Exascale Catalytic Chemistry (ECC) Project

SAND2019-10671PE

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Midterm Review
September 18, 2019
Virtual

Exascale Catalytic Chemistry

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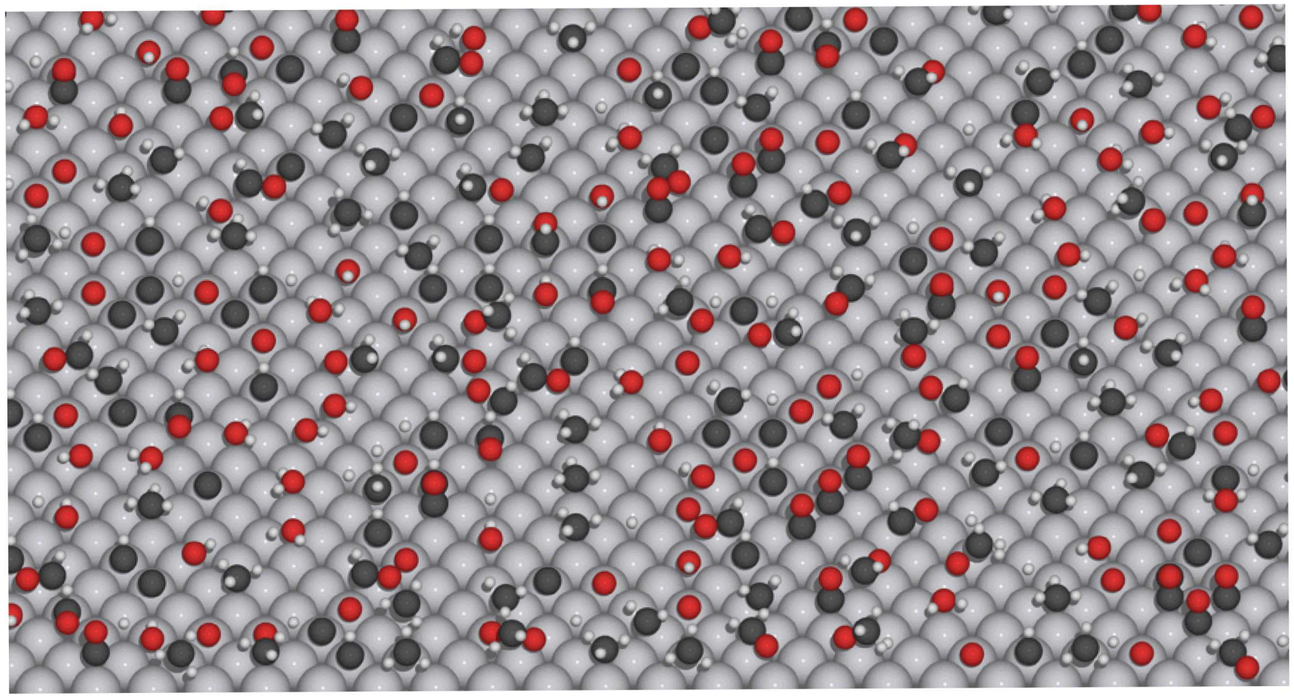
Outline

- Introduction to the ECC project and team
- Research thrusts, progress and plans
- Summary



Mission, vision, and goals of the ECC project

Develop an exascale-ready software ecosystem that enables the characterization of catalytic processes in coupled gas/solid systems faster and more accurately.

Long-term vision

- Enable the characterization of the catalytic activity of nanoparticles

Overall science goal of ECC

- Enable the automated characterization of coupled catalytic reaction systems on single facets

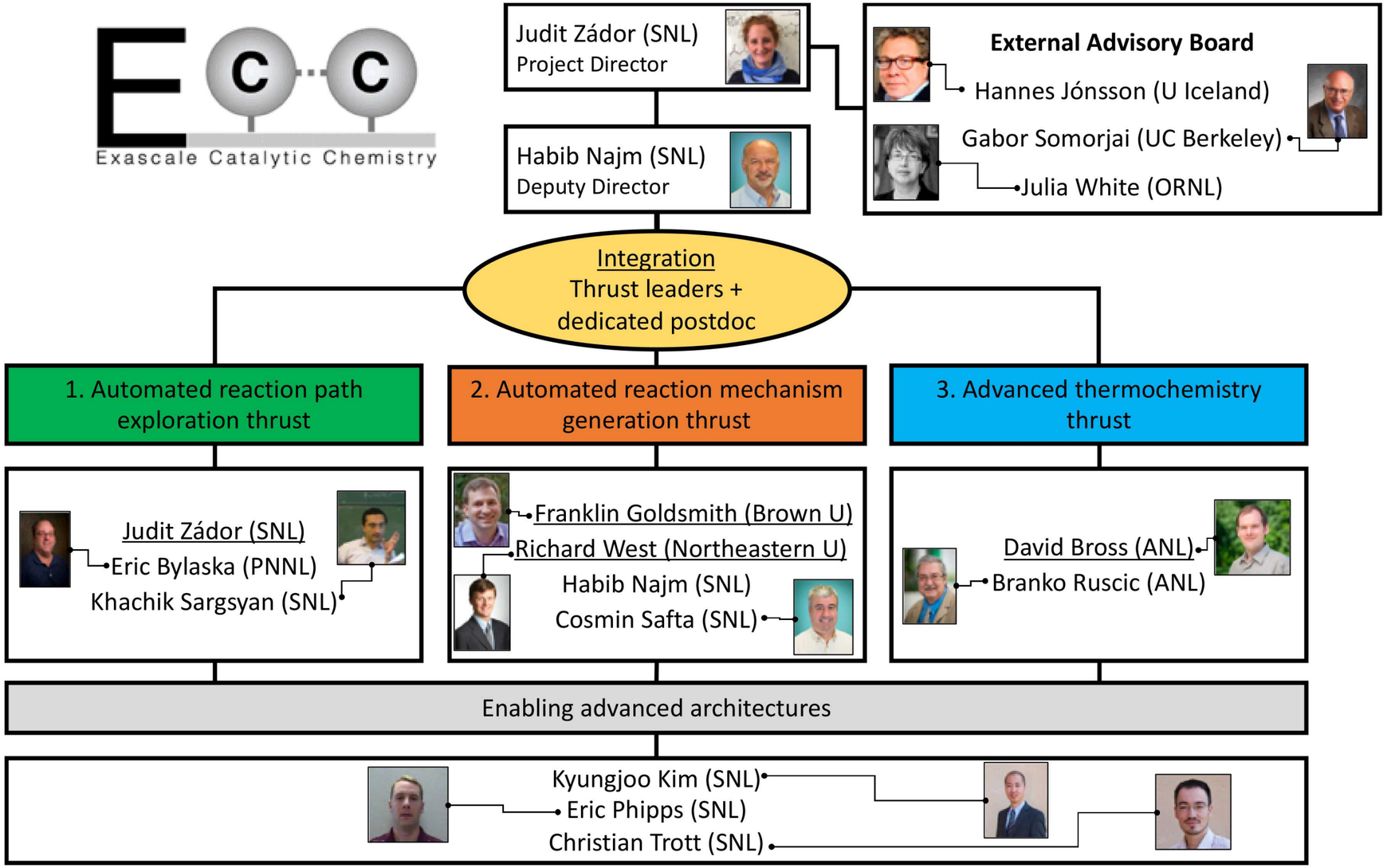
Specific scientific problems to be solved

- Comprehensively explore reaction channels for elementary reactions in catalysis
- Systematically construct microkinetic models
- More accurately determine the underlying thermochemistry

Software goals

- Develop and/or improve a set of open source codes targeting exascale hardware that can be used together or separately by the heterogeneous catalysis community

ECC organizational structure along and across thrusts



Management and roles

Project director: Zádor (SNL)

Overall direction of the project

- keep the team focused on the goals
- encourage collaboration
- adjust scientific goals and management approaches
- ensure integration among the thrusts

Organizational

- organize meetings
- make hiring and other staffing decisions
- track the budget
- bureaucratic duties, e.g. travel approval

Reporting

- write abstracts and review documents
- give presentations

Scientific

- the thrust lead for Automated reaction path exploration

Deputy director: Najm (SNL)

- main advisor to the project director in strategic planning
- acting project director while the project director was on maternity leave

Thrust leads: Zádor (SNL), West (NEU), Goldsmith (BU), Bross (ANL)

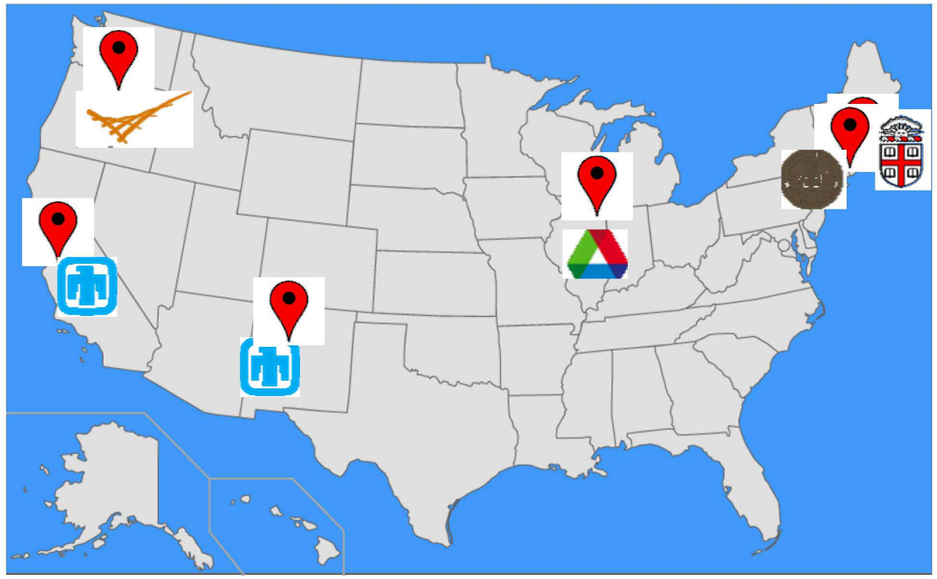
- coordinate work within the thrust
- work together on the overall integration
- arrange subteam meetings
- writing the technical portions of the review documents

Postdocs and students

- focus their attention on scientific research
- write codes and papers

+ dedicated postdoc starting in January 2020 to focus on integration

Communication strategies are crucial for our diverse and geographically spread-out team



Face-to-face “deep” meetings

- annual meetings
- technical conferences and other venues
- site visits

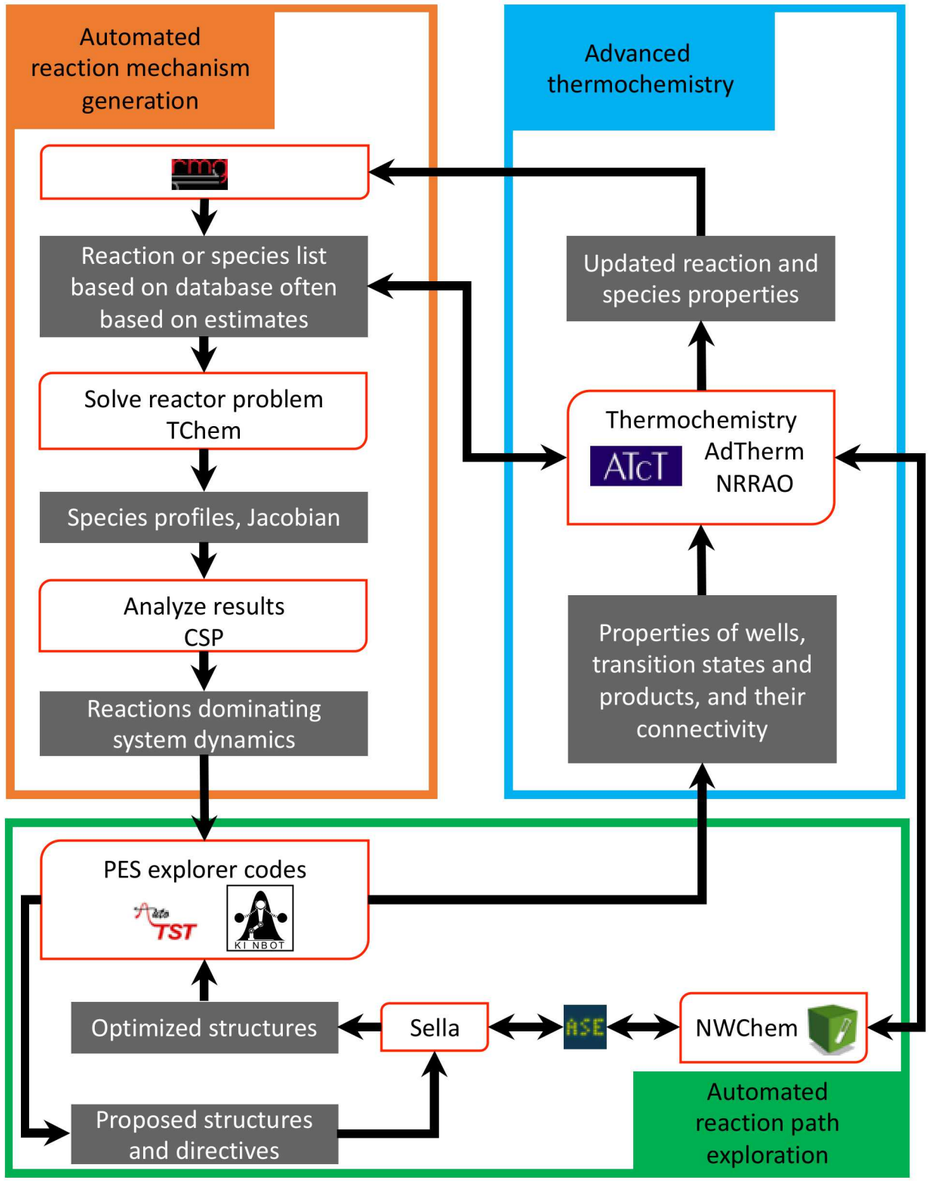
Regular technical meetings

- online every two weeks
- weekly in-person

Project management tools for fast and archived communication

- Kanban boards
- Slack channel
- gitter (for users)

Integrated technical plan



This is our roadmap.

Years 1-2

- Develop the codes within each thrust
- Intra-thrust integration

Years 3-4

- Further coupling and calculations for actual catalytic systems are largely the goal for the second half of ECC project

By the end of the project

- Generate microkinetic models and their parameters automatically
- All tools demonstrate their
  - individual capabilities
  - coupling
  - performance
  - scalability on heterogeneous architectures.

Target test catalytic systems with coupled gas-phase and heterogeneous chemistry are for instance synthesis of higher alcohols from syngas or dehydrogenation of methanol.

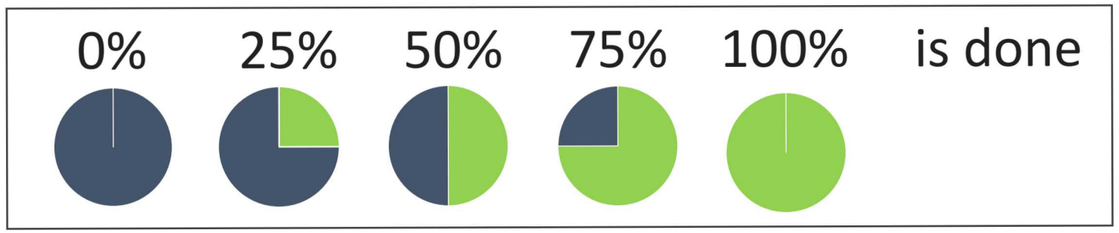
Structure of thrust descriptions

Automated reaction path exploration

Automated reaction mechanism generation

Advanced thermochemistry

1. Goals and participants
2. Detailed view of intra-thrust integration
3. Progress and plans
4. Summary of progress

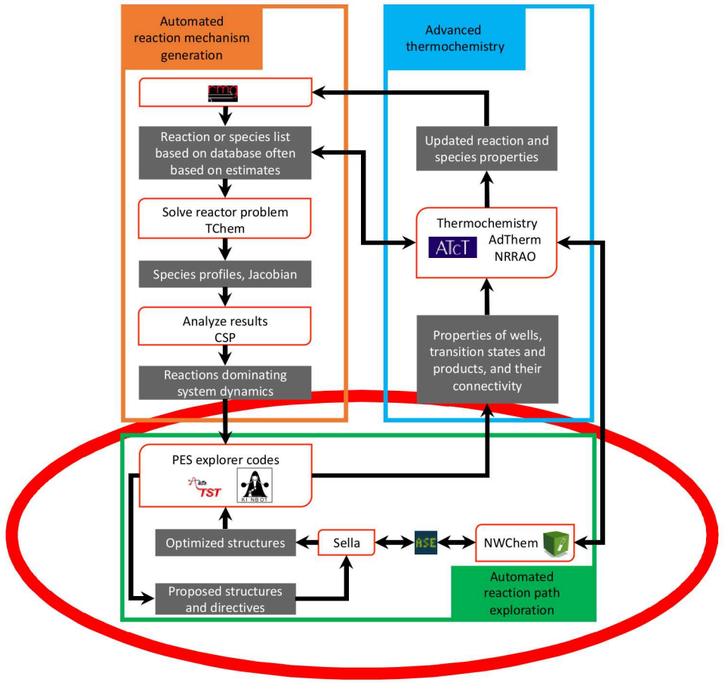


X Existing

P Past (Years 1-2)

