Automated exploration of the mechanism of elementary reactions

Sandia National Laboratories
Judit Zádor (PI) and Habib N. Najm (co-PI)

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SAND2012-7845P
LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT
Early Career R&D Program

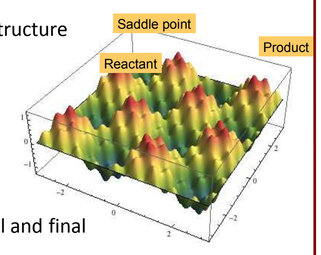
Problem

- **Optimization of new transportation fuels and engine technologies requires the characterization of the combustion chemistry of a wide range of fuel classes.**
- **Theoretical studies of elementary reactions — the building blocks of complex reaction mechanisms — are essential to accurately predict important combustion processes such as autoignition of biofuels.**
- **The current bottleneck for these calculations is a user-intensive exploration of the underlying potential energy surface (PES), which relies on the "chemical intuition" of the scientist to propose initial guesses for the relevant chemical configurations.**
- **For newly emerging fuels, this approach cripples the rate of progress because of the system size.**
- **The KinBot program package aims to accelerate the detailed chemical kinetic description of combustion, and enables large-scale systematic studies on the sub-mechanism level.**

Approach

Fundamental approaches to explore a network of reaction pathways on a PES

- Grid approach: Maps out the energy landscape of the full 3N-6 dimensional space on a dense grid
- Global approach: Determines all possible structures and their connections on a combinatorial basis
- Growing Network approach: Grows the reaction network starting form a seed structure



It is an extremely difficult task to search in this 3N-6 dimensional space!

Fundamental methods to find saddle points

- Local Optimization methods: Walk uphill starting at a reactant
- Double-Ended methods: Create a good guess by averaging or morphing the initial and final structures
- Chemistry-Based methods: Model chemical intuition based on topological analysis and geometrical manipulation

KinBot 1.0 = Growing Network approach + Chemistry-Based method

Gas-phase kinetics have accumulated an enormous amount of chemical knowledge about reaction pathways, which can be efficiently utilized using computer codes.

Automation makes reaction pathway exploration:

- faster
- less human-resource intensive
- systematic
- error-free

KinBot is a parallel C-code coupled to Gaussian09, which automatically explores reaction pathways relevant in gas-phase chemical kinetics, with emphasis on combustion-related reactions.

KinBot finds the lowest energy conformers using random sampling in the dihedral space. The structures are analyzed, and when certain motifs are detected, a transition-state search is initiated by the code. The transition states are found by robust geometrical manipulation of the structures using redundant internal coordinates and stepwise relaxation.

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*** OVERALL PROGRAM STRUCTURE ***

read keywords and seed geometry

analyze seed
  make distance matrix D
  make bond matrix B based on D
  determine if structure is unimolecular or bimolecular
  find radical center R using B and D
  determine whether the it is TS, using B and D
  find cyclic substructures in seed, stored in C
  find all dihedral angles in seed, stored in H

optimize seed /G09
  read optimized seed geometry and analyze optimized seed

perform reaction pathway search
  if R and beta bond exists:
    search for beta scission pathways /G09

  if R and contains hydrogen atoms:
    search for internal hydrogen abstraction pathways /G09

if peroxy radical:
    search for direct HO2 elimination pathway /G09

  if hydroperoxy alkyl radical:
    search for cyclic ether formation pathway /G09

  output optimized geometries, frequencies and rotational
  constants of both products and transition states for all
  pathways found

create conformational sample of seed
  optimize structures /G09
  analyze results

create 1-D hindered rotor scan for the lowest energy conformers
  perform 1-D scans /G09
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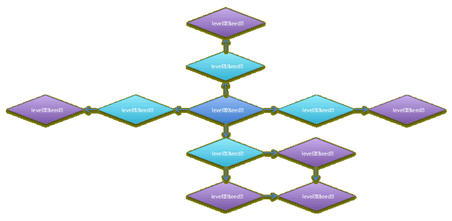
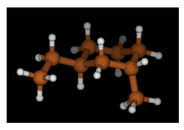
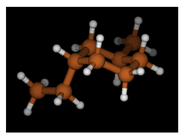






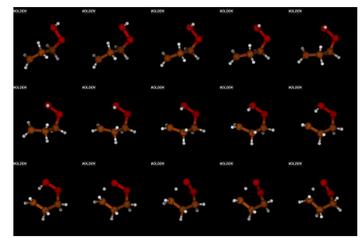
KinBot can handle cyclic structures as well

