atomic reaction sequences.

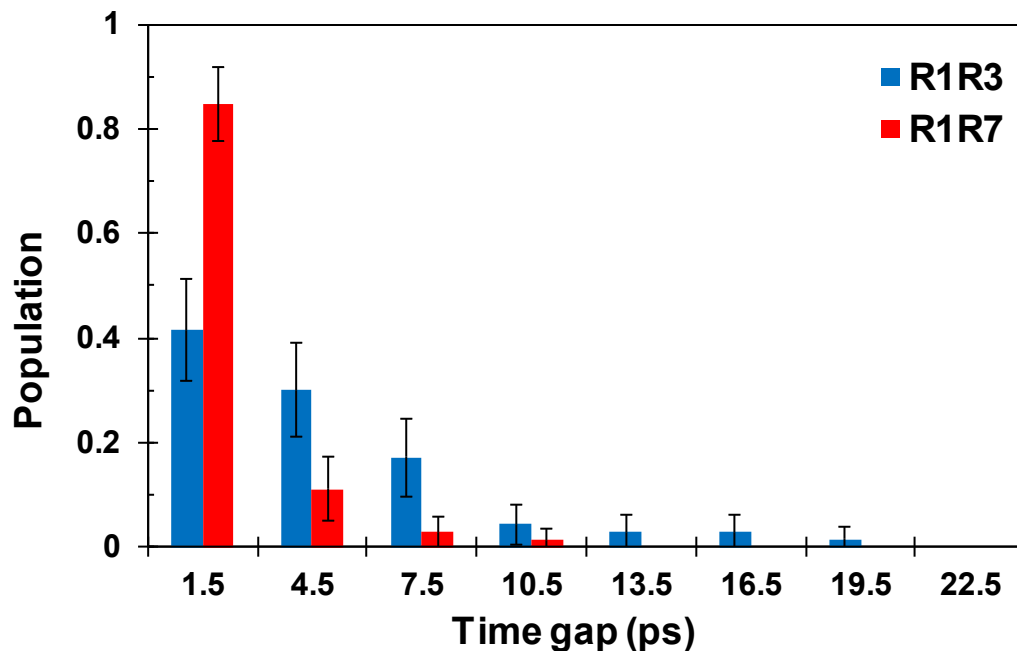


Figure 2. The distributions of time gaps for two sequences of length two that transmits hydrogen atoms from H_2O_2 to H_2O . While both sequences begin with the dissociation of a H_2O_2 molecule (R1), the OH radical undergoes (blue) $\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$ (R3) or (red) $\text{OH} + \text{HO}'\text{H}' \rightarrow \text{O}'\text{H}' + \text{HOH}$ (R7) to produce H_2O . These two sequences were observed equally frequently; see Table I. The time gap between the two sequential reactions in R1-R7 is 3.1 ps lower than that in R1-R3.

Project Summary - Grant # W911NF-14-1-0359 (MURI Sub)
Reporting Period: September 1, 2019 – December 31, 2019
Effort Title: *New Theoretical and Experimental Methods for Predicting Fundamental Mechanisms of Complex Chemical Processes*

Statistical dynamics of complex chemistry (MURI sub)

Jason R. Green
Departments of Chemistry and Physics
University of Massachusetts Boston * Boston, MA 02125

Relevance to Army

Efficiently harnessing the heat produced by combustion to do useful work requires accurate predictions of bulk chemistry from molecular dynamics. This project will provide DoD researchers with new theory and computationally effective strategies for predicting the combustion chemistry that underlies numerous applications. For example, hydrogen is a high-profile, targeted source of clean energy that still requires the development of measures to mitigate unintended ignition. Explosion limits and the energetic fluctuations that spark explosions are central to these safety measures. The project here targets reliable predictions of autoignition from simulations that will inform such measures and enable the broader application of hydrogen as a zero-emission/clean, renewable fuel. Another aim of the project is to transform our theoretical view of how the macroscopic phenomenon of ignition emerges from the statistics of molecular events and, ultimately, impact the development of the improved measures for storing and transporting hydrogen safely.

Accomplishments for Reporting Period

- *Classical speed limit on stochastic thermodynamic observables (rate of heat release):* We have derived an Ehrenfest-like equation of motion for the expectation of stochastic thermodynamic observables and found that the analog of the quantum-mechanical commutator is the covariance between the observable and the rate of change of the information content in the underlying nonequilibrium distribution (Figs. 1 and 2). The energy exchanged as heat between a system and its surroundings, for example, can then be interpreted as a measure of the linear relationship between energy and information. An uncertainty relation follows that bounds the time that elapses before the change in the mean of any observable has the same magnitude as its standard deviation. Analogous to the Mandelstam-Tamm form of the time-energy uncertainty relation in quantum mechanics, this inequality bounds the speed of arbitrary stochastic thermodynamic observables, independent of the dynamics, system size, and nonequilibrium conditions (heat, entropy production/flow, chemical/dissipative work).
- *Dynamic scaling laws for complex chemistry:* By formulating the dynamics of fluctuations as a nonequilibrium surface-growth, we have shown that dynamic scaling features are apparent in the stochastic thermodynamic observables of well-mixed chemical kinetic systems. From a survey of the stochastic kinetics for chemical reactions at and away from chemical equilibrium with stochastic chemical kinetics (home-built code), we have found universality

classes for the dynamical activity and the entropy flow defined by kinetic molecularity and dynamic scaling relations.

Collaborations and Technology Transfer

We are disseminating the final results of this project through the publication of high-quality papers in selective peer-reviewed journals.