F Future (Years 3-4)

contributors, incl. PDs and students



Automated reaction path exploration

Automated reaction path exploration

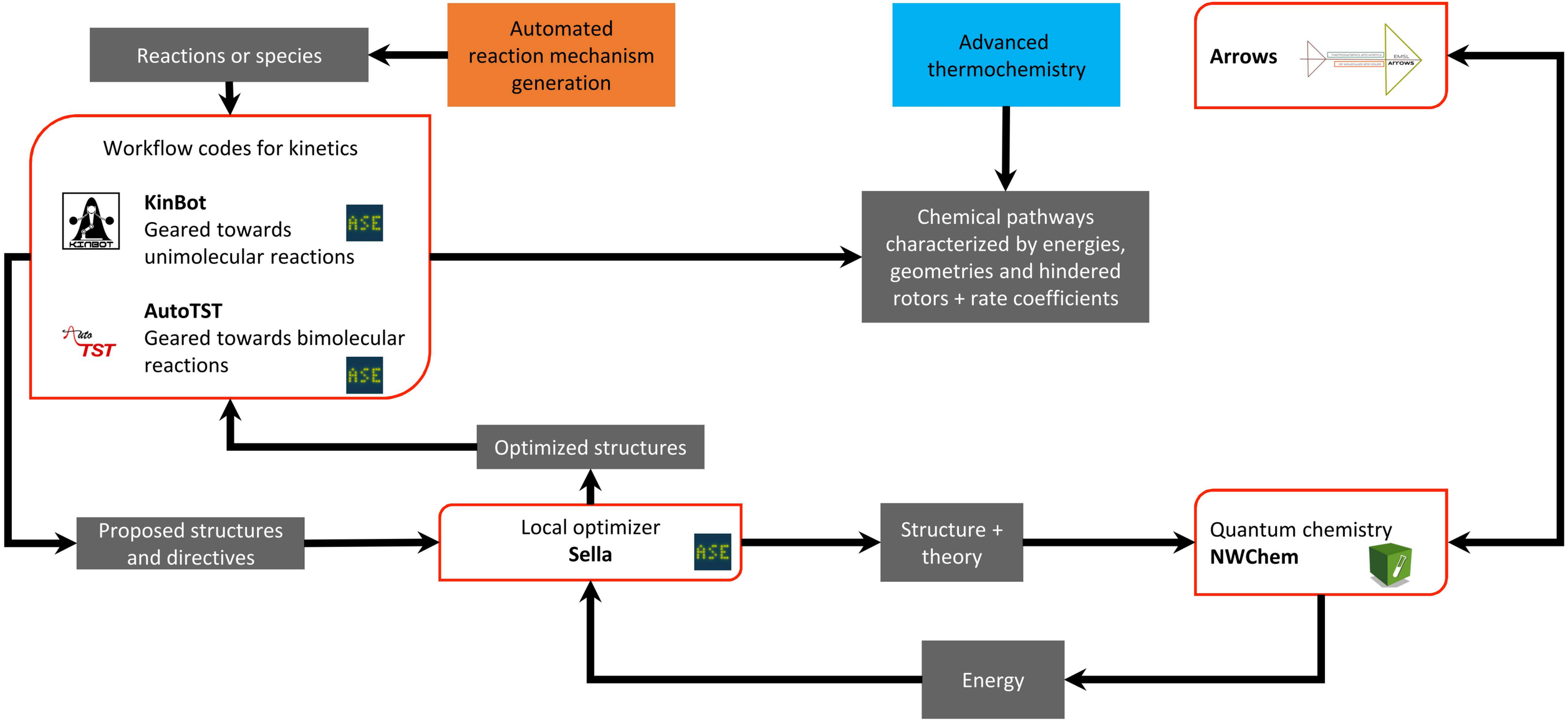
Creation and improvement of codes that take us from a proposed chemical reaction or a proposed species to a rate coefficient for gas/solid catalytic systems.

Goals

- Create tools to explore PESs of adsorbates
- Create robust and flexible open-source saddle-point optimizer
- Improve electronic structure code to treat heterogeneous catalytic systems
- Create web-based flexible interfaces for catalytic systems
- Couple and interface the above capabilities

Zádor, West, Bylaska, Najm, Sargsyan, Hermes, Harms

Automated reaction path exploration



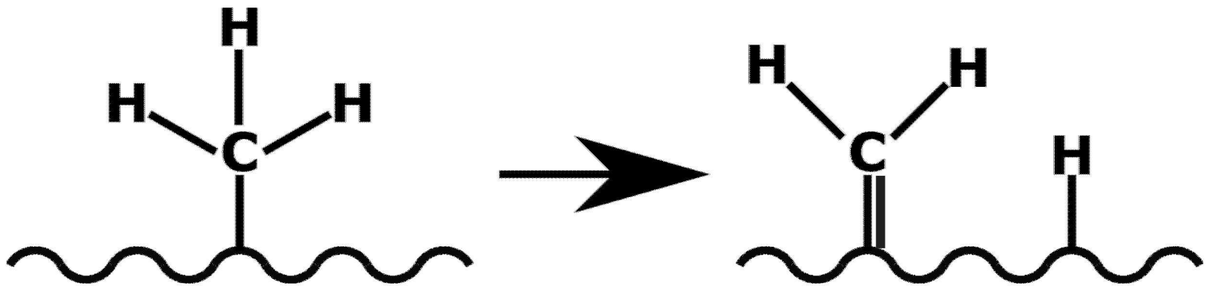
From formal catalytic reactions to *ab initio* kinetics

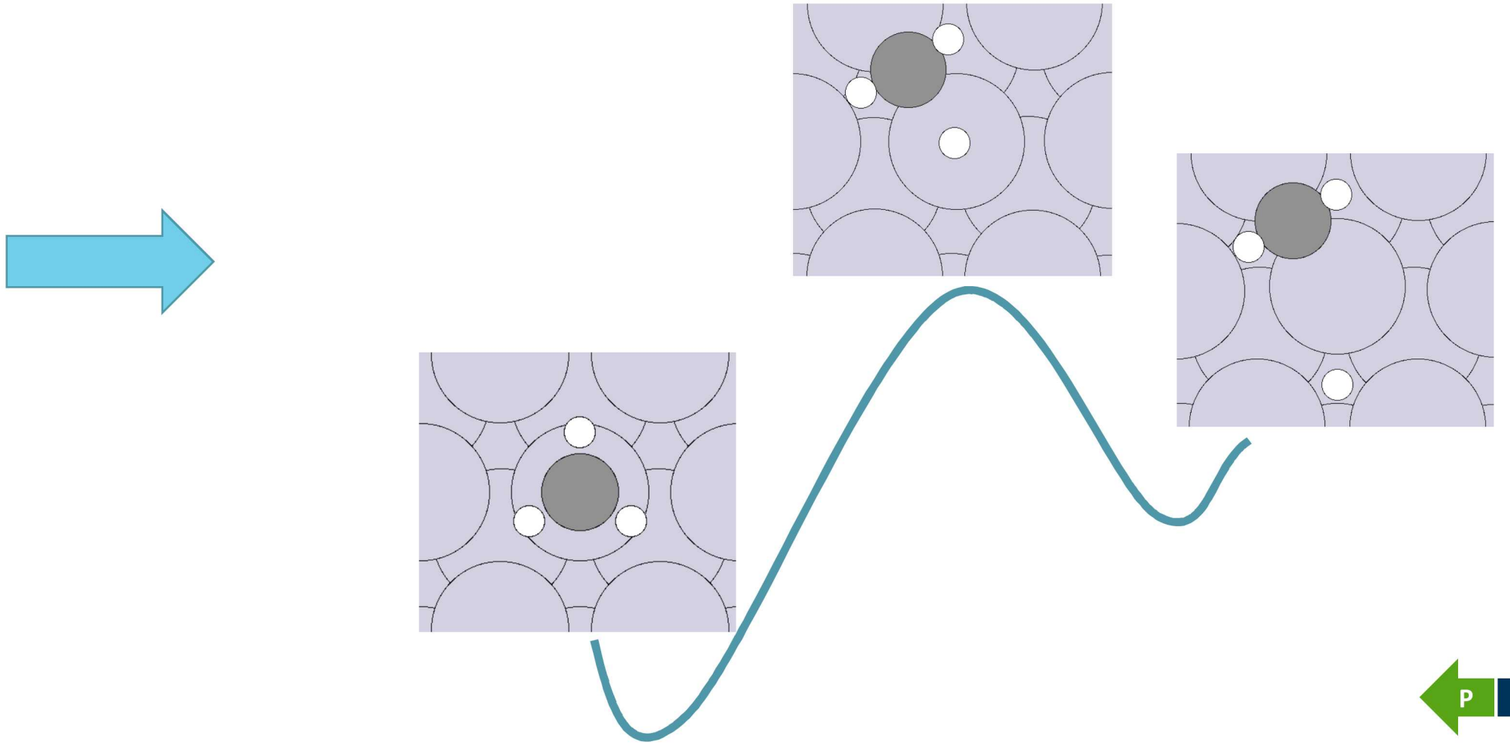
RMG reaction representation

```
- index: 0
  reaction: CH3X + X <=> CH2X + HX
  reaction_family: Surface_Abstraction
  reactant: |

    1 *1 C u0 p0 c0 {2,S} {3,S} {4,S} {5,S}
    2 *2 H u0 p0 c0 {1,S}
    3   H u0 p0 c0 {1,S}
    4   H u0 p0 c0 {1,S}
    5   X u0 p0 c0 {1,S}
    6 *3 X u0 p0 c0
  product: |

    1 *1 C u0 p0 c0 {3,S} {4,S} {5,D}
    2 *2 H u0 p0 c0 {6,S}
    3   H u0 p0 c0 {1,S}
    4   H u0 p0 c0 {1,S}
    5   X u0 p0 c0 {1,D}
    6 *3 X u0 p0 c0 {2,S}
```



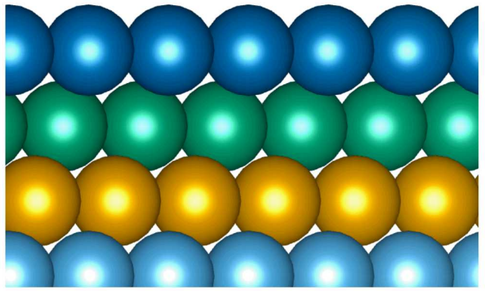


Hermes, Sargsyan, Najm, Zádor

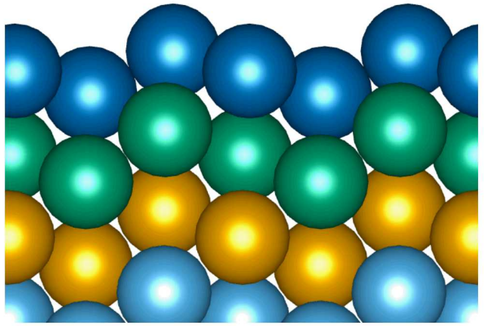
There are many potential binding sites even for simple surfaces

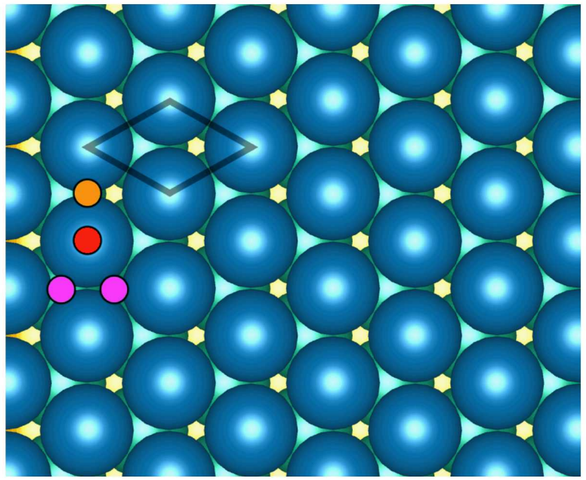
FCC(111)

FCC(211)

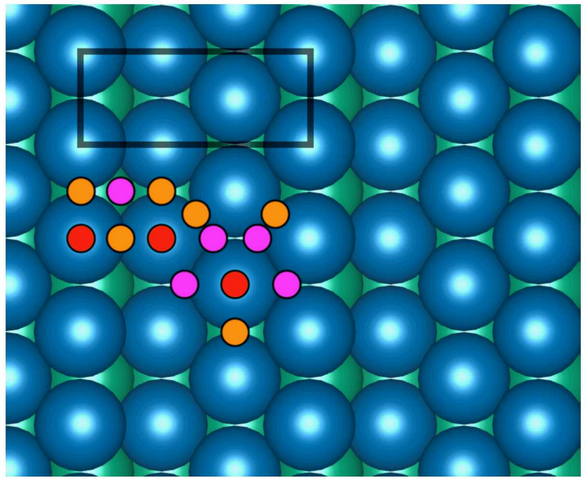


Side view





Top view

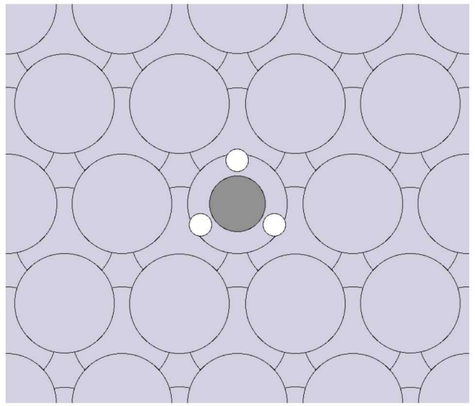


...and there are even more for high-index metal facets or nanoparticles.

