An open-source toolchain from molecular vibrations to detailed combustion: how (some) physical chemists and chemical engineers have escaped proprietary software

Mark E. Fuller, Ph.D. and Kfir Kaplan

March 4, 2022

About Us

Mark and Kfir are both active in developing and contributing to FOSS projects within the scientific community including CANTERA, the REACTION MECHANISM GENERATOR, and the AUTOMATIC RATE CALCULATOR.

Mark:

- **Ph.D. in chemical engineering**
- **Linux/FOSS user and contributor over 15+ years**
- **Research foci are combustion chemistry, batteries, fuel cells, and heat transfer**
- **Currently employed in DevOps**

Kfir:

- **fourth-year undergraduate student at the Technion in chemical engineering**
- **...**

GitHub: mefuller & kfir4444

Introduction

Computational chemistry is essential to current and future development

Just a few examples:

- **Alternative bio and manufactured fuels**
- **Batteries and Fuel cells**
- **Drug and pharmaceutical manufacturing and degradation**
- **Proteins and organic molecules**
- **Refining and materials synthesis**

We are moving from postdictive to predictive computational capabilities[1]

[1] Green, W. H. AIChE Journal **2020**, *66*, 1–16.

Toolchain overview: macro to micro-scale

“Complete” simulation of a chemical reactor:

- **Global/macroscopic: temperature, pressure, chemical composition (TPX)**
- **Reactor/condition-specific implementation of laws of thermodynamics, conservation equations**
- **Chemical reactions for all chemical species**
- **Thermodynamic properties for all chemical species**

Toolchain overview: computing and sourcing properties

Various computational approaches:

- **“Guess” new species and thermodynamic properties from tabulated rules**
- **Estimate reaction rates by analogy to other reactions**

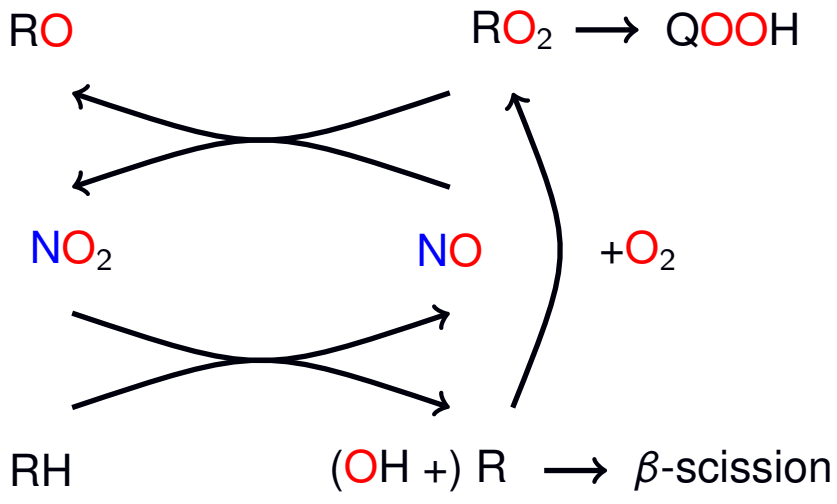
or

- **Compute molecular structures (many different methods)**
- **Calculate thermodynamic properties and reaction rates**

{Cheap and fast} versus {expensive and slow},
but we need both approaches to solve real problems