Resulting Journal Publications During Reporting Period

- Schuyler B. Nicholson, Luis Pedro Garc'ia-Pintos, Adolfo del Campo, Jason R. Green "Time- information uncertainty relations in thermodynamics" *Nat. Physics*. **2020**
Conditionally accepted.
- Luke W. Bertels, Lucas B. Newcomb, Mohammad Alaghemandi, Jason R. Green, Martin Head-Gordon "Benchmarking the performance of the ReaxFF reactive force field on hydrogen combustion systems" *J. Phys. Chem. A* **2020** Accepted.
- Zachary G. Nicolau, Takashi Nishikawa, Schuyler B. Nicholson, Jason R. Green, Adilson E. Motter, "Non-normality and non-monotonic dynamics in complex reaction networks" *Submitted 2020*

Graduate Students Involved During Reporting Period

Ph.D students

- Rebecca A. Bone (Ph.D. current)

Masters students

- Michael E. Marucci (M.S. current)

Students

Number of undergraduate participants: 0

Number of graduate participants: 2

Number of participants that received a STEM degree (in this past year): 0

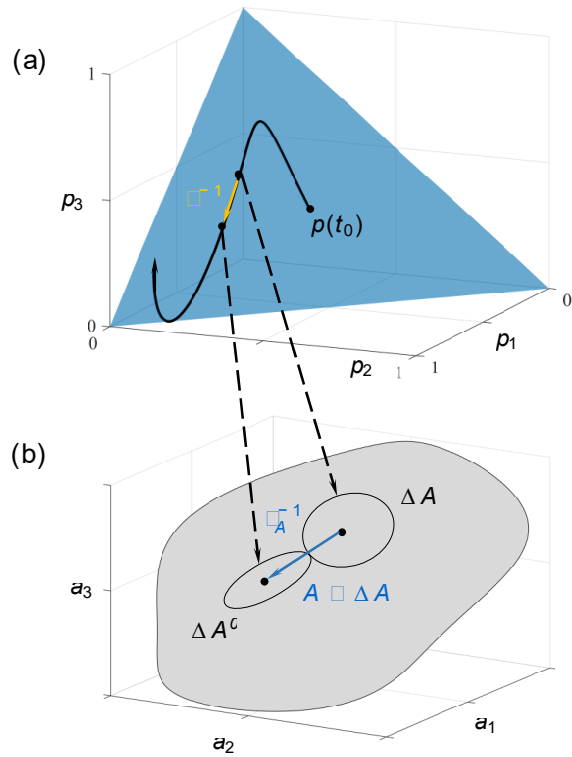


Figure 1 Statistical distinguishability of thermodynamic observables. As a result of an (a) underlying stochastic dynamics and probability distribution over configurations, an (b) observable A of a system evolves in time away from thermodynamic equilibrium. The distributions of A at two times are distinguishable when their standard deviations do not overlap. The time to reach a distinguishable state is when the path function has the magnitude of one initial standard deviation ΔA .

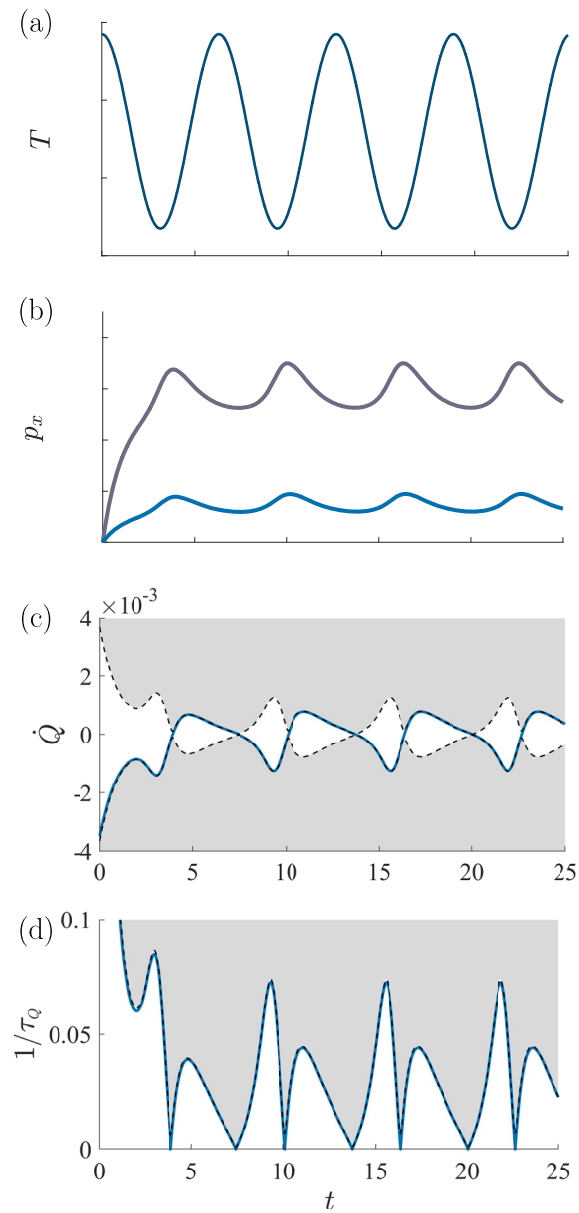


Figure 2 Illustration of time-information uncertainty relation and speed limit on the dissipation of heat for a three-state Markov model. (a) Periodic temperature protocol. (b) Probability of two states as a function of time. (c) Heat flux as a function of time (blue) bounded by the time-information uncertainty relation (dashed). (d) Speed of the heat exchanged as a function of time (blue) is tightly bounded by the speed limit time set by the Fisher information (dashed).

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Berkeley Subcontract

Martin Head-Gordon
Department of Chemistry
University of California, Berkeley, CA 94720.