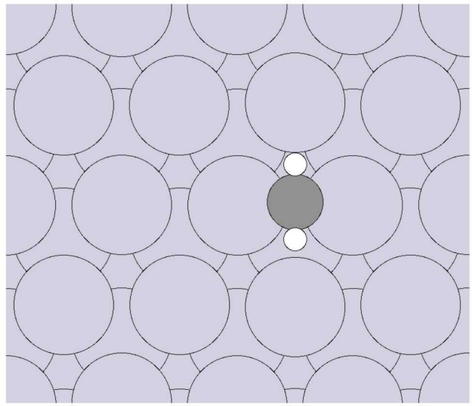
Hermes, Sargsyan, Najm, Zádor

There are only a few sites that are minima on Pt(111) for these species

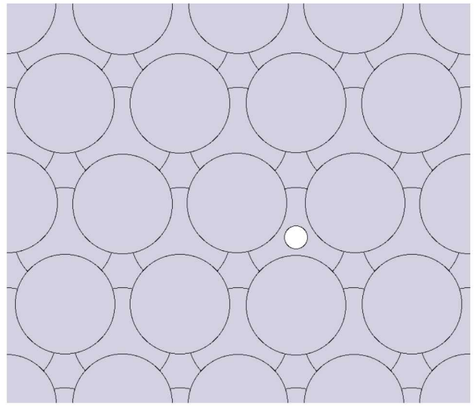
CH_3

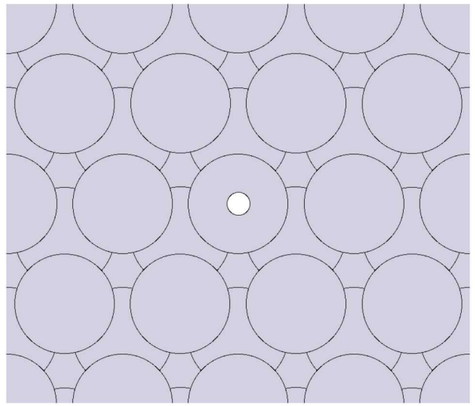


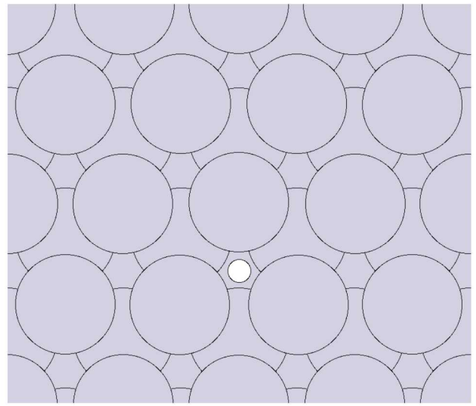
CH_2



H

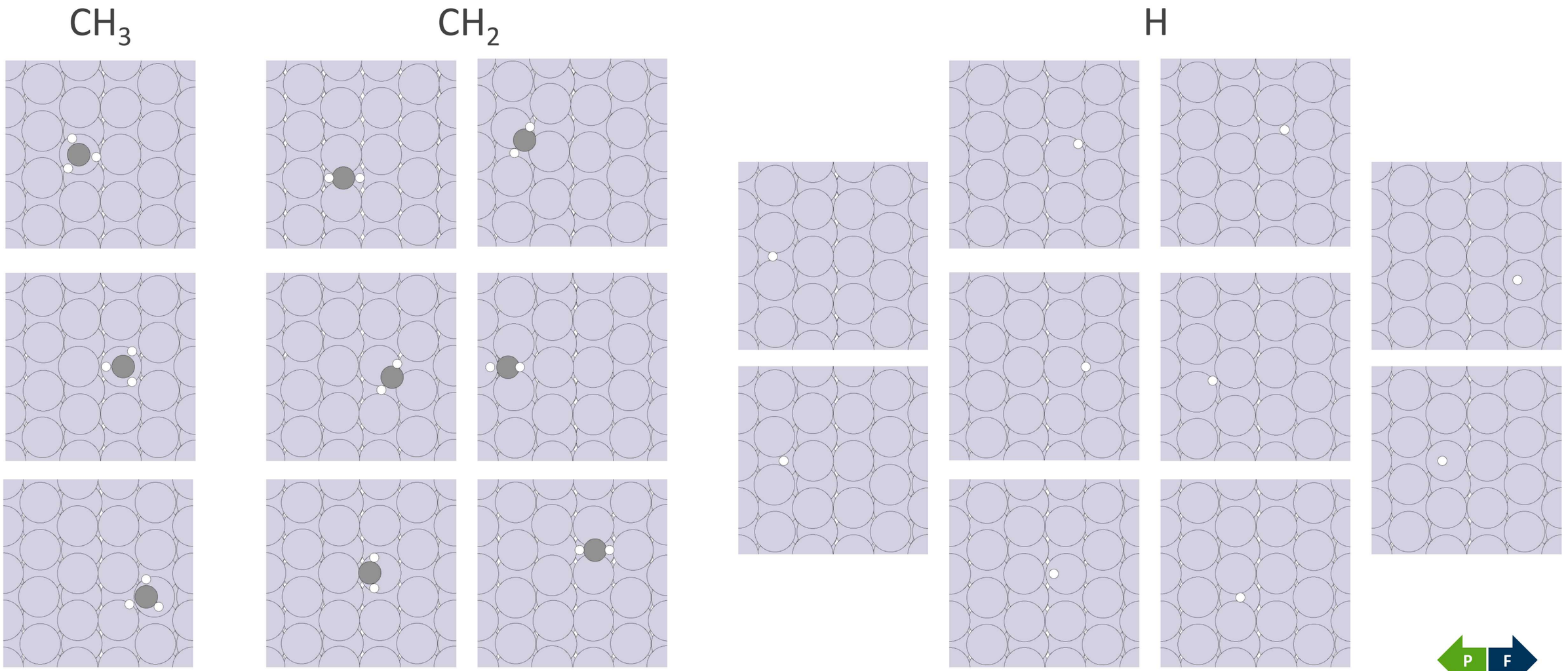






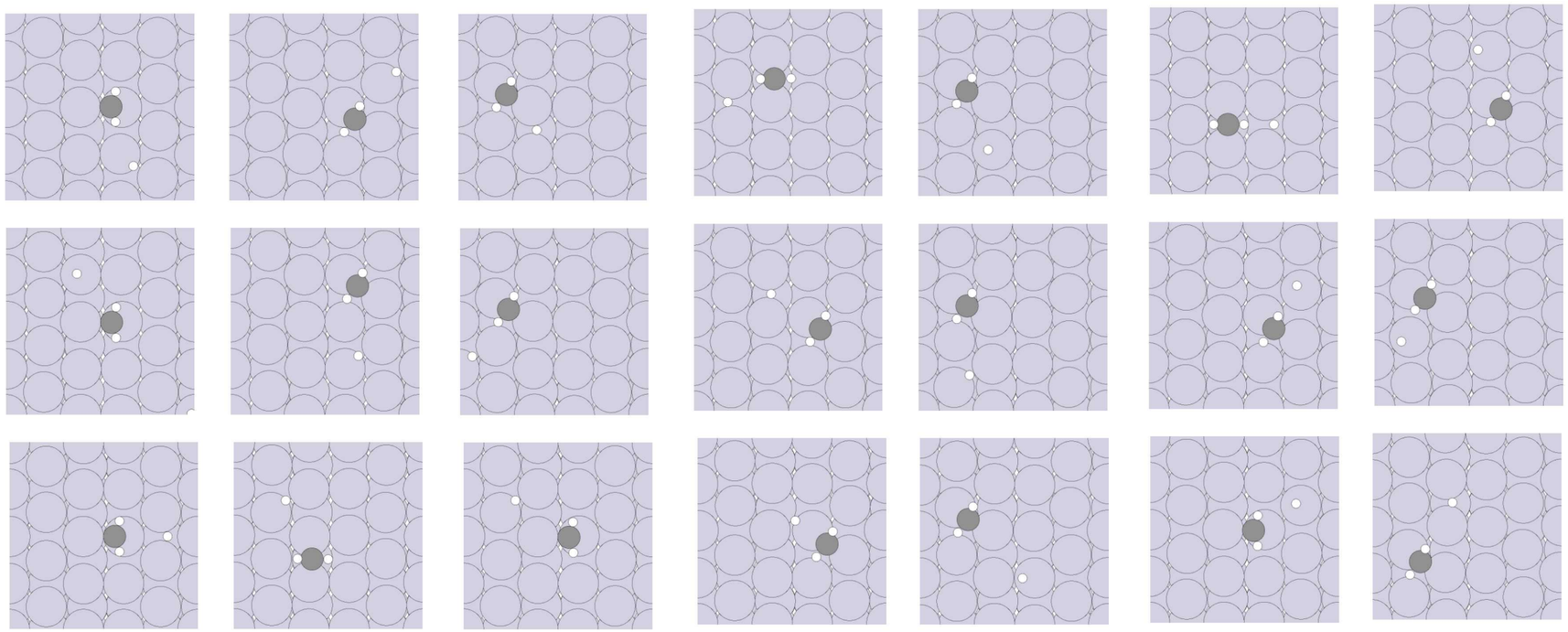
P F

But there are a lot more already on Pt(211)



Hermes, Sargsyan, Najm, Zádor

CH_2 + H co-adsorbed minima on Pt(211)



…There are **73** total minima!

It is difficult or impossible to know a priori which minima are directly connected to the reaction of interest, and which involve diffusion of adsorbates in addition to reaction.

Hermes, Sargsyan, Najm, Zádor

From structures to saddle points

Pt(111):

$\Delta_r E$: 0.267 +/- 0.053 eV

Pt(211):

$\Delta_r E$: 0.064 +/- 0.415 eV

- There are a few hundred possible proposed pathways just for CH_3 → CH_2 + H on Pt(211)
- We implemented ASE NEB in the workflow, but it is too expensive even with PBE functional
- Gaussian process (GP) NEB[1]: training the GP quickly overtakes the cost of the QC calculation
- We are working on own GP NEB implementation with active learning

FitPy

Lightweight Python library as a wrapper to established machine learning (ML) and uncertainty quantification (UQ) libraries (UQTk, PyTorch, Keras, SciKit-Learn)

- Inclusion of **gradients**
- Evaluation of predictive **uncertainties**
- **Adaptive** construction, locality, trust region

These algorithms will live in KinBot.

P F

Hermes, Sargsyan, Najm, Zádor

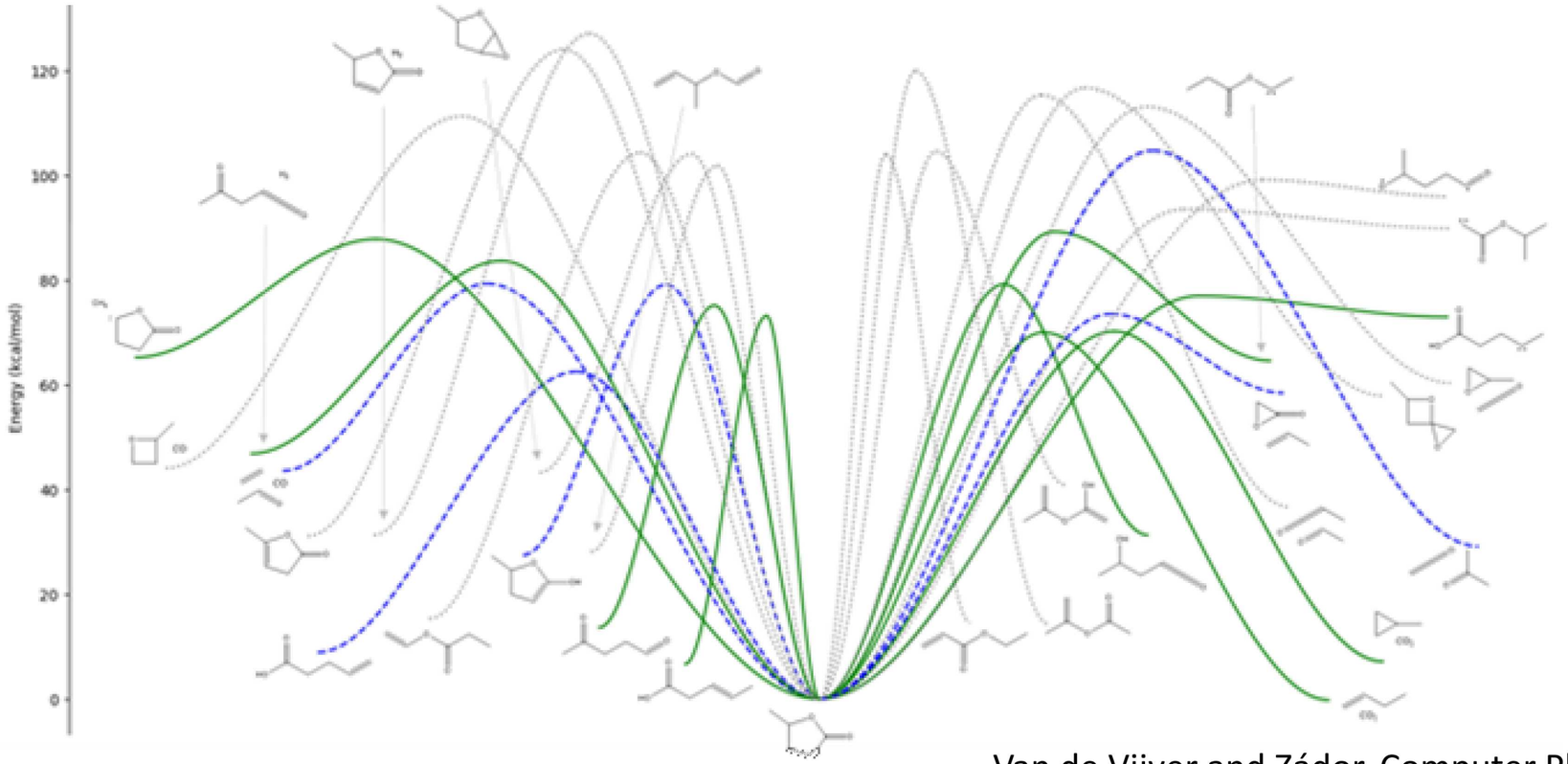
[1]Low-Scaling Algorithm for Nudged Elastic Band Calculations Using a Surrogate Machine Learning Model
José A. Garrido Torres, Paul C. Jennings, Martin H. Hansen, Jacob R. Boes, and Thomas Bligaard
Phys. Rev. Lett. **122**, 156001 – Published 15 April 2019

KinBot 2.0: Translating chemistry into computer codes

Find and characterize reaction pathways all the way to rate coefficients in a convenient workflow.

KinBot has been ported to several HPC clusters.

This code is an existing capability for gas-phase systems.



github.com/zadorlab/KinBot

Van de Vijver and Zádor, Computer Physics Communications, 2019

KinBot has an extensive, kinetics-oriented file handling infrastructure that will be adapted to reaction searches for catalysis when integrated with currently stand-alone scripts for surface reactions.

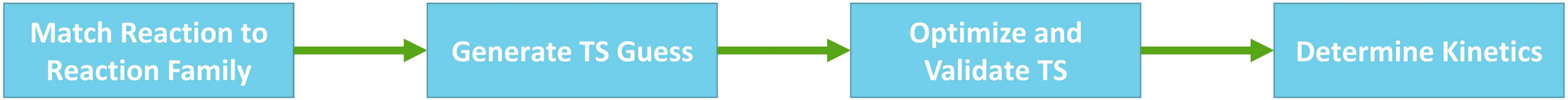
Zádor

AutoTST: An automated transition state theory kinetics calculator

This project has supported:

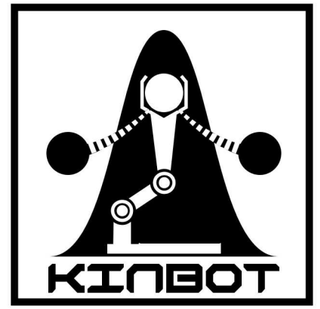
1. Creation of AutoTST as an **independent codebase**
   www.github.com/ReactionMechanismGenerator/AutoTST
2. Added systematic **conformer search**, **1D hindered rotor scans**, and **normal mode analysis**.
3. Added ASE to support numerous electronic structure calculators (and Sella)
4. Added job management framework to better utilize computational resources

Benchmarked against known data, 84% success



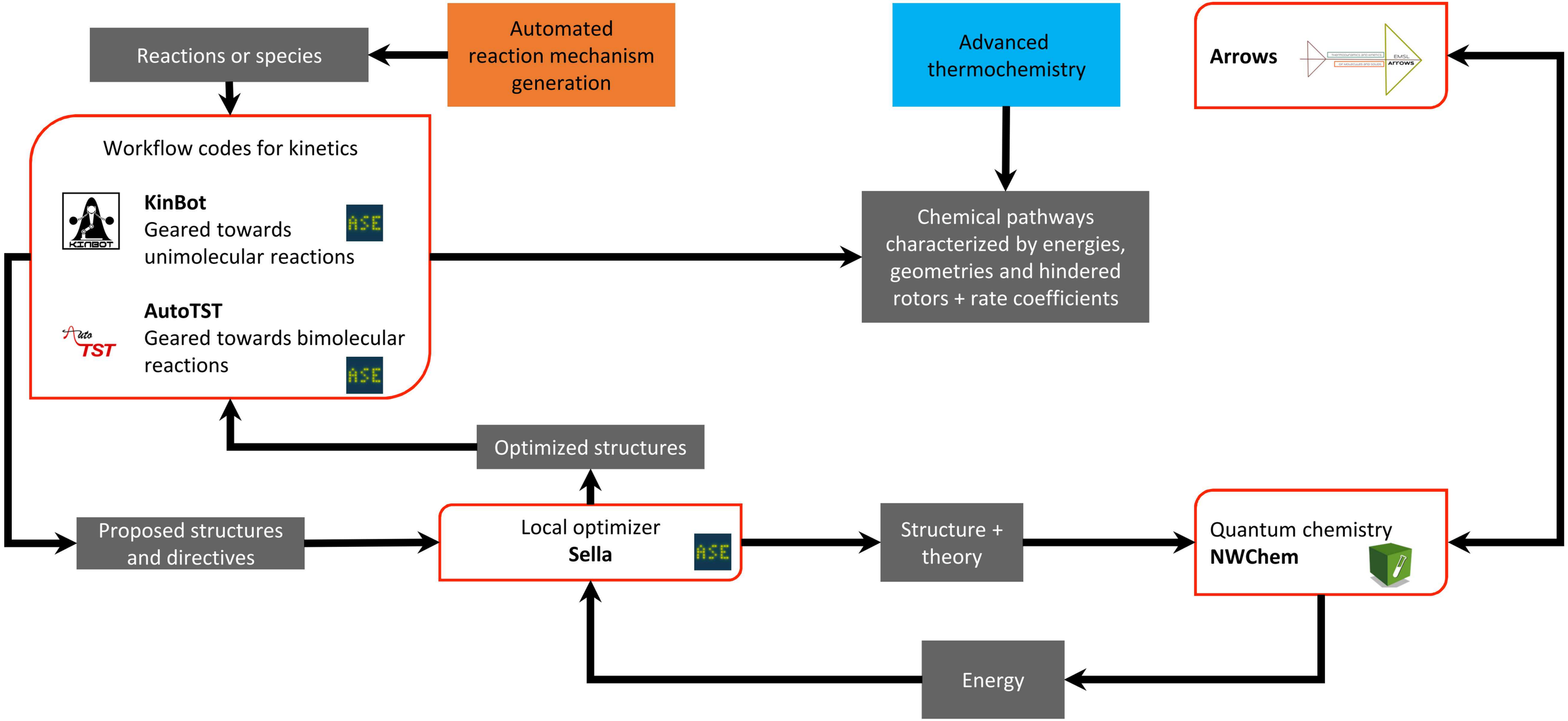
ASE: Larsen et al., J. Phys: Condens. Matter (2017)

Future work on AutoTST and KinBot



- Interface with and use our own new optimizer, Sella
  - Partially implemented, functionality to be further tested
- Use NWChem for electronic structure calculations (through ASE and Sella)
- Add catalytic reaction families to perform automatic transition searches on surfaces

Automated reaction path exploration

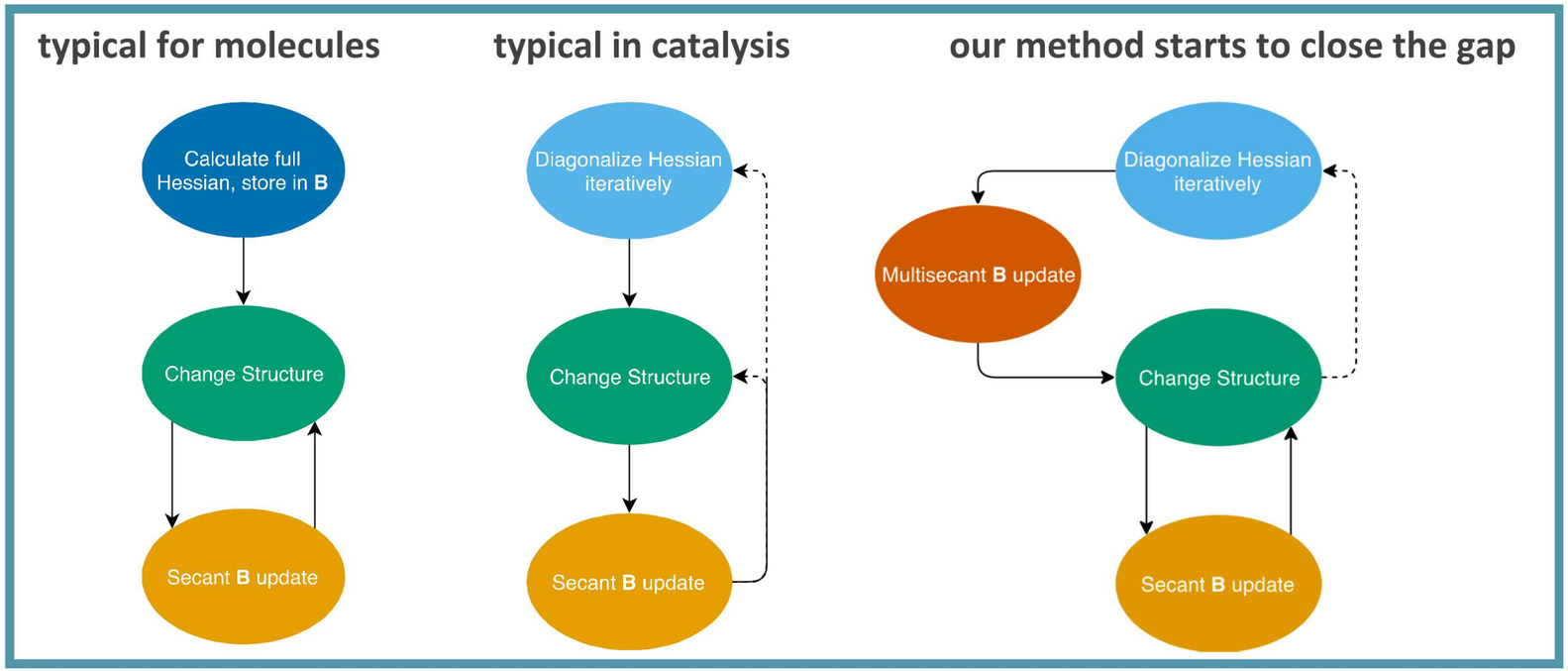


Sella: Accelerated saddle point refinement through full exploitation of partial Hessian diagonalization

Locating saddle points (SP) is a computational bottleneck in the characterization of reaction pathways.