Guessing Species and Reactions

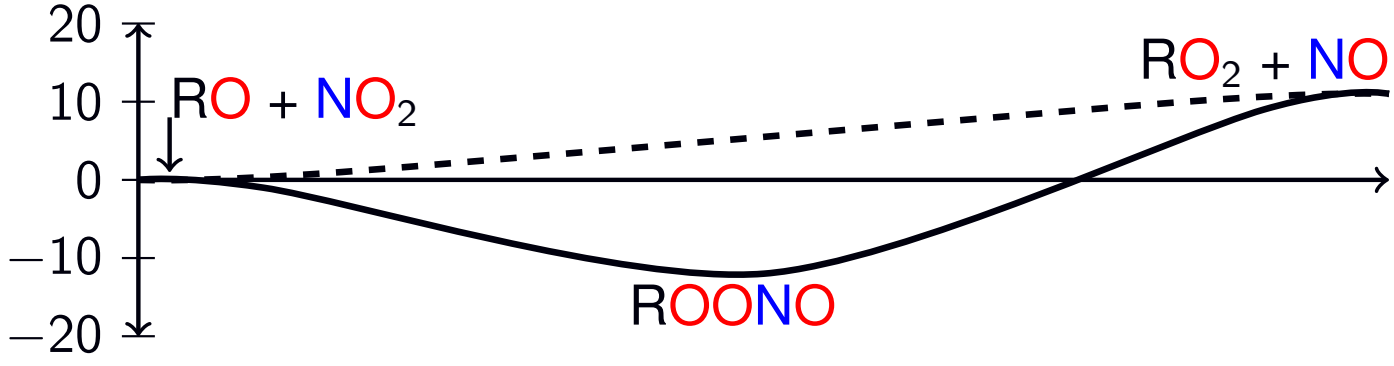
- **Hydrogen abstractions**
  - → $RH + NO_2 \rightleftharpoons R + HONO$
  - → $RH + NO_2 \rightleftharpoons R + HNO_2$
  - → $RH + NO \rightleftharpoons R + HNO$
- **Nitrite/Nitrate/Nitro-/Nitroso-Compounds**
  - → $RONO \rightleftharpoons RO + NO$
  - → $RONO_2 \rightleftharpoons RO + NO_2$
  - → $RNO_2 \rightleftharpoons R + NO_2$
  - → $RNO \rightleftharpoons R + NO$
- **Isomerizations**
  - → $RONO \rightleftharpoons RNO_2$
- **HONO elimination**
  - → $RONO \rightleftharpoons$ alkene + HONO
- **NO_x cycling**
  - → $RO_2 + NO \rightleftharpoons RO + NO_2$
  - → $R + NO_2 \rightleftharpoons RO + NO$



Adding NO_x to a combustion process[2]

[2] Fuller, M. E. et al. Reaction Chemistry & Engineering **2021**, *6*, 2191–2203.

Calculating Species and Reactions



Generalized potential energy surface for alkoxy radical (RO) + NO_2 system. Energies in kcal/mol. Well-skipping occurs at virtually all combustion-relevant temperatures and pressures.

Reaction	A	n	E_a
$CH_3O_2 + NO \rightleftharpoons CH_3O + NO_2$	4.62E+15	-0.38	97.8
$C_2H_5O_2 + NO \rightleftharpoons C_2H_5O + NO_2$	2.11E+14	-0.12	-470.6
n-$C_3H_7O_2 + NO \rightleftharpoons n$-$C_3H_7O + NO_2$	1.07E+14	-0.25	-1302.0

Units: centimeters, kelvin, calories, moles

Software

Our toolchain

- Electronic structure calculations of individual molecules with PSI4
- Conversion of individual molecule results to thermodynamic properties and reaction rates with ARC
- Automated model construction including estimating properties with RMG
- Automating decisions to refine estimates with computations using T3
- Reactor simulations with CANTERA
- Comparing to experimental data with standardized formatting (CHEMKED)

Psi4

RMG

ARC

T3

Cantera

ChemKED

Technical - bake in above

-how is software developed and distributed? -include links to source code, binaries

Help wanted

-where can technical/software people contribute without knowing chemistry? -what challenges do we foresee?

Q&A

Q&A

(1) Green, W. H. AIChE Journal **2020**, *66*, 1–16.

(2) Fuller, M. E.; Morsch, P.; Goldsmith, M. P. C. F.; Heufer, K. A. Reaction Chemistry & Engineering **2021**, *6*, 2191–2203.

Mark E. Fuller, Ph.D. and Kfir Kaplan – fuller@fedoraproject.org

Dana Research Group
Fundamental and Applied Chemical Kinetics
The Technion
Haifa, IL

dana.net.technion.ac.il