Accomplishments for Reporting Period (insert into “What was accomplished toward achieving these goals”)

- **Polarized many-body expansion (PolBE) for electronic structure of large systems (completed):** The Many-Body Expansion (MBE) is a useful tool to simulate condensed phase chemical systems, often avoiding the steep computational cost of usual electronic structure methods. However, it often requires higher than 2-body terms to achieve quantitative accuracy. Therefore we developed the Polarized MBE (PolBE) method where each MBE energy contribution is treated as an embedding problem. In each energy term, a smaller fragment is embedded into a larger, polarized environment and only a small region is treated at the high-level of theory using embedded mean-field theory. The role of polarized environment was found to be crucial in providing quantitative accuracy at the 2-body level.
- **Assessment of REAXFF using electronic structure theory (interaction with Jason Green) (completed)** Three variants of ReaxFF were assessed along reaction paths for key elementary reactions in hydrogen combustion, including in some cases, 2-d grid scans to understand the origin of breakdowns. High level benchmarks reveal that state-of-the-art DFT shows errors that are roughly 10 times smaller than current versions of REAXFF, which motivates future improvements to reactive force fields.
- **Provision of electronic structure data for development of a reactive force field (interaction with Igor Mezc) (on-going):** The potential stitching tools developed by the Mezc group provide an alternative path to a reactive force field, and we have provided the Mezc group with intrinsic reaction coordinates and high quality electronic structure energies along pathways for roughly twenty important elementary reactions involved in hydrogen combustion. We have continued to have bi-weekly meetings, and the project is progressing.

Resulting Journal Publications During Reporting Period

[1] “Making Many-Body Interactions Nearly Pairwise Additive: The Polarized Many-Body Expansion Approach”, S. Prasad Veccham, J. Lee and M. Head-Gordon, J. Chem. Phys. 151, 194101 (2019); doi: 10.1063/1.5125802

[2] “Benchmarking the Performance of the ReaxFF Reactive Force Field on Hydrogen Combustion Systems”, L.W. Bertels, L.B. Newcomb, M. Alaghemandi, J.R. Green, and M. Head-Gordon, J. Phys. Chem. A (in press, accepted June 8, 2020); DOI: 10.1021/acs.jpca.0c02734

[3) Thesis: “Postmodern Electronic Structure Theory,” University of California, Berkeley.
Joonho Lee, completed August 2019

Graduate Students Involved During Reporting Period

- Luke Bertels (Ph.D, current)
- Joonho Lee (Ph. D, graduated)
- Jonathan Wong (Ph. D, current)
- Josie Hendricks (Ph. D, current)

Students

Number of undergraduate and graduate STEM participants: 2

Number of participants that received a STEM degree: 1

Awards, Honors and Appointments

- Schrodinger Medal of the World Association of Theoretical and Computational Chemists (WATOC) (2020).
- APS Justin Jankunas Doctoral Dissertation Award in Chemical Physics (to Joonho Lee for the thesis listed above) (American Physical Society, 2020).