New method for locating first order SPs:

- Can be effectively deployed in an automated computational frameworks
- Targets catalytic systems

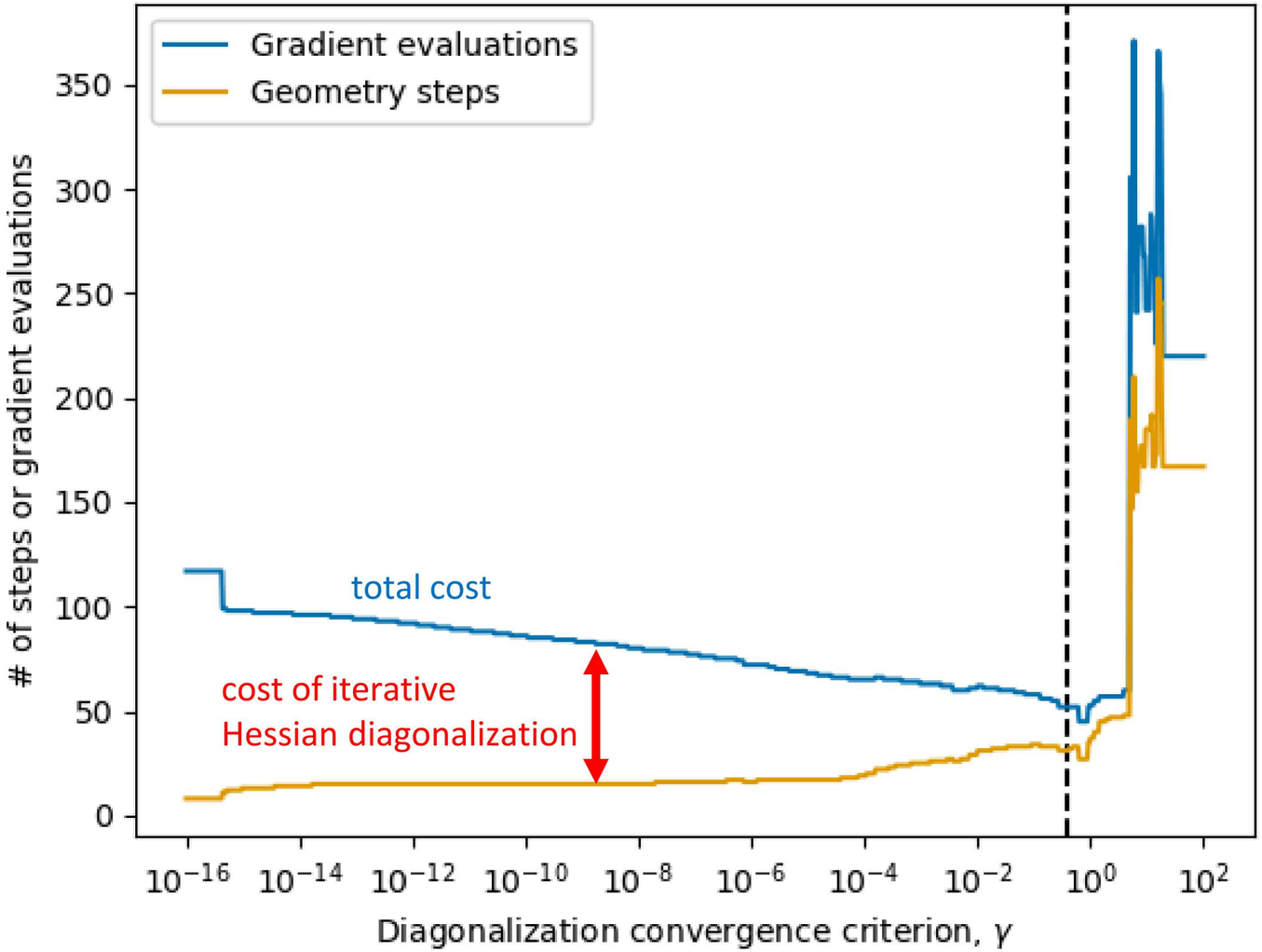


- Many MD and electronic structure codes implement own SP refinement
- Quality varies greatly
- Poses a problem to scientists who wish to choose the best software package
- Splintering of SP refinement strategies between codes designed for small gas-phase molecules and codes designed for larger condensed-phase systems

- We use all curvature information from the iterative eigensolver to construct the approximate Hessian.
- Our approximate Hessian's accuracy depends on how many steps are performed by the iterative eigensolver, which in turn depends on the diagonalization convergence criterion.

Hermes, Sargsyan, Najm, Zádor

It is possible to minimize the cost using a single hyperparameter γ, the diagonalization convergence criterion



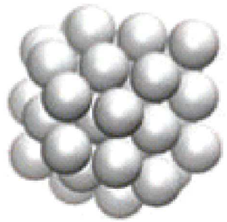
γ = 0.4 is an overall optimum for the systems tested.

Hermes, Sargsyan, Najm, Zádor

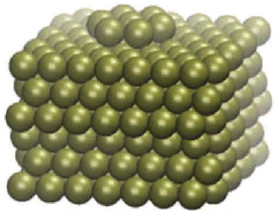
Sella outperforms established benchmark by 25-50%

Optbench.org performance (Chill et al., JCTC 2014)

Goal: find a saddle point with the least number of gradient evaluations starting from a large set of initial geometries.



Benchmark test	Program	Mean	Minimum	Maximum
38-atom LJ clusters	Optim	145	57	565
	Sella	70	24	159



Pt(111) with 7-atom island	Optim	71	43	143
	Sella	53	31	108

```
pip install sella
```

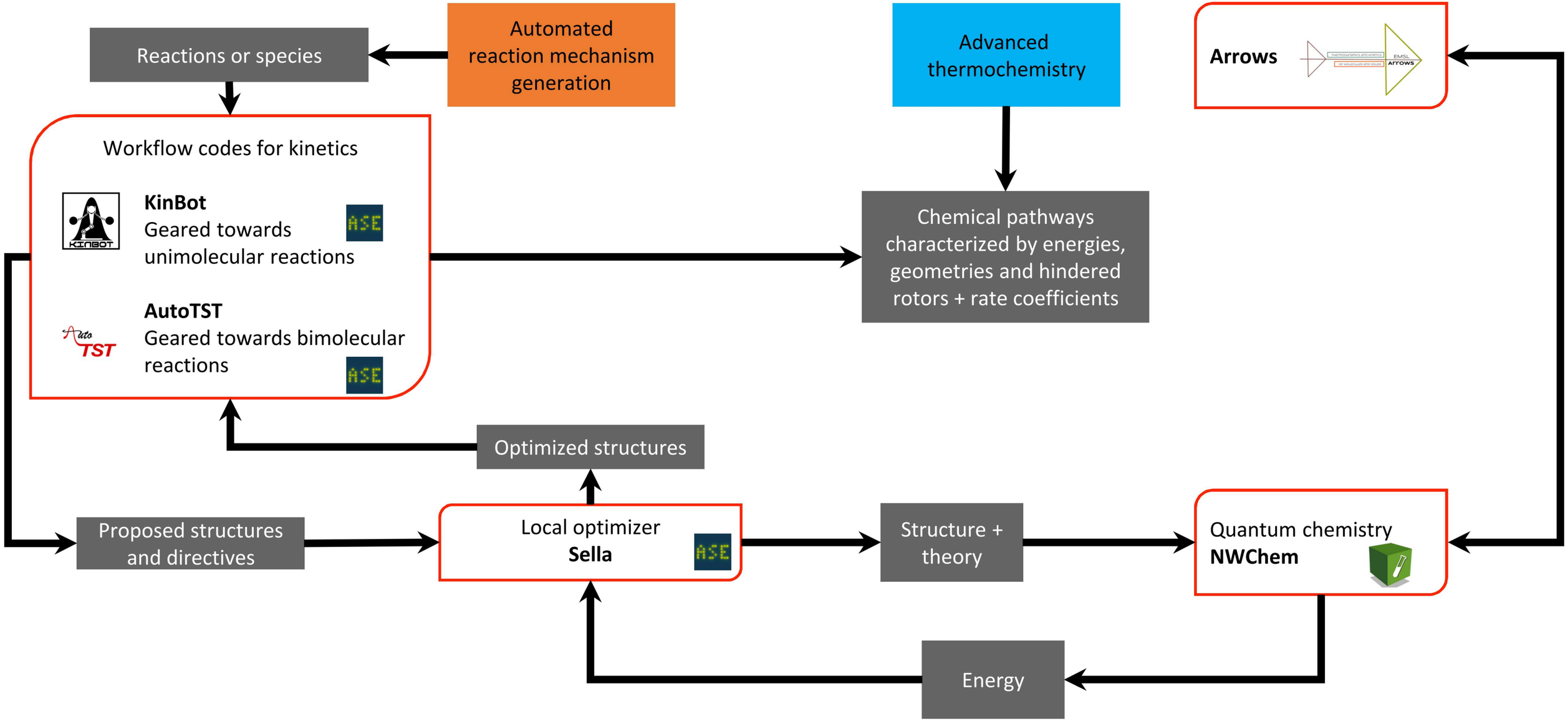
github.com/zadorlab/sella

Paper is submitted to JCTC and is available on ChemRxiv.

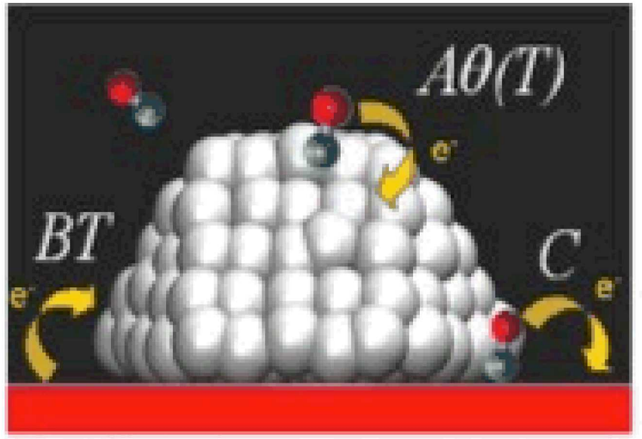
Sella is fully ASE compatible and is open source.

Hermes, Sargsyan, Najm, Zádor

Automated reaction path exploration



Integration with new beyond DFT developments in NWChem (and NWChemEx) plane-wave codes for HPC

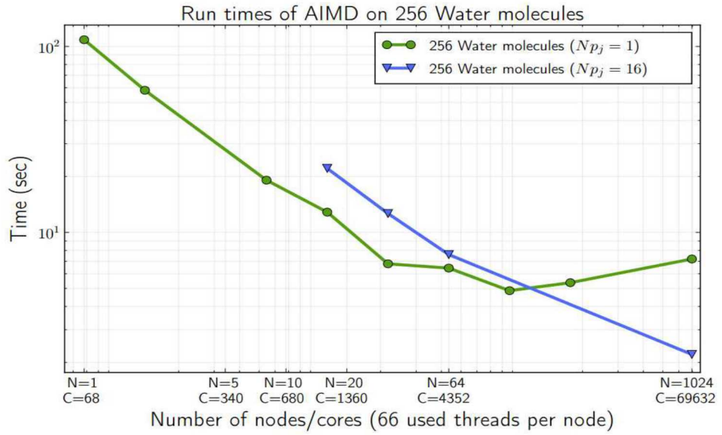


New functionals in NWChem's plane-wave code

- **Added Meta-GGAs VS98, M06, TPSS, SCAN,…** P
  - Formulas rewritten to be significantly more stable and efficient.
  - Note Perdew and Suns' Meta-GGA code uses quadruple precision!

- **Implemented vdw-DF and vdw-DF2 dispersion functionals and various GGAs for catalysis, e.g. BEEF** P

- **Finishing initial development of a periodic RPA method** P F
  - It is anticipated that the initial development of this code will be finished by October 2019.



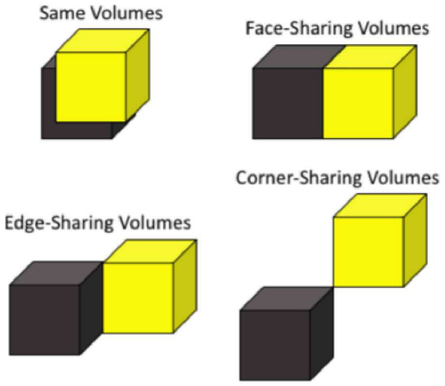
Other Developments

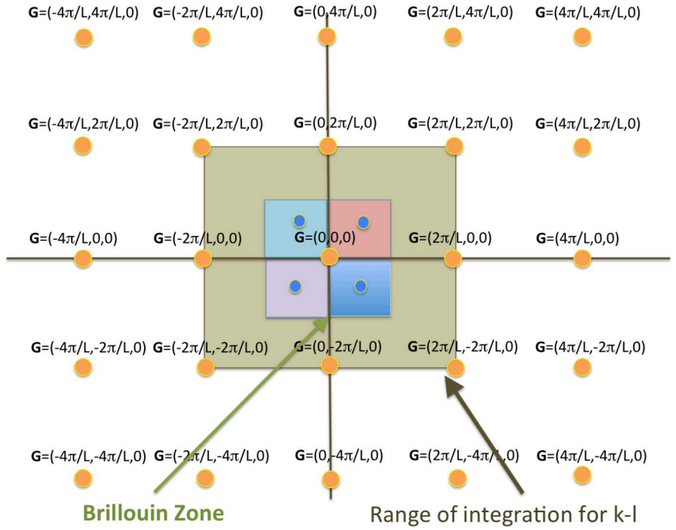
- We have implemented new **fractional occupation** optimizers and fixed various bugs for metallic systems,
- Fully implemented **space group symmetry**,
- Interfaced the **ONCV pseudopotentials**,
- Developed a Python code interface and added a **socket interface** to work with the ASE Python library for NWChem to better interact with the other parts of the project.

Bylaska

Screened potentials defined solely from periodic boundary conditions

- Simple approximations for 2-el. int. over Brillouin zone is very inaccurate, simple Γ-point approximation → infinity!
- The condensed phase community typically introduces a screened Coulomb interaction to calculate the 2-el. int.
- **We have developed a new approach using Filon's integration**
  - no need to use large numbers of *k*-points
  - overcomes limitations of highly-engineered approaches
  - makes chemistry many-body calculations (e.g QIS, CCSD(T)), MCSCF) tractable in periodic boundary conditions.