Results

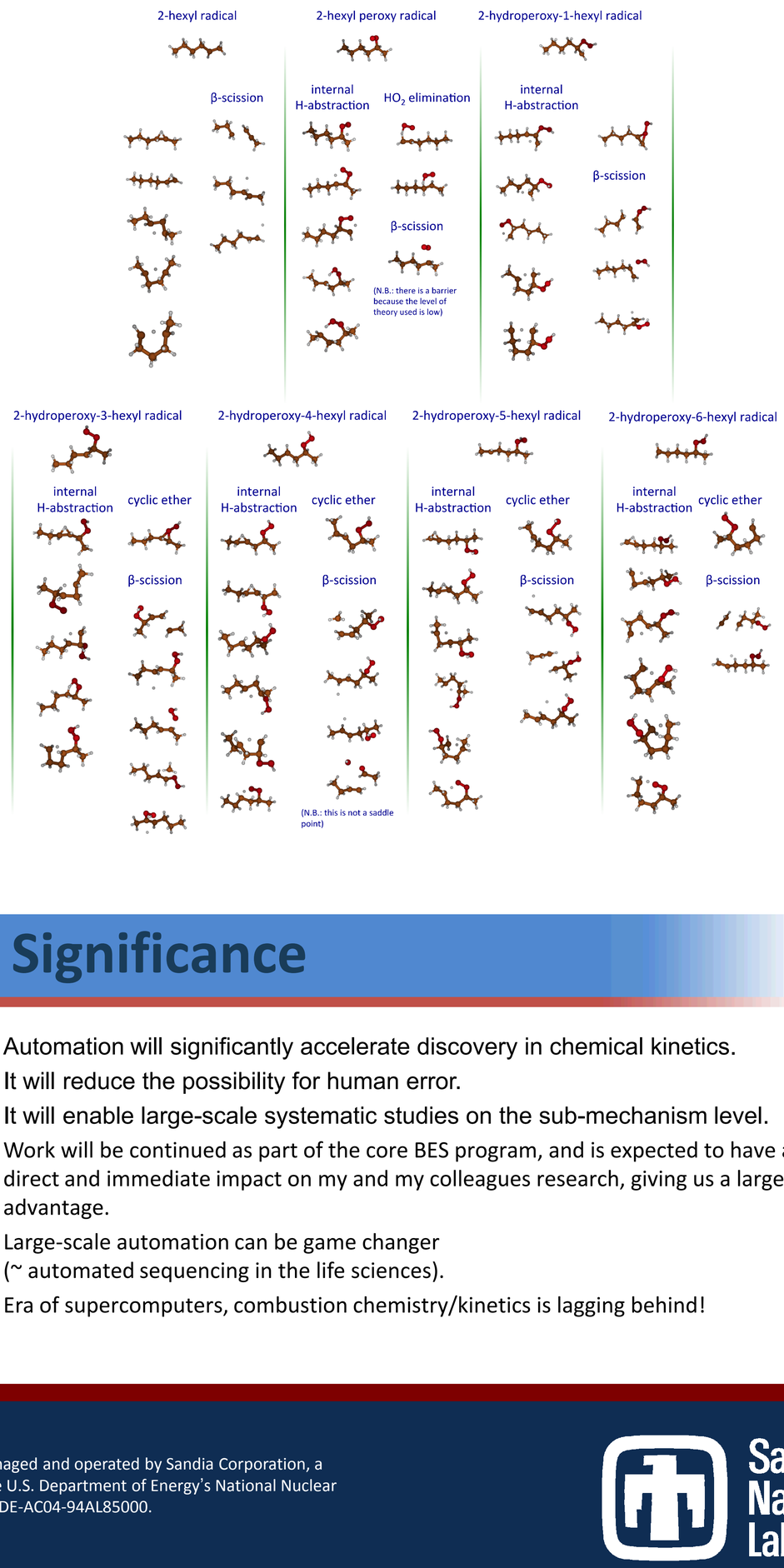
Currently implemented reactions

The first targeted group of reactions are the ones related to low-temperature autoignition. Despite the complicated reaction pathways on the PES, the steps can be categorized into a handful of topological types, which also cover reactions not typical on these PESs.

- General β-scission pathways
  - simple C-C bond cleavage
  - H-atom elimination
  - ROO dissociation
  - QOOH ⍰ HO_2 + alkene
  - aldehyde/ketone formation from alkoxy
  - etc.
- Internal H-abstraction
  - alkyl radical isomerization
  - ROO / QOOH isomerization
- Direct HO_2 elimination
- Cyclic ether formation (of any size)



Illustrative example: All "trivial" pathways discovered from 2-hexyl, 2-hexyl peroxy and 2-hydroperoxyhexyl radicals (B3LYP/6-31G*)



Significance

- Automation will significantly accelerate discovery in chemical kinetics.
- It will reduce the possibility for human error.
- It will enable large-scale systematic studies on the sub-mechanism level.
- Work will be continued as part of the core BES program, and is expected to have a direct and immediate impact on my and my colleagues research, giving us a large advantage.
- Large-scale automation can be game changer (~ automated sequencing in the life sciences).
- Era of supercomputers, combustion chemistry/kinetics is lagging behind!

NNSA National Nuclear Security Administration
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SAND 2012-xxxP

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