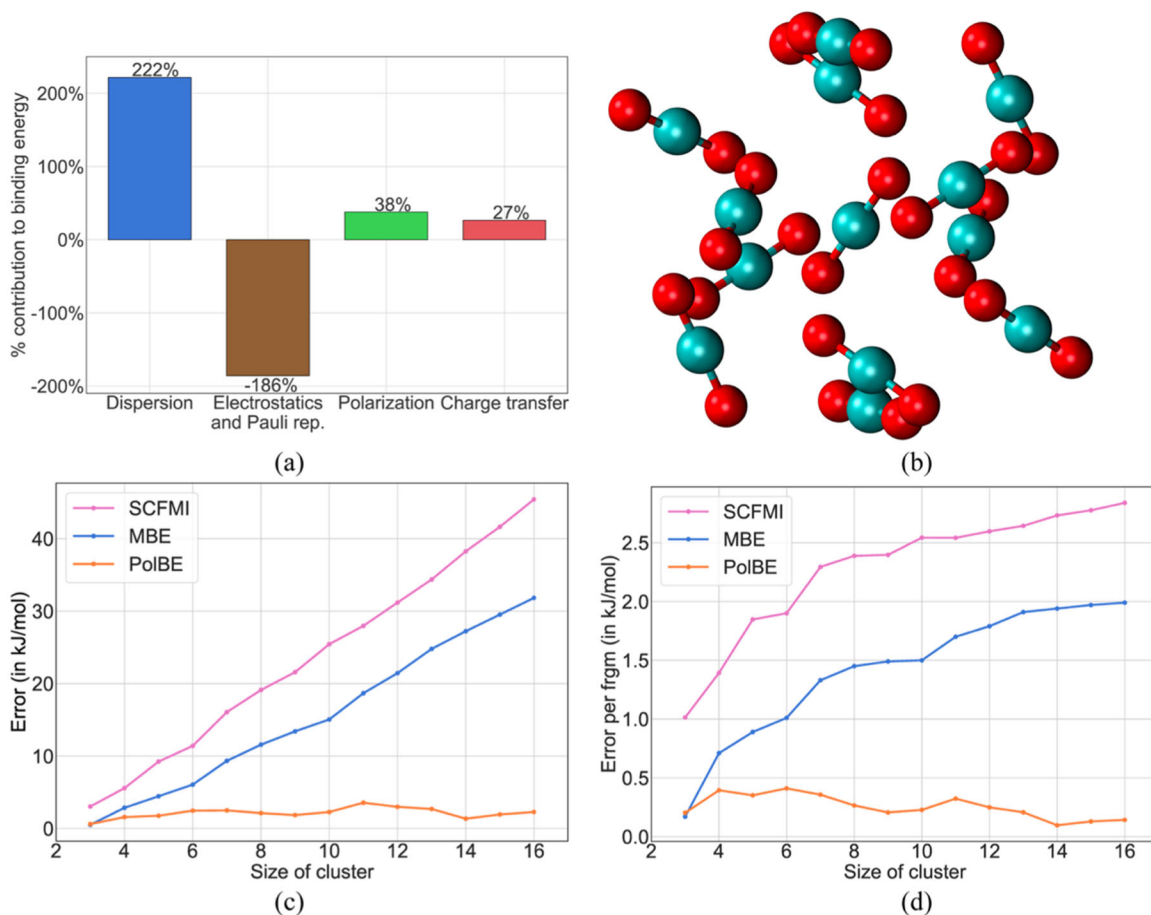
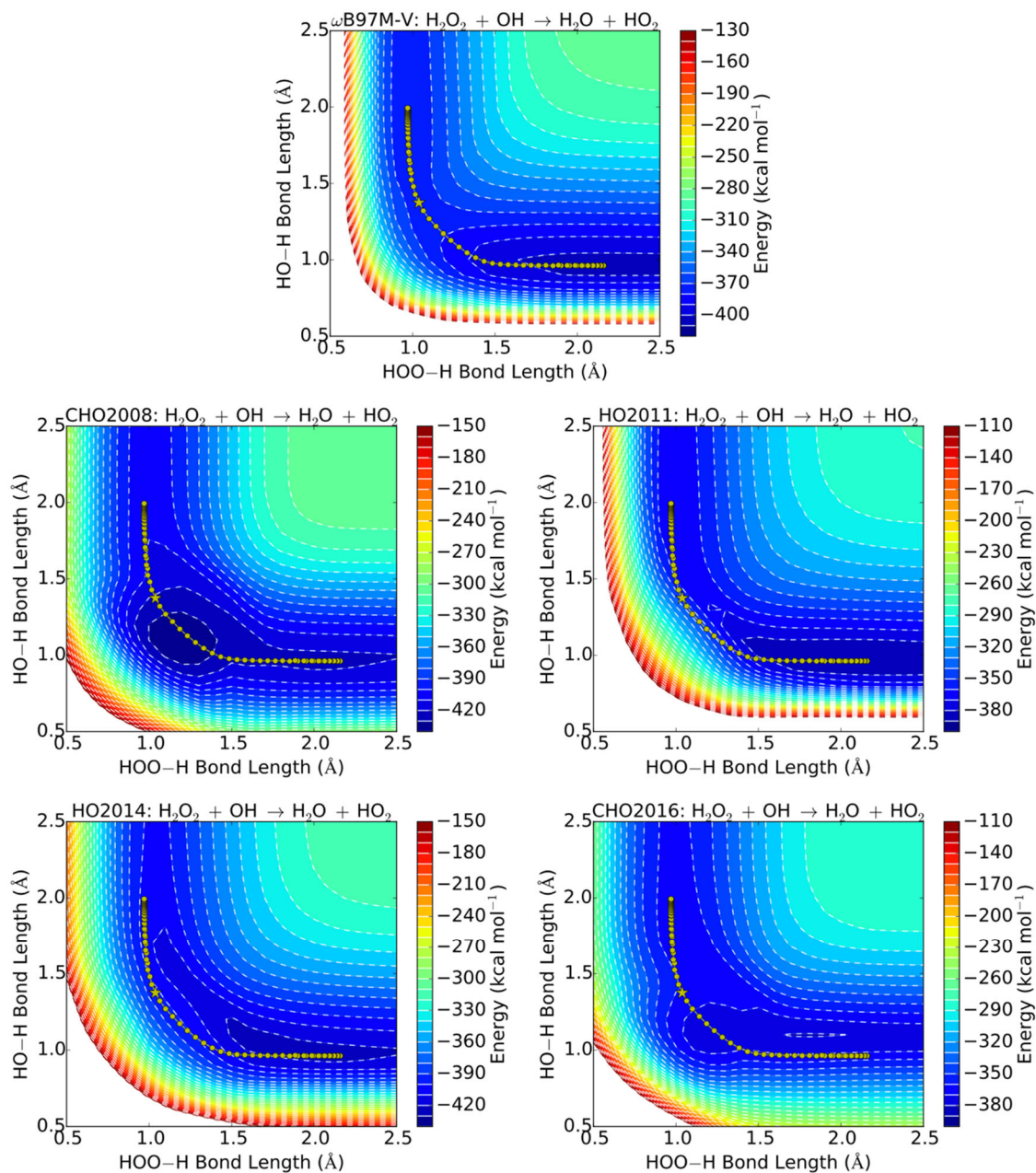


FIG. 4. (a) Energy decomposition analysis for all CO₂ clusters considered in this study. Dispersion is the interaction between induced dipoles of different fragments. Pauli repulsion is the steric energetic penalty that occurs when two nonbonded atoms are forced to occupy the same space. Electrostatics is the energy associated with the Coulombic interactions between fragments. Polarization is the energy associated with relaxation of molecular orbitals. Charge transfer is the energy associated with the flow of electrons between the fragments. (b) A CO₂ cluster containing 13 molecules. (c) SCFMI, vacuum MBE, and PolBE errors as a function of CO₂ cluster size. (d) SCFMI, vacuum MBE, and PolBE errors per fragment as a function of CO₂ cluster size. For comparison, the reference binding energy for the 16-mer is 225.3 kJ/mol.

Illustrations of the reduced error using the polarized many-body expansion (PolBE) to describe a model system consisting of 3-16 carbon dioxide molecules. The results are dramatically better than the conventional MBE.