Example of screened potential for G-point exchange calculation – note $V_{SCR}(G=0)$ is not infinite

$$-\frac{1}{2\Omega}\left(\frac{1}{(V_{BZ})^2}\right)\int d\boldsymbol{k}\int d\boldsymbol{l}\sum_{\boldsymbol{G}}\left[\frac{4\pi}{|\boldsymbol{G}-\boldsymbol{k}+\boldsymbol{l}|^2}\right]\rho^{\sigma}_{\boldsymbol{ml};\boldsymbol{nk}}(-\boldsymbol{G})\,\rho^{\sigma}_{\boldsymbol{nk};\boldsymbol{ml}}(\boldsymbol{G})$$

$$\approx -\frac{1}{2\Omega}\left(\frac{1}{(V_{BZ})^2}\right)\sum_{\boldsymbol{G}}\rho^{\sigma}_{\boldsymbol{ml}=\boldsymbol{0};\boldsymbol{nk}=\boldsymbol{0}}(-\boldsymbol{G})\rho^{\sigma}_{\boldsymbol{nk}=\boldsymbol{0};\boldsymbol{ml}=\boldsymbol{0}}(\boldsymbol{G})\left[\iint\frac{4\pi}{|\boldsymbol{G}-\boldsymbol{k}+\boldsymbol{l}|^2}\,d\boldsymbol{k}d\boldsymbol{l}\right]$$

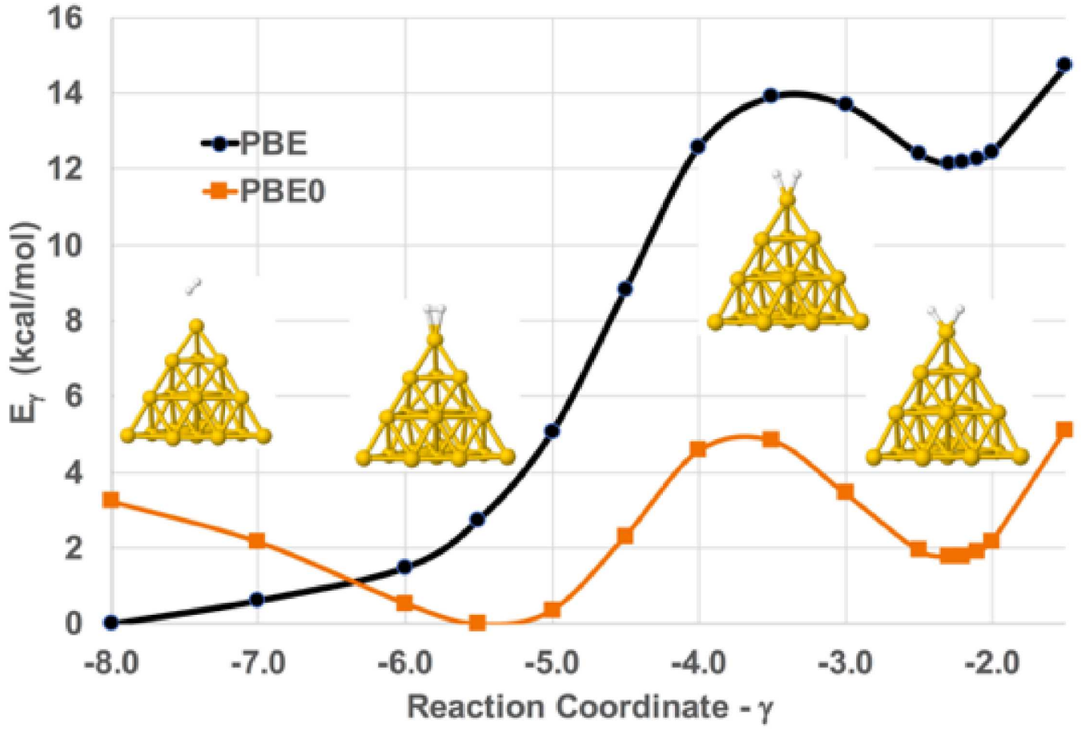
$$=-\frac{1}{2\Omega}\left(\frac{1}{(V_{BZ})^2}\right)\sum_{\boldsymbol{G}}\rho^{\sigma}_{\boldsymbol{ml}=\boldsymbol{0};\boldsymbol{nk}=\boldsymbol{0}}(-\boldsymbol{G})\rho^{\sigma}_{\boldsymbol{nk}=\boldsymbol{0};\boldsymbol{ml}=\boldsymbol{0}}(\boldsymbol{G})[V_{SCR}(\boldsymbol{G})]$$

- Accurate and efficient integration strategies have been developed for generating screened potentials.
- Algorithm works for general shaped unit cells.

Bylaska

Application of screened potentials

example: $Au_{20}^- + H_2 \rightarrow Au_{20}H_2^-$



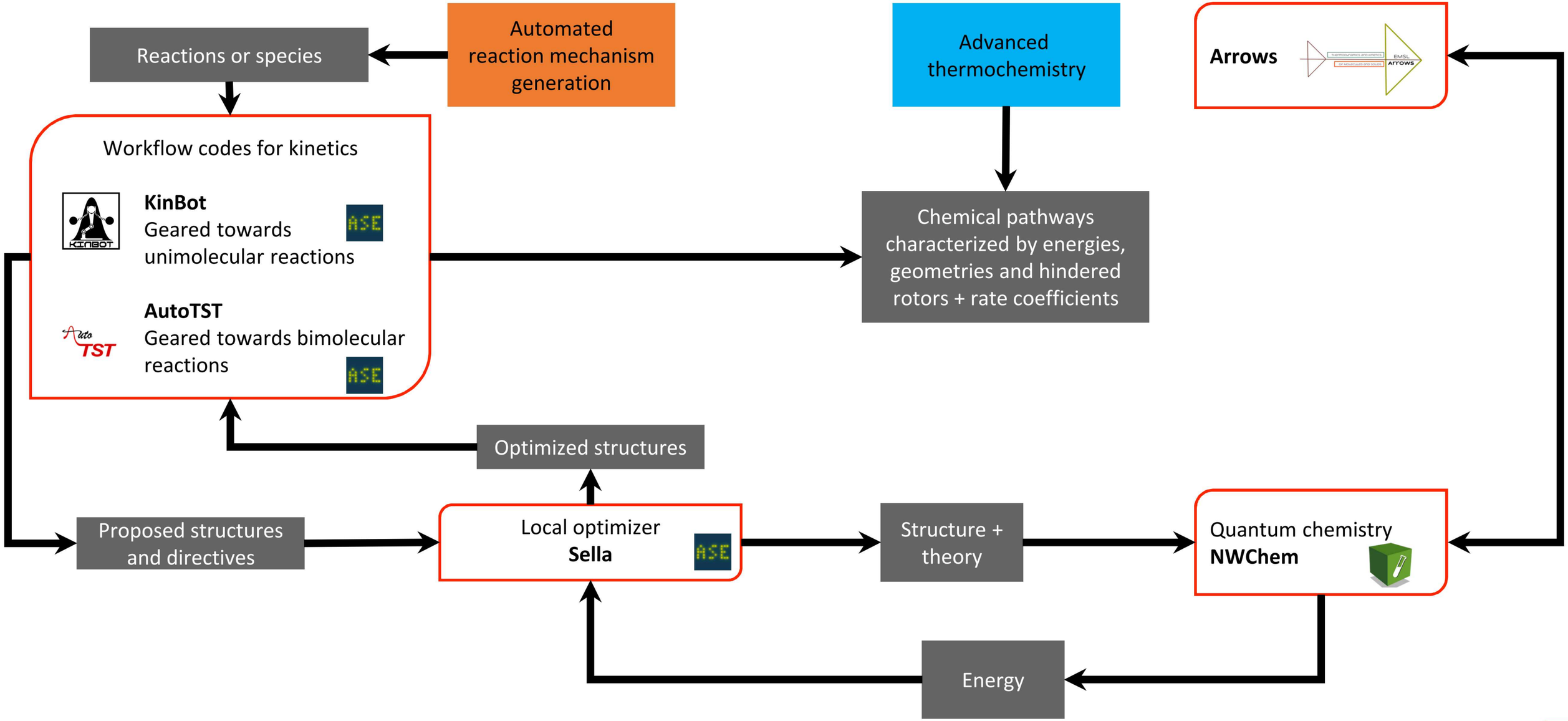
Future work:

Other approaches for estimating the correlation energy

- Random phase approximation (RPA)
- Multi-Configurational Self-Consistent Field (MCSCF)

Bylaska

Automated reaction path exploration

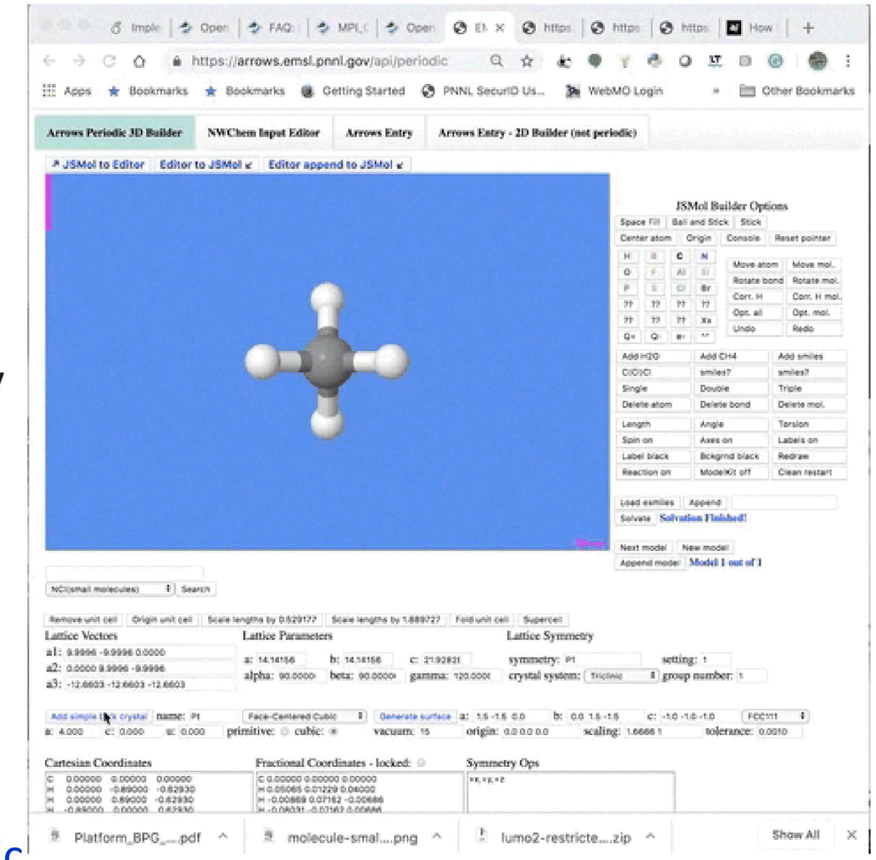


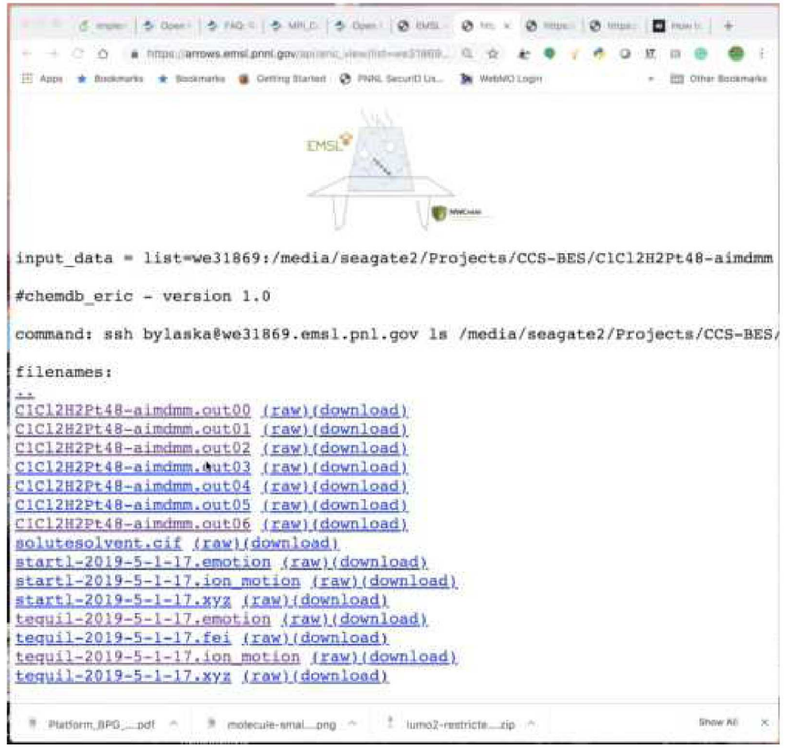
Visual workflow and builders to make complex electronic structure simulations more accessible

A periodic builder and simulation workflow have been developed and added to the recently developed **EMSL Arrows web interface**. Current features include

- Works on **any web browser** on workstations, laptops, tablets, smart phones,…
- **Web**-accessible and **stand-alone** versions available

- Generates and cleaves surfaces in seconds
- Options for setting up initial reaction pathways, free energy simulations, electron transfer calculations
- Understands space-group symmetry
- Text and spreadsheet editors
- MM optimization, solvation for periodic systems via web API



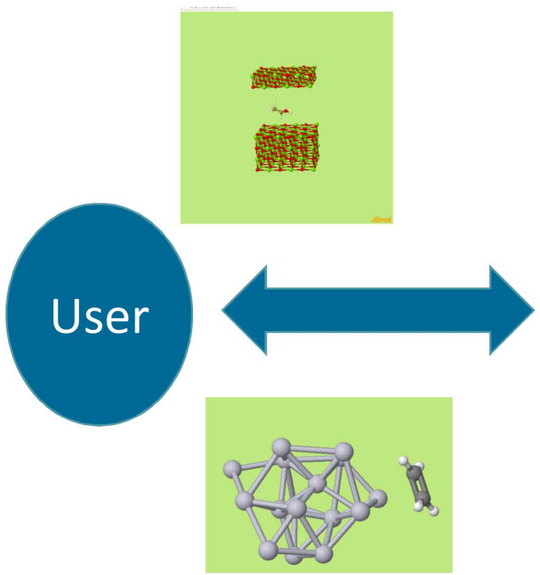


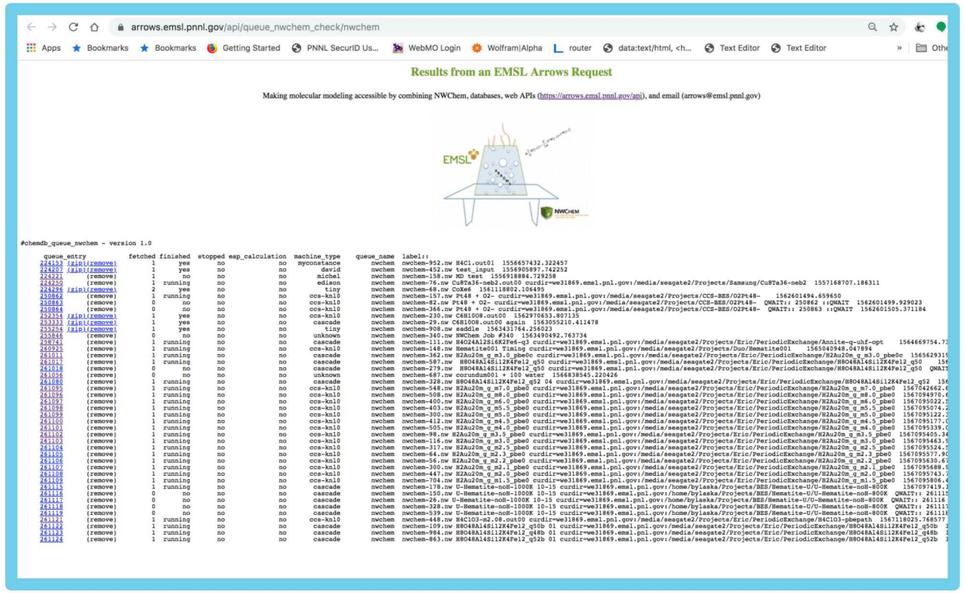
- Extensive options to build and modify periodic and cluster systems.
- Create, edit, load and save NWChem input decks and submit jobs.
- View NWChem output, structures, trajectories, Gaussian cube files, free-energy surfaces, various graphing,…

https://arrows.emsl.pnnl.gov/api/periodic

Arrows Queue

- We developed a web-based queue system that works with DOE HPC computers without the need for protocols that rely on unsecure passwords storage.

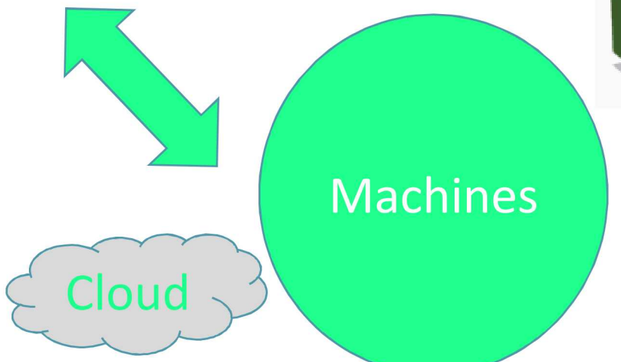




- Login to HPC machine in the usual way.
- Use a terminal or cron jobs to access arrows with standard GET and POST.
- Python scripts developed to help automate submission on HPC machine
- Arrows does not store user passwords!

- User uses web-API to create NWChem input deck
- Submit input decks to Arrows Queue with optional one-time target phrase so only specified users can see the submitted input deck

Arrows Queue seamlessly copies data back and forth. Movement of data is driven by user not by Arrows.