Unrelaxed potential energy surfaces for the $\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$ reaction, in kcal mol⁻¹, are presented for $\omega\text{B97M-V}$ and four ReaxFF parameter sets. Here the $\text{HOO}\cdots\text{H}\cdots\text{OH}$ angle is linearized while all other geometric parameters are held fixed in the transition state configuration as optimized at the $\omega\text{B97M-V}/\text{cc-pVTZ}$ level of theory. The interatomic distances for points along the intrinsic reaction coordinate calculated at the $\omega\text{B97M-V}/\text{cc-pVTZ}$ level of theory are overlaid on each surface. The energies presented are relative to the energies of the isolated atoms.

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Igor Mezic
Department of Mechanical Engineering
University of California-Santa Barbara
Santa Barbara, California 93106

Relevance to Army

Development of the theory of description of reaction processes leads to increased accuracy of combustion process models. Their use in conjunction with fluid dynamical codes that add the description of dynamical evolution in engine combustors should result in better combustor designs, increased engine efficiency, and reduction in energy use.

Accomplishments for Reporting Period

- 1) Developed further a systematic procedure based on programmable potentials for learning coarse-grained reaction EST (A. Avilla, with M. Head-Gordon).

Collaborations and Technology Transfer

- With M. Head-Gordon secured a DARPA project for design of materials using the EST/Programmable Potentials methodology.
- Shared data with AFRL Materials team

Resulting Journal Publications During Reporting Period

- Mezić I. Spectrum of the Koopman operator, spectral expansions in functional spaces, and state-space geometry. *Journal of Nonlinear Science*. 2019 Oct 17:1-55.
- Korda M, Putinar M, Mezić I. Data-driven spectral analysis of the Koopman operator. *Applied and Computational Harmonic Analysis*. 2020 Mar 1;48(2):599-629.
- Book: Mauroy A, Susuki Y, Mezić I. *The Koopman Operator in Systems and Control 2020* (pp. 3-33). Springer, Cham.

Graduate Students Involved and current During Reporting Period

- Allan Avila , Cory Brown

In this period we developed theory of Koopman operators powerful enough to describe state space of complex dynamical systems that occur in the context of programmable potential methodology for description of chemical processes developed in this project.

We examined spectral operator-theoretic properties of linear and nonlinear dynamical systems with globally stable attractors. Using the Kato decomposition, we developed a spectral expansion for general linear autonomous dynamical systems with analytic observables and define the notion of generalized eigenfunctions of the associated Koopman operator. We interpret stable, unstable and center subspaces in terms of zero-level sets of generalized eigenfunctions. We then utilize conjugacy properties of Koopman eigenfunctions and the new notion of open eigenfunctions—defined on subsets of state space—to extend these results to nonlinear dynamical systems with an equilibrium. We provide a characterization of (global) center manifolds, center-stable, and center-unstable manifolds in terms of joint zero-level sets of families of Koopman operator eigenfunctions associated with the nonlinear system. After defining a new class of Hilbert spaces, that capture the on- and off-attractor properties of dissipative dynamics, and introducing the concept of modulated Fock spaces, we develop spectral expansions for a class of dynamical systems possessing globally stable limit cycles and limit tori, with observables that are square-integrable in on-attractor variables and analytic in off-attractor variables. We discuss definitions of stable, unstable, and global center manifolds in such nonlinear systems with (quasi)-periodic attractors in terms of zero-level sets of Koopman operator eigenfunctions. We define the notion of isostables for a general class of nonlinear systems. In contrast with the systems that have discrete Koopman operator spectrum, we provide a simple example of a measure-preserving system that is not chaotic but has continuous spectrum, and discuss experimental observations of spectrum on such systems. Such systems are common among those representing chemical reactions via a suitable programmable potential Hamiltonian. We also provide a brief characterization of the data types corresponding to the obtained theoretical results and define the coherent principal dimension for a class of datasets based on the lattice-type principal spectrum of the associated Koopman operator.

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Effort Title: New Theoretical & Experimental Methods for Predicting Fundamental Mechanisms of Complex Chemical Processes (MURI sub)

Co-PI Name: Adilson E. Motter
Department: Physics and Astronomy
Northwestern University, Evanston, IL 60208

Objective

The Northwestern University group has focused on the network analysis and control of combustion reaction systems. The main objectives are to 1) infer the state of the chemical network, 2) determine the impact of unknown intermediate reactions/species, 3) rationally manipulate the behavior of the reaction network, and 4) discover general relations between network structure and dynamics.

Approach

The current reporting period was focused on the fourth objective, namely the discovery general relations between network structure and dynamics. This was pursued by combining current results in network theory, spectral analysis, and dynamical systems methods. As further elaborated below, this work allowed us to investigate the relation between the non-normality of the relevant coupling matrix and non-monotonicity of the dynamics using a master equation representation of combustion reaction systems (see **Figure 1**).

Relevance to Army

The research completed over the reporting period helped identify universal relations between network structure and combustion dynamics. This is relevant to fundamental the challenges involved in modeling, predicting, and designing combustion reaction processes that have higher efficiency, higher yield, reduced costs, more controllable dynamics, and reduced emissions. It will also assist the identification of key elements for model construction, including the identification of dominant pathways. Ultimately, the research is of relevance for the development of combustion-powered systems for military and commercial purposes.

Accomplishments for Reporting Period

The research was oriented by the following questions. What is the relation (if any) between non-normality and non-monotonicity in complex reaction systems? For example, is the transient presence of intermediate species related to the coupling matrix being non-normal? These questions are motivated by practical implications of intermediate species in ignition and other key steps of the reaction process. Here, we used a master equation to model the reaction dynamics to derive a general condition for observing non-monotonic dynamics of individual species, establishing that non-normality promotes non-monotonicity but is not a requirement for it. In contrast, we show that non-normality is a requirement for non-monotonic dynamics to be

observed in the Renyi entropy. Using H₂/O₂ combustion as an application, we demonstrate that non-monotonic dynamics under experimental conditions are supported by a linear chain of connected components, in contrast with the dominance of a single giant component observed in typical random reaction networks. This indicates that our approach can also inform dimension reduction in the analysis of very large complex reaction networks. These results were derived in collaboration with Prof. Jason Green's group and are currently under consideration for publication in Physical Review Research.

Research plans for next reporting period

Even though the project is over, we still have papers in the process of being published, which we plan to share with the rest of the team once they appear.

Resulting Journal Publications During Reporting Period

Non-normality and non-monotonic dynamics in complex reaction networks, Physical Review Research,

Z. G. Nicolaou, T. Nishikawa, S. B. Nicholson, J. R. Green, and A. E. Motter (currently under peer review).

Graduate Students Involved During Reporting Period

N/A

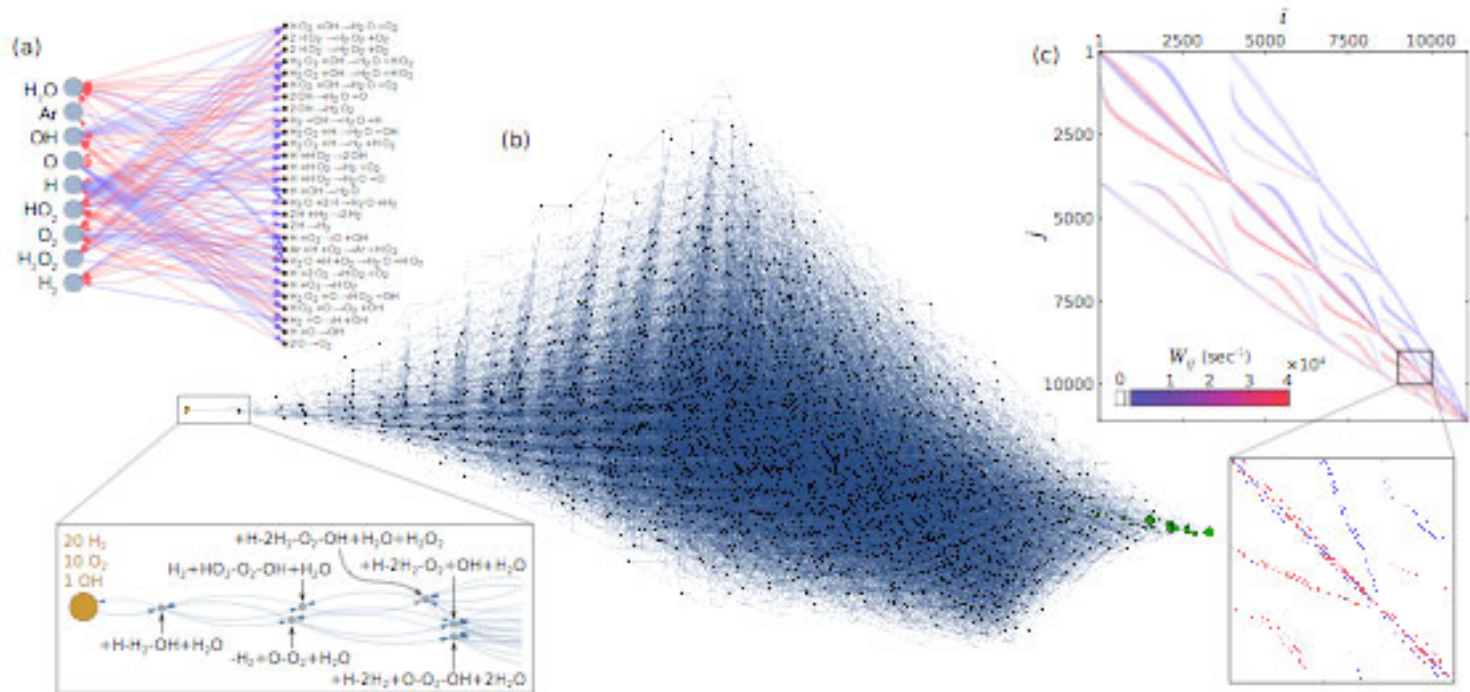


Figure 1. Network representations of the H₂/O₂ combustion process. (a) Conventional bipartite graph representation, in which the nodes representing reactions (black dots) have incoming links (blue arrows) from the nodes representing the reactant species and outgoing links (red arrows) to those representing the product species. (b) Master-equation representation, in which each node represents a state defined by the number of molecules of all species and a weighted link the rate of transition between two states. The network shown encompasses the 11,106 states accessible from the initial state (orange node on the left) with 20 H₂, 10 O₂, 1 OH, and 200 Ar molecules. The green nodes on the right indicate the states with strictly positive probability of occupancy in the steady-state distribution of the chemical master equation. All the other states are indicated by black dots, and the (reversible) transitions between the nodes are represented by links. The inset shows a zoom-up of the initial state and its neighboring states, which are labeled with the changes in species composition relative to the initial state. The link strengths in the inset are proportional to the transition rates. (c) Transition rate matrix, where the states are indexed by the order of discovery in the state enumeration algorithm based on depth-first search.