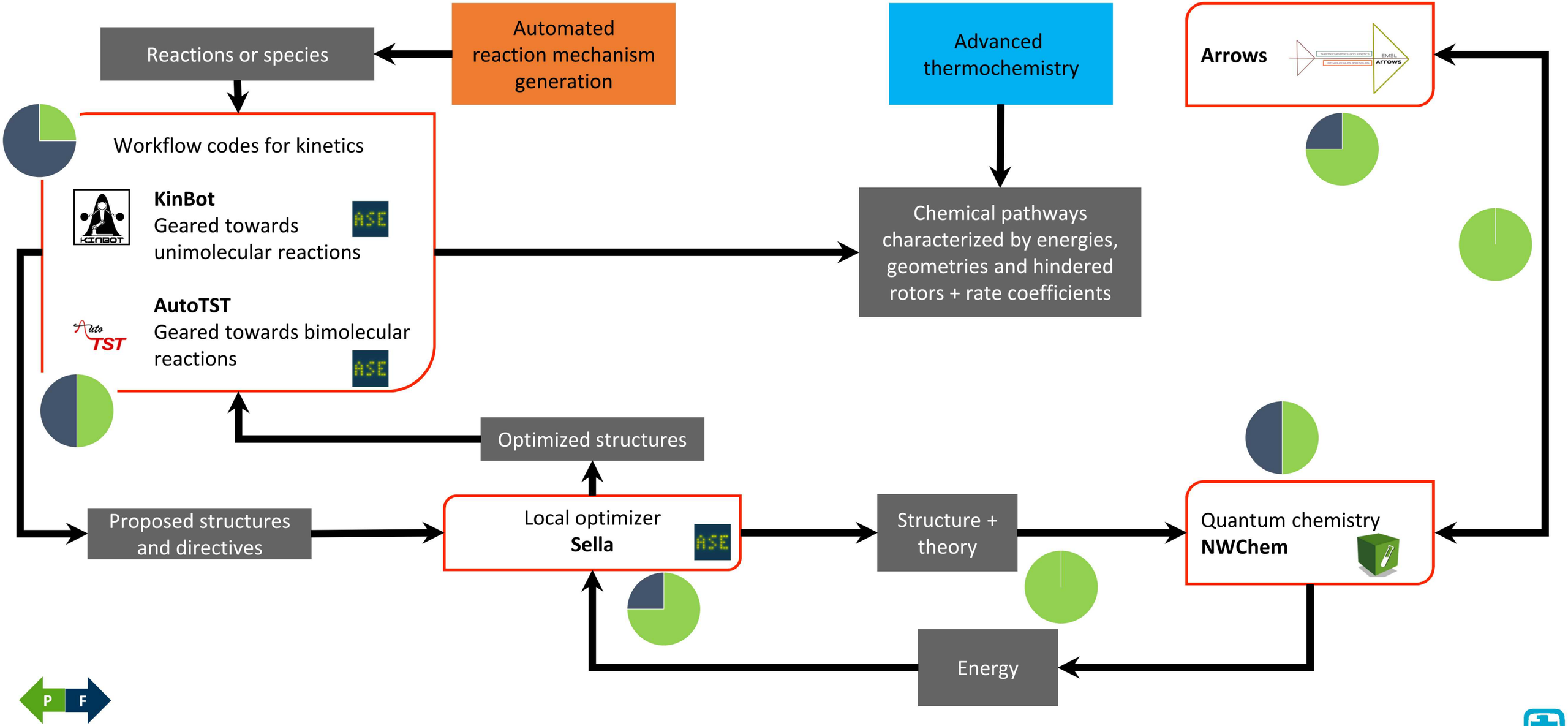


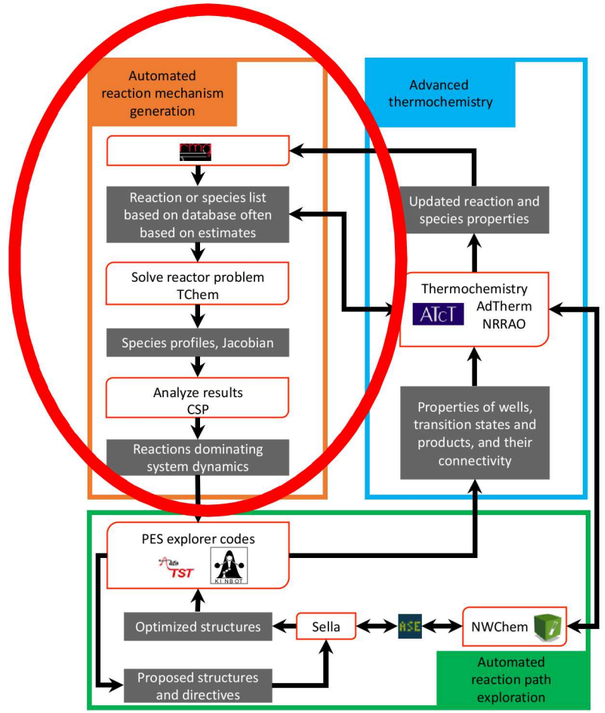
Cori

NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

Bylaska

Automated reaction path exploration





Automated reaction mechanism generation

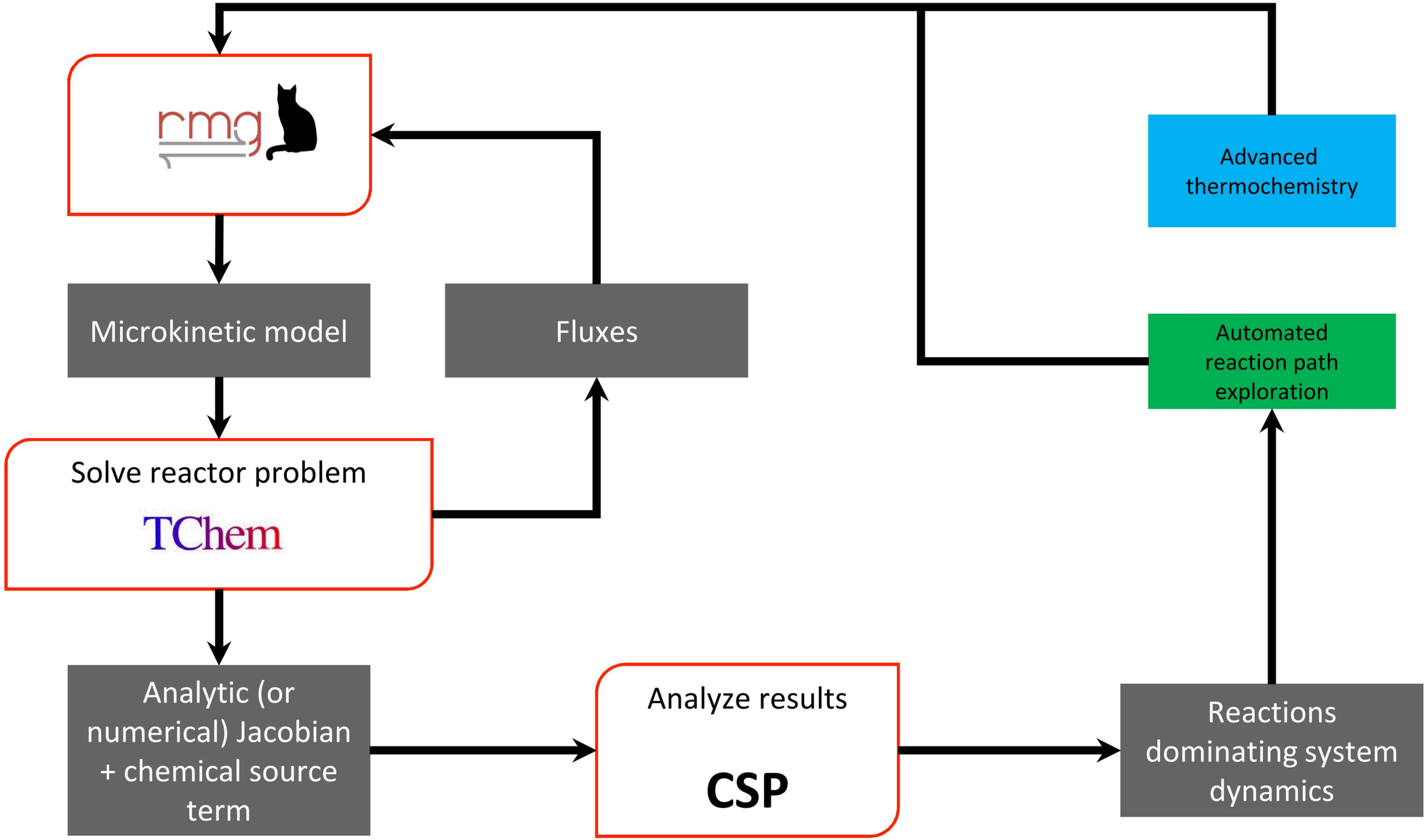
Automated reaction mechanism generation

Building, running, and analyzing microkinetic models for gas/solid catalytic systems

- For more accurate microkinetic mechanisms on a wider variety of metal surfaces improve RMG-Cat
- Rewrite TChem in object-oriented C++ using the Kokkos framework, and extend it to heterogeneous catalysis chemistry.
- Develop a Kokkosified and open-source C++ library for CSP analysis of chemical systems
- Couple codes

Goldsmith, West, Safta, Najm, Kim, Rob, Mazeau, Blondal

Automated reaction mechanism generation



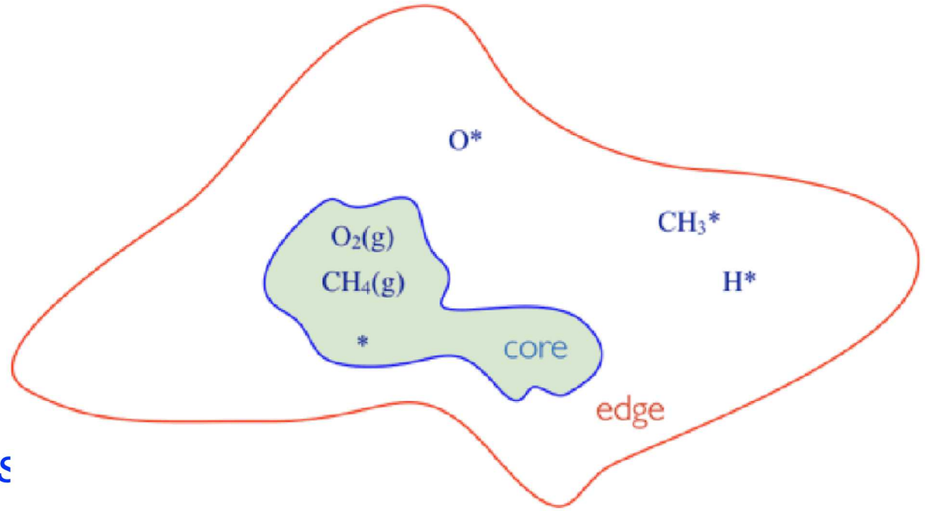
Let's use computers to build microkinetic mechanisms!

$$R_1 + R_2 \rightleftharpoons P$$

$$\begin{bmatrix} R_1 + R_2 \rightleftharpoons I_1 + I_2 \\ I_1 \rightleftharpoons I_3 \\ I_2 + I_3 \rightleftharpoons P \end{bmatrix}$$

Code needs to

1. represent species
    - *use chemical graph theory*
2. propose new reactions
    - *use reaction families*
3. estimate thermodynamic + kinetic properties
    - *use precompiled databases and estimation methods*
4. keep only the important reactions
    - *use flux-based algorithm*



Mazeau, West
Blondal, Goldsmith
X

We have made 5 significant improvements to RMG's capabilities for heterogeneous catalysis

1. all heterogeneous capabilities are now included in RMG 2.4 and above
2. inclusion of nitrogen chemistry
3. updated thermodynamic database
4. seamless inclusion of gas-phase kinetics
5. linear scaling relations

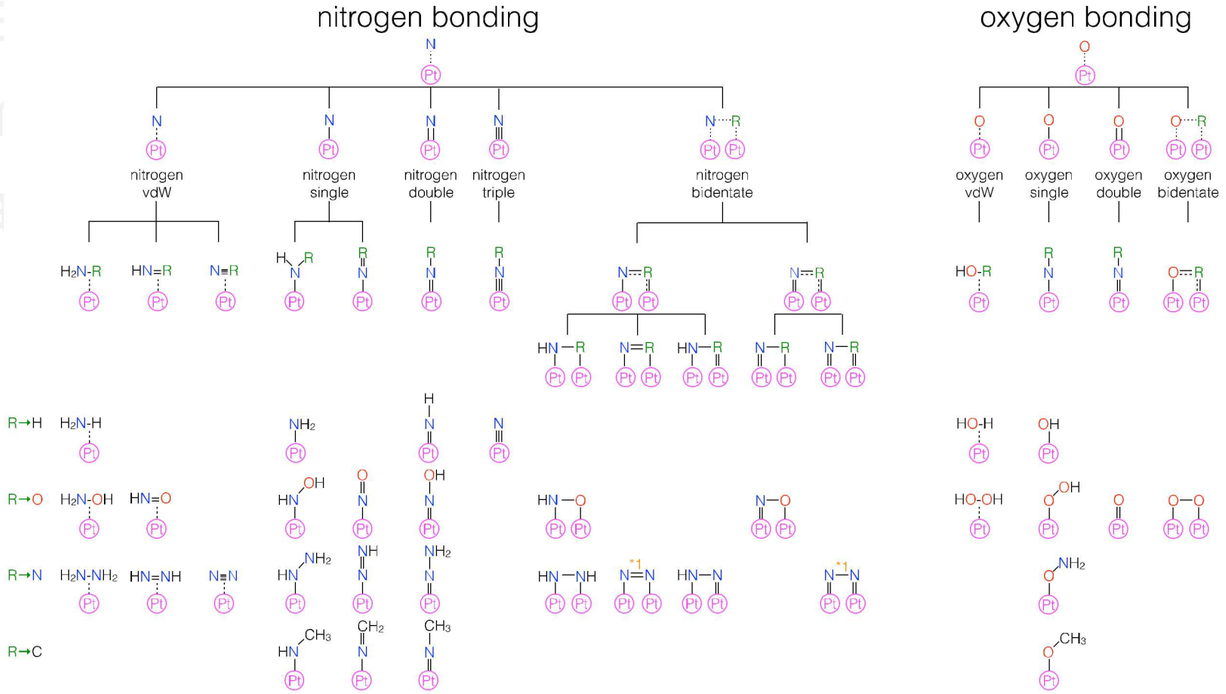
is based upon Reaction Mechanism Generator (RMG)

- open source, Python based
- developed for combustion
- mature (~50+ graduate-student years of development)
- https://rmg.mit.edu/

Mazeau, West
Blondal, Goldsmith

We have made 5 significant improvements to RMG's capabilities for heterogeneous catalysis

1. all heterogeneous capabilities are now included in RMG 2.4 and above
2. inclusion of nitrogen chemistry
3. upda
4. sean
5. linea



Mazeau, West
Blondal, Goldsmith

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69 specific HCNO adsorbates were computed on Pt(111) using BEEF-vdW functional

P

Mazeau, West
Blondal, Goldsmith

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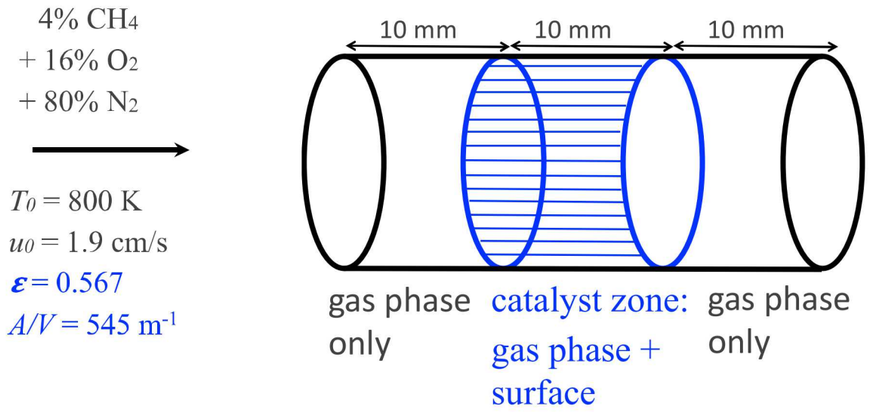
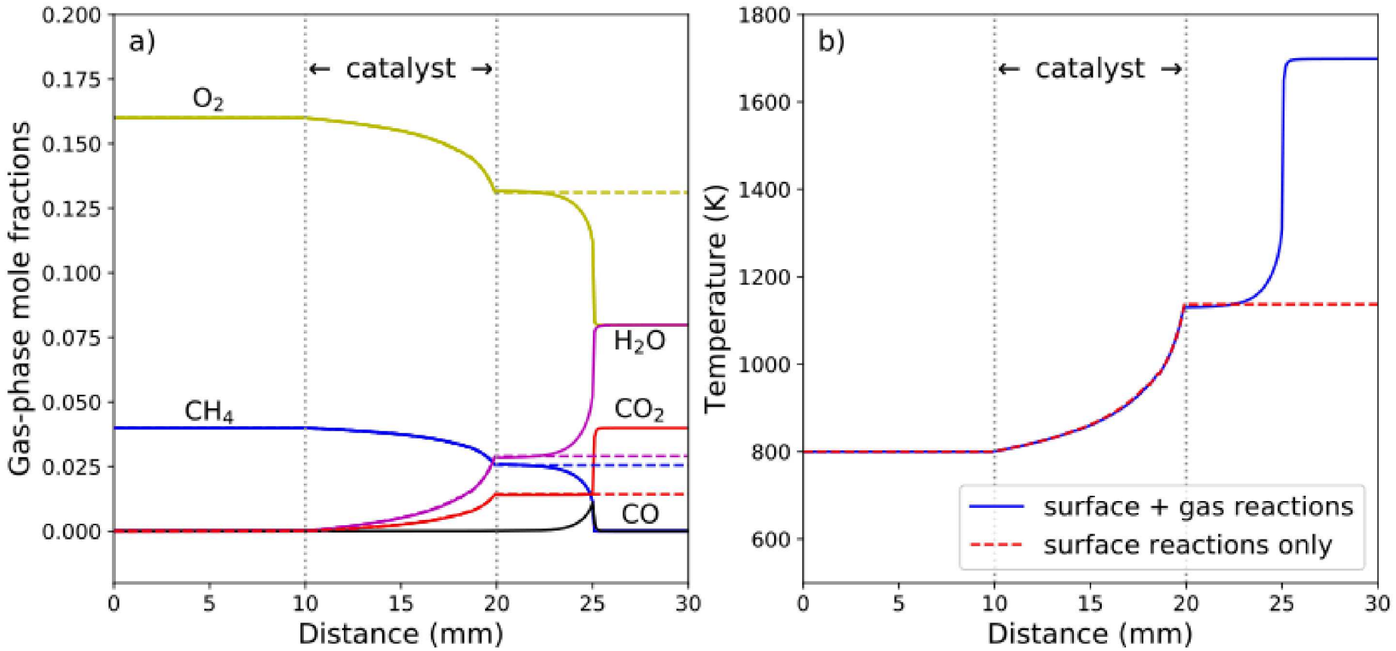
Mazeau, West
Blondal, Goldsmith

Example: RMG generated a mechanism for methane oxidation on Pt(111)

- fuel lean conditions for T = 500, 1500, 1800 K & P = 1 bar
- core:
  - 21 adsorbates + 51 surface reactions
  - 38 gas-phase species + 340 reactions
- edge:
  - 196 species + 298 reactions





We demonstrated the coupled gas-surface capabilities of RMG.
Such coupling is necessary to predict correct behavior.