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Angela Violi
Department of Mechanical Engineering
University of Michigan * Ann Arbor, MI 48109

Accomplishments for Reporting Period

1. Combined machine learning and combustion chemistry to analyze reaction networks.
2. Developed a novel computational tool based on sparse learning theory to analyze complex reaction networks
3. Trained and mentored postdoc

Resulting Journal Publications During Reporting Period

Journal publications:

1. Farshad Harirchi, Doohyun Kim, Omar Khalil, Sijia Liu, Paolo Elvati, Mayank Baranwal, Alfred Hero, Angela Violi, On Sparse Identification of Complex Dynamical Systems: A Study on Discovering Influential Reactions in Chemical Reaction Networks, *Fuel*, [To appear]
2. Mayank Baranwal, Jacob Saldinger, Paolo Elvati, Alfred O Hero, Angela Violi, SPIN: SParse IdeNtification of large chemical reaction networks, *Combustion and Flames*, [Under review]

Products/tools:

1. Mixed integer linear programming (MILP) reduction solver
2. Centrality reduction solver

Graduate Students Involved During Reporting Period

No students

Awards, Honors and Appointments

- **Angela Violi:** Thurnau Professorship University of Michigan
- **Angela Violi:** 2020 Aspire, Advance and Achieve Mentoring Award from University of Michigan Women in Science and Engineering Program

Additional Figures

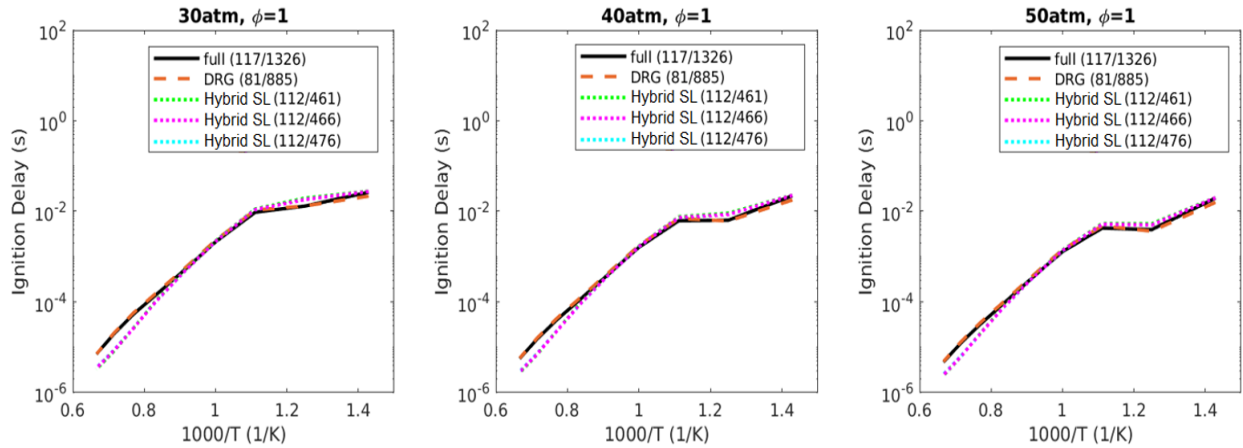


Figure 1: Reduction of the full mechanism of propane combustion (117 species, 1326 reactions). Our Hybrid Sparse learning scheme can reduce the number of reactions to 461 with only negligible deviation in ignition delay compared to the full mechanism. Other competing methods, such as, DRG-reduced mechanism consist of nearly twice as many reactions.