Mazeau, West
Blondal, Goldsmith

K. Blondal, J. Jelic, E. Mazeau, F. Studt, R. H. West, and C. F. Goldsmith. Computer-generated kinetics for coupled heterogeneous/homogeneous systems: A case study in catalytic combustion of methane on platinum, Indust. Eng. Chem. Res. accepted

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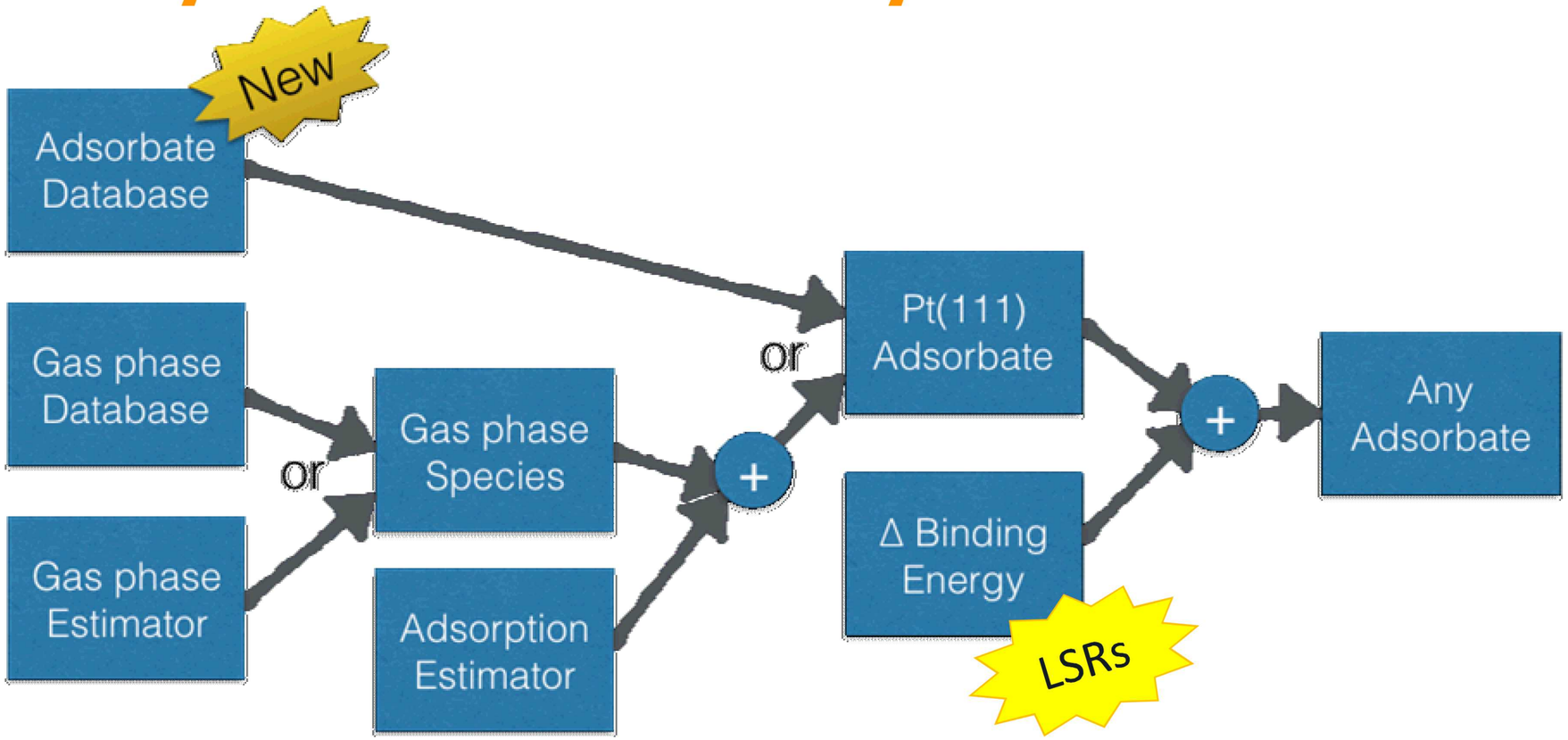
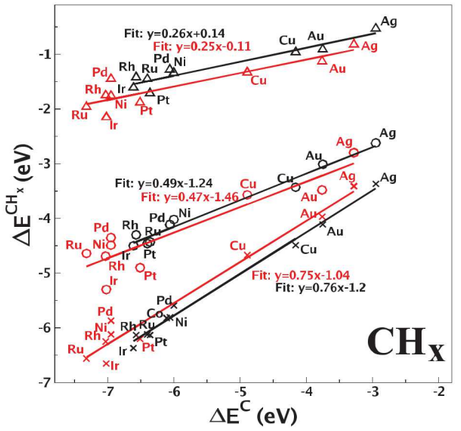
Mazeau, West
Blondal, Goldsmith

We can now estimate thermochemistry of any adsorbate on any metal



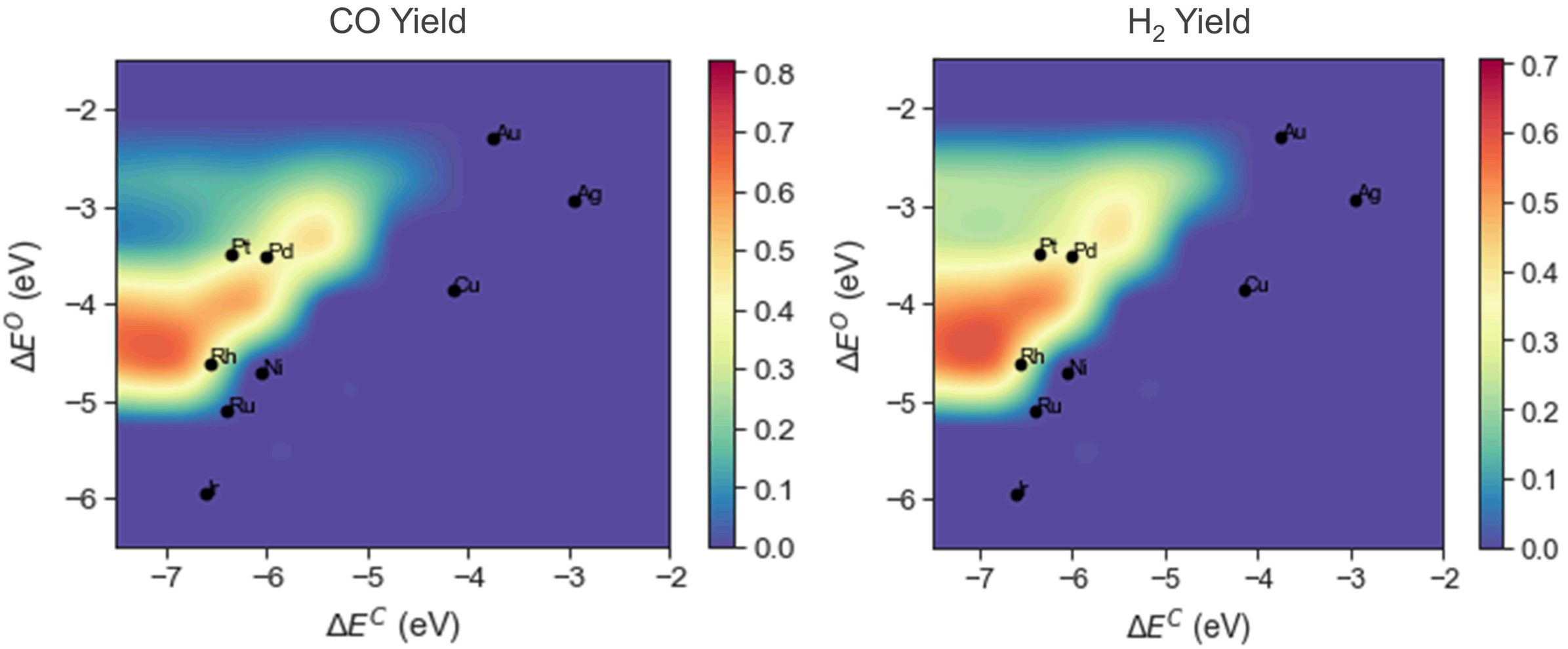


Abild-Pedersen et al., Phys. Rev. Lett. (2007)

- On many metals, simple rules can predict the (change in) binding energy.
- Now implemented in RMG.

Mazeau, West Blondal, Goldsmith

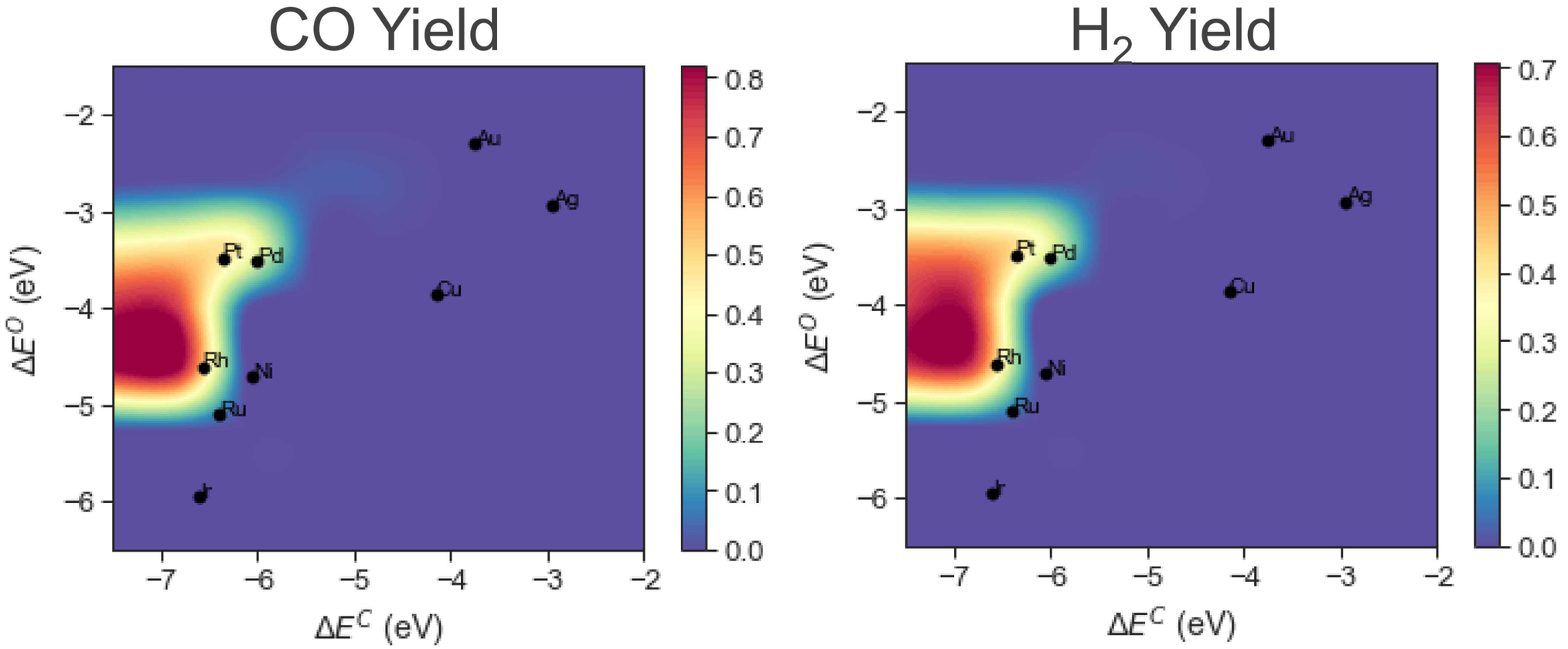
RMG allows systematic and automatic investigation of many metals
Example: Synthesis gas on different metal surfaces



Some metals have higher selectivity but lower yield.

Mazeau, West
Blondal, Goldsmith

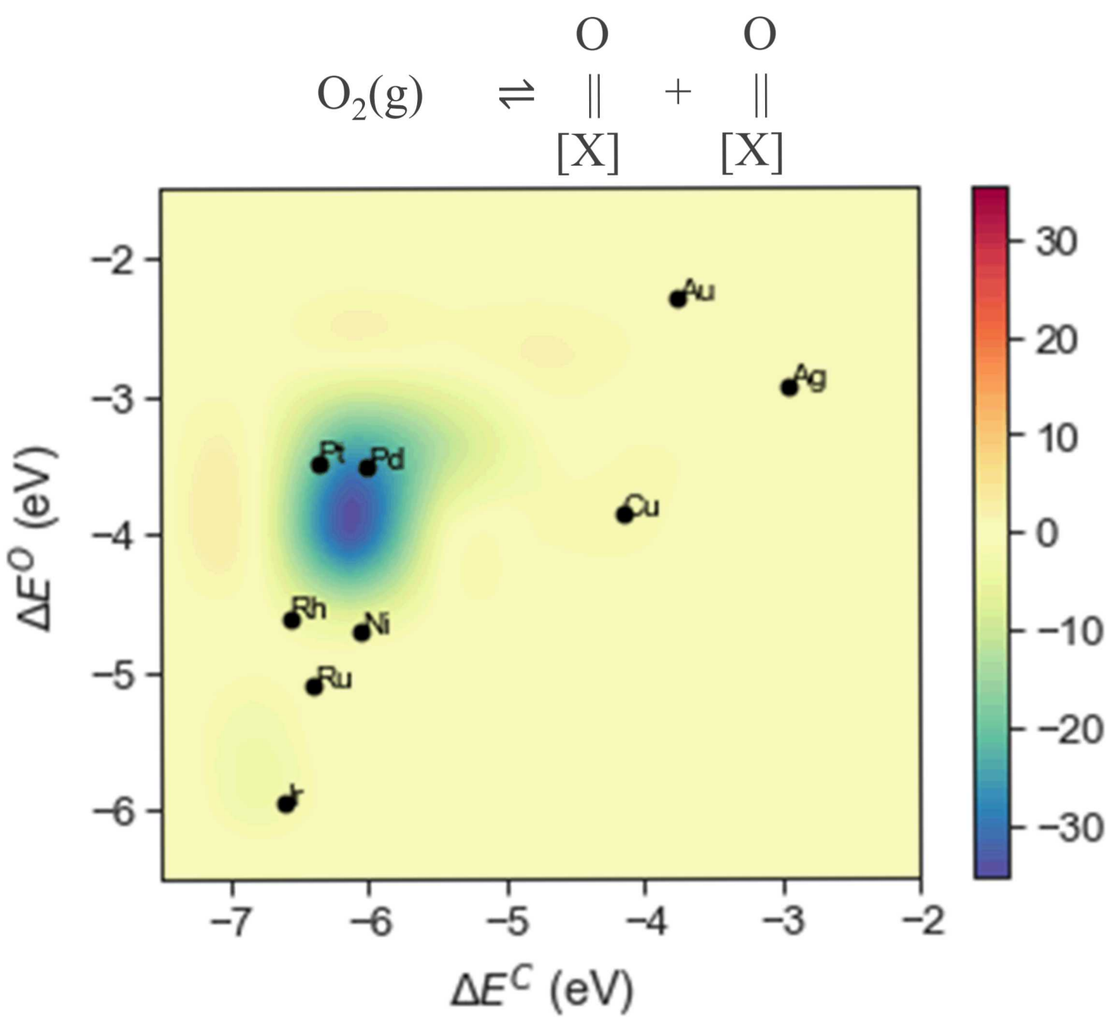
Automated investigation of the effect of the inlet composition