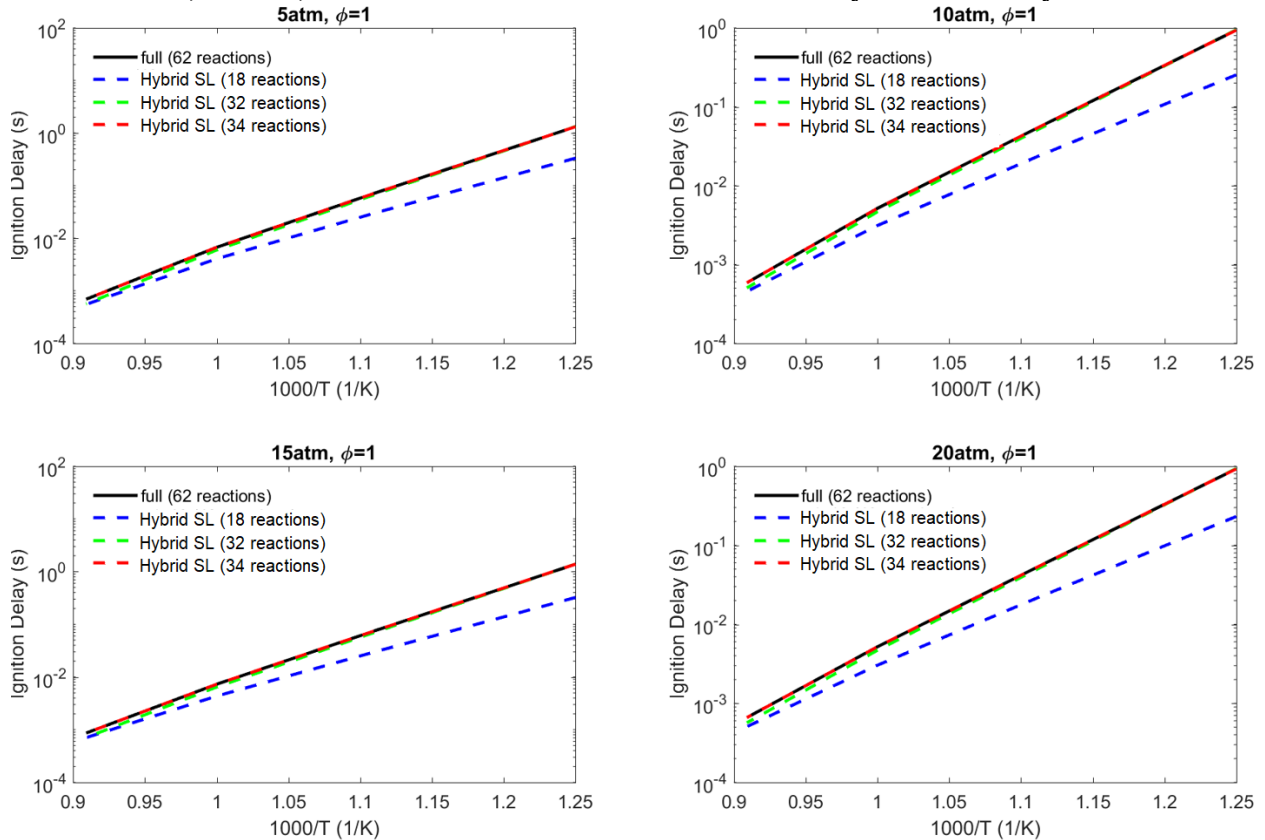


Figure 2: Reduction of the full mechanism of hydrogen combustion (9 species, 62 reactions). Our Hybrid Sparse learning scheme can reduce the number of reactions to 32 with a maximum deviation of 0.41% in ignition delay

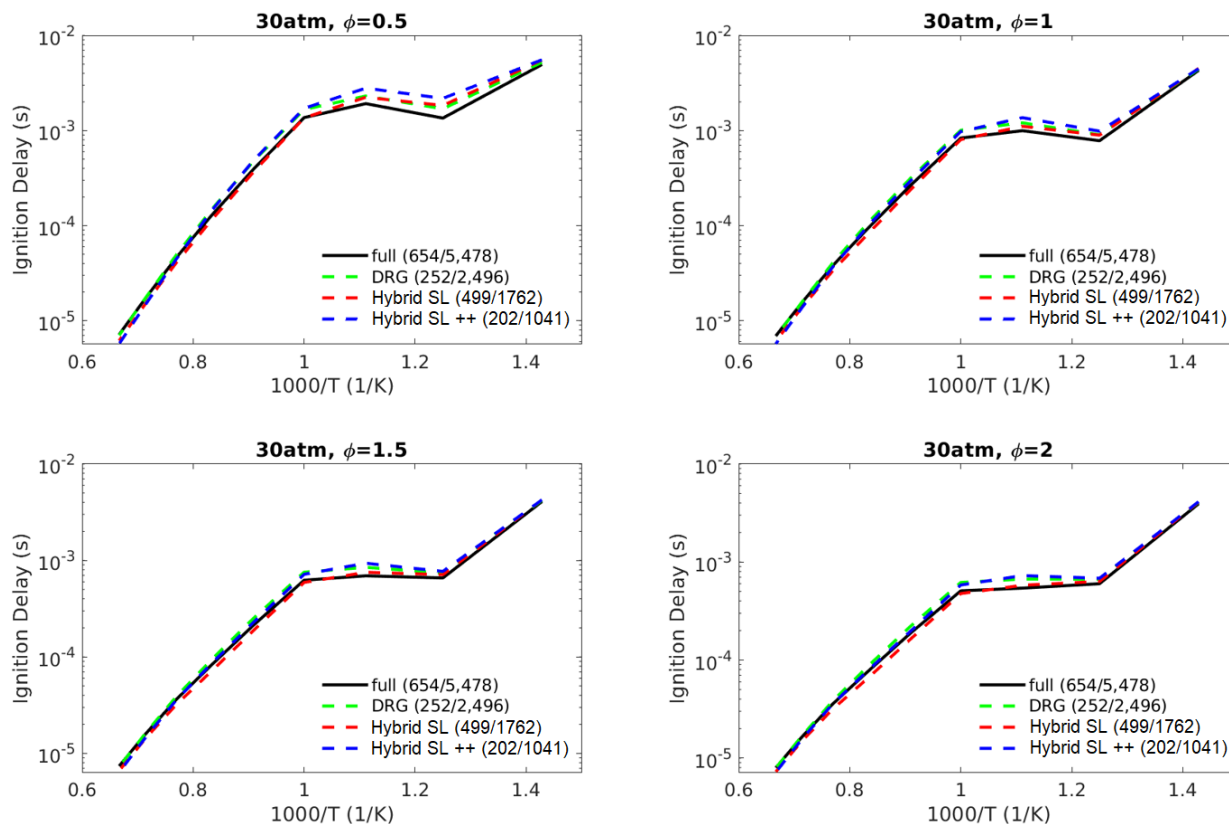


Figure 3: Reduction of the full mechanism of n-heptane combustion (654 species, 5478 reactions). Our Hybrid SL approach significantly reduces the number of reactions to 1762. We also propose an improved mechanism which further reduces the number of species and reactions to 202 and 1041, respectively.

Summary

Many important chemical processes are characterized by complex reaction networks. Properly understanding the complex interplay of diverse species and chemical dynamics can allow for better utilization of these processes. Numerical modeling has proved a valuable tool in the analysis of these reactive systems; however, it comes at greatly increased computational cost. In order to alleviate this increased computational complexity, we have developed a principled, data driven approach for identifying underlying chemical mechanisms and removing reactions and species with minimal contributions to the reaction model. This is achieved using a combination of tools from multiple domains - (a) Wiener filters for linear system identification, (b) mixed-integer optimization and relaxation, and (c) hybridization with other model-free reduction solvers. Compared to existing approaches which rely on iterative evaluations of successively reduced mechanisms in an ad hoc manner, our approach is a single-shot method that leverages these tools to reduce a large mechanism into a meaningful smaller mechanism up to specified error tolerance.