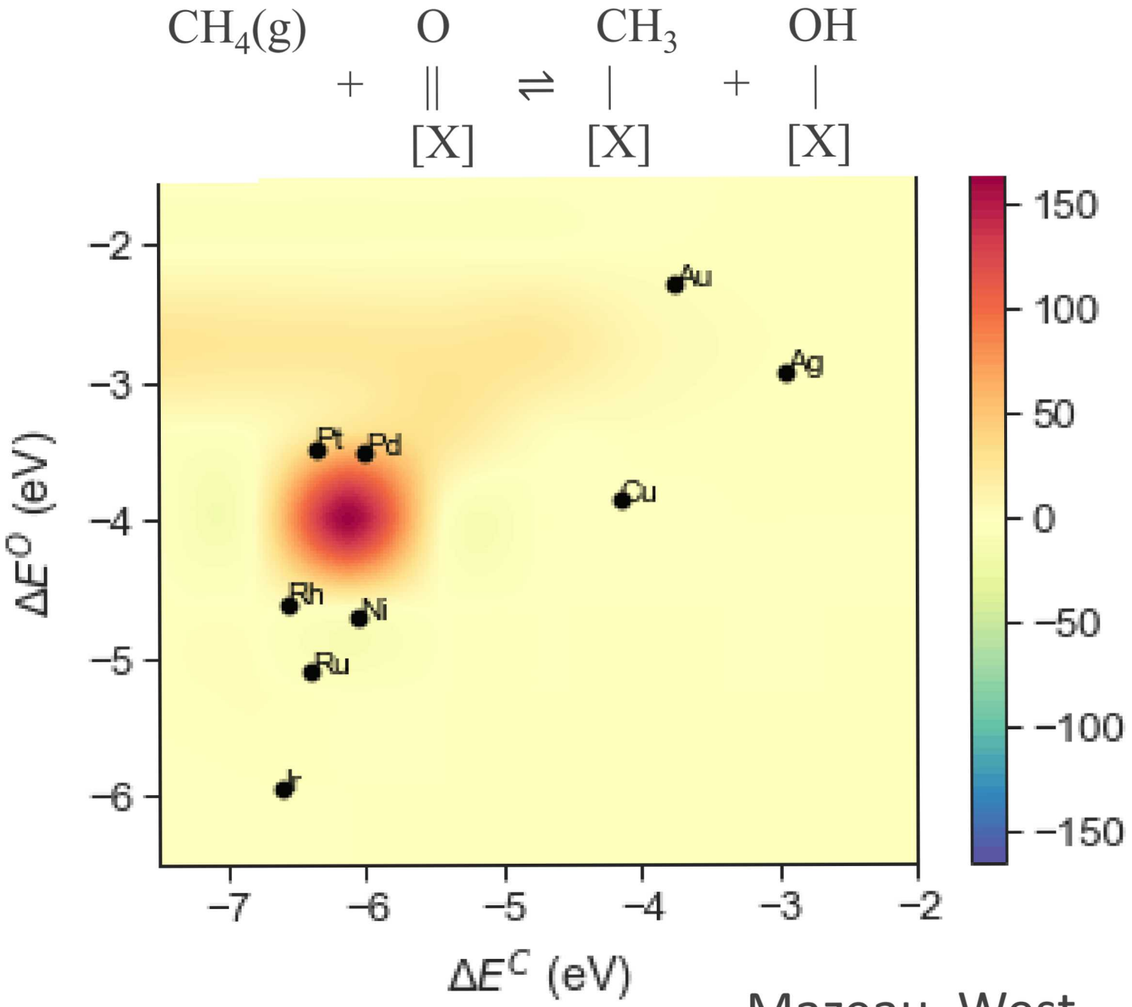


Not only does each metal affect yield, feed gas composition does as well

Mazeau, West
Blondal, Goldsmith

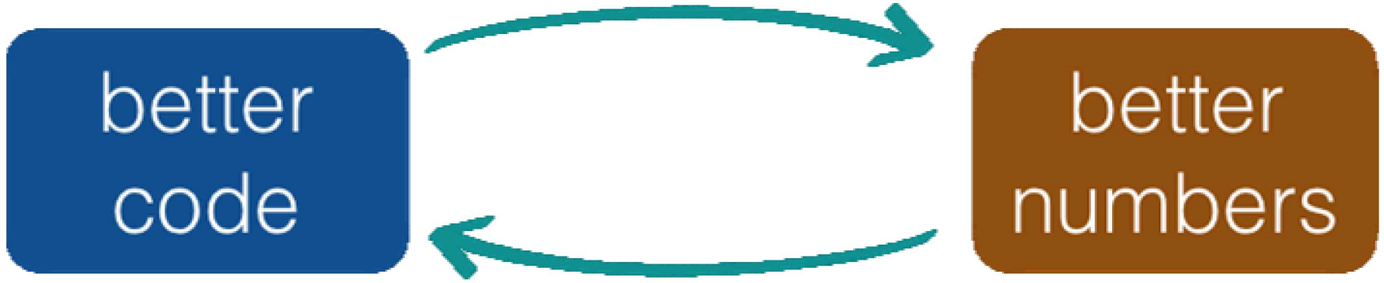
Volcano plots for the sensitivity of a reaction on H_2 yield as a function of atomic binding energies





Mazeau, West
Blondal, Goldsmith

RMG-Cat works, but we have work to do



- Coverage dependence
- Bifunctional materials, oxides
- Kinetic Monte Carlo simulations

- Better thermodynamic properties

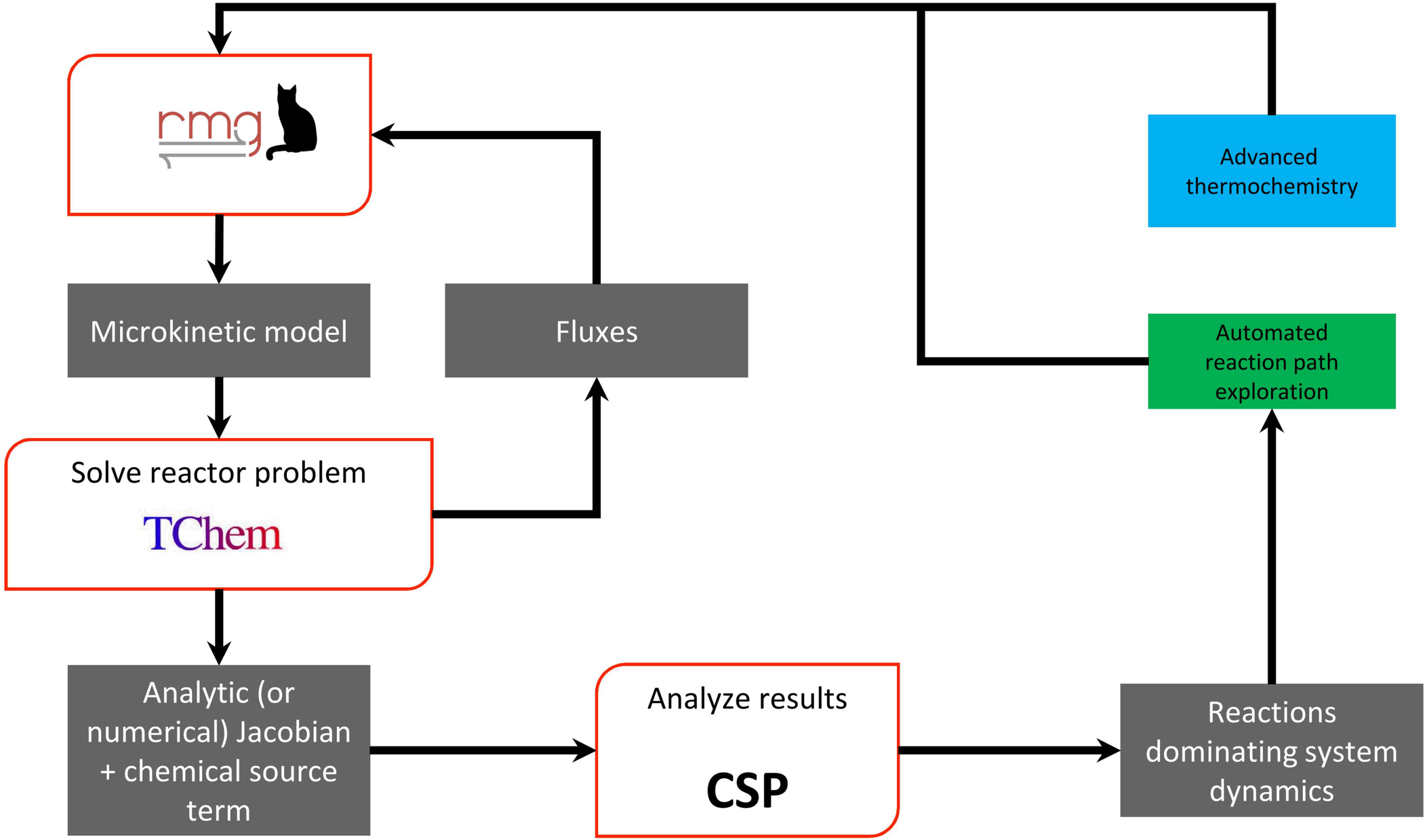
➔ Thrust #3

- Add more reaction families
  - *Bi-dentate*
  - *Eley-Rideal*
- Kinetics calculations

➔ Thrust #1

Mazeau, West
Blondal, Goldsmith

Automated reaction mechanism generation



TChem

TChem is a software library that enables numerical simulations using complex chemistry and facilitates the analysis of detailed kinetic models written in C++.

Activities under ECC:

1. Kokkos integration for performance-portability on future exascale computing platforms 

2. Include heterogeneous catalytic capabilities in the toolkit 

3. Couple with RMG-Cat, CSP and ATcT 

Safta, Rob, Kim

Refactoring TChem using Kokkos

Improvements:

- TChem was completely redesigned using Kokkos. https://github.com/kokkos/kokkos
- A single Kokkos version of TChem works for diverse advanced computing systems

- Hierarchical parallelism
  - Batch parallelism is exploited for the efficient use of GPUs.
  - For additional performance, team-level hierarchical parallelism is implemented.

- Using Intel Xeon Skylake 2x24 processor, TChem+Kokkos achieves 7x – 8x speedup for large batch sizes when GPUs are enabled

Microkinetic model capabilities

- Parser for surface species and reactions as specified by RMG 

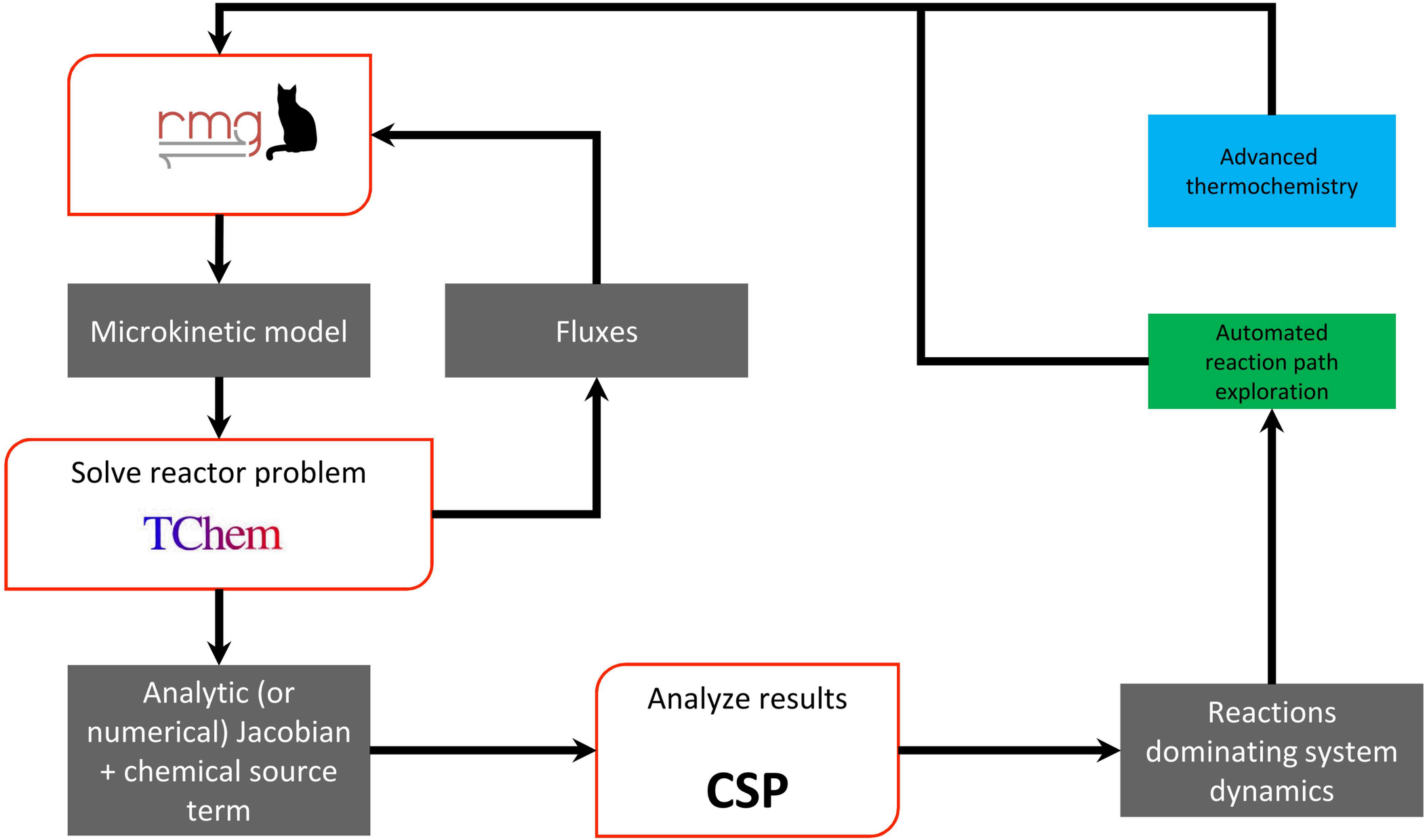
- Functions handling thermodynamic properties, equilibrium constants, stick coefficients, and species productions rates of adsorbates 

- Plug flow reactor (PFR) model implemented 

  - Parse gas-phase and microkinetic models output from RMG
  - Differential Algebraic Equations (DAEs) solved with IDA (LLNL's Sundials package)
  - Provide source terms and numerical Jacobian to CSP (in progress)

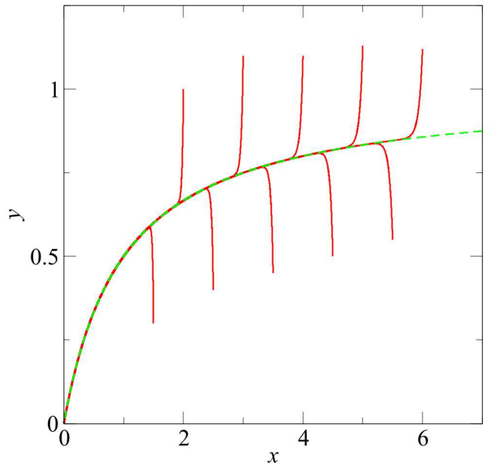
Safta, Rob, Kim

Automated reaction mechanism generation



Stiff chemical systems & Computational Singular Perturbation (CSP)

- Stiff chemical system kinetics exhibit a large range of time scales
- Progression to equilibrium proceeds as a cascade down to lower dimensional slow manifolds – 0 dim at equilibrium
- CSP basis vectors decouple the fast and slow subspaces
- Projection of the dynamics on the fast and slow subspaces enables analysis

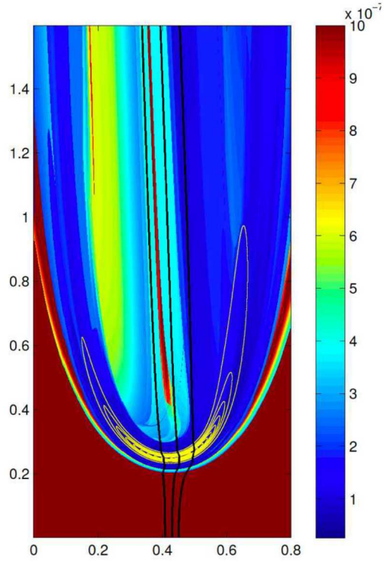


Goal

- Develop **open source** C++ library for CSP analysis of chemical systems
- Target development at heterogeneous **CPU-GPU** architectures

Approach

- Design an object oriented software structure given CSP capabilities
- Implement latest CSP developments for both gas phase & catalysis
- Use *Kokkos* for low-level mixed-architecture operations
- Demonstrate utility and scalability of the new analysis capabilities
  - High-end heterogeneous computational hardware
  - Range of chemical model complexity
  - Gas phase and catalytic systems



Driving chemical timescale in a methane edge flame.

Najm, Rob, Kim

CSP Progress – open-source software including capabilities for catalysis

- Extended mathematical formulation for CSP analysis from ODE to DAE systems P
- Developed C++ CSP library for dynamical analysis of general ODE/DAE systems P
  - Couples with TChem for kinetics & thermodynamics
    - Requires source term and Jacobian for given state vector
    - Can be easily coupled to other chemical libraries
  - Extensive validation and testing in final stages
  - Provides cause-and-effect information while decoupling fast/slow processes
    - Reliable sensitivity information in stiff systems
    - Identification of key processes governing partial-equilibration and quasi-steady state behavior
    - Identification of important processes/reactions driving predicted dynamical system response
  - Soon open-source release F

P Najm, Rob, Kim

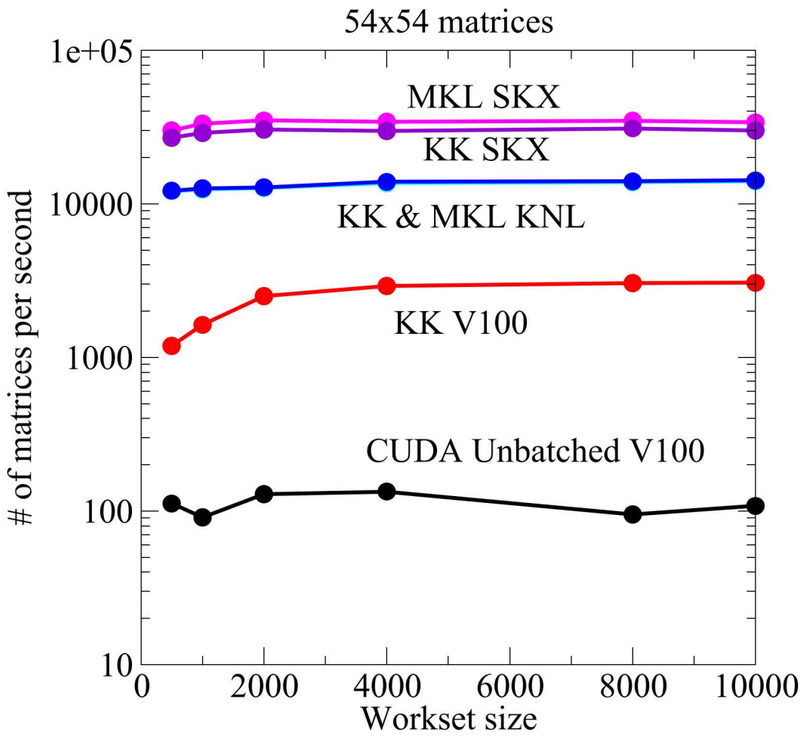
CSP on heterogeneous exascale hardware using Kokkos

Key computational cost in CSP analysis is eigen-decomposition of Jacobian matrix for any given chemical state

Batched linear algebra routines allow effective massively-parallel GPU utilization

- Batching necessary for small-moderate size matrices
- No available open-source GPU batched eigensolvers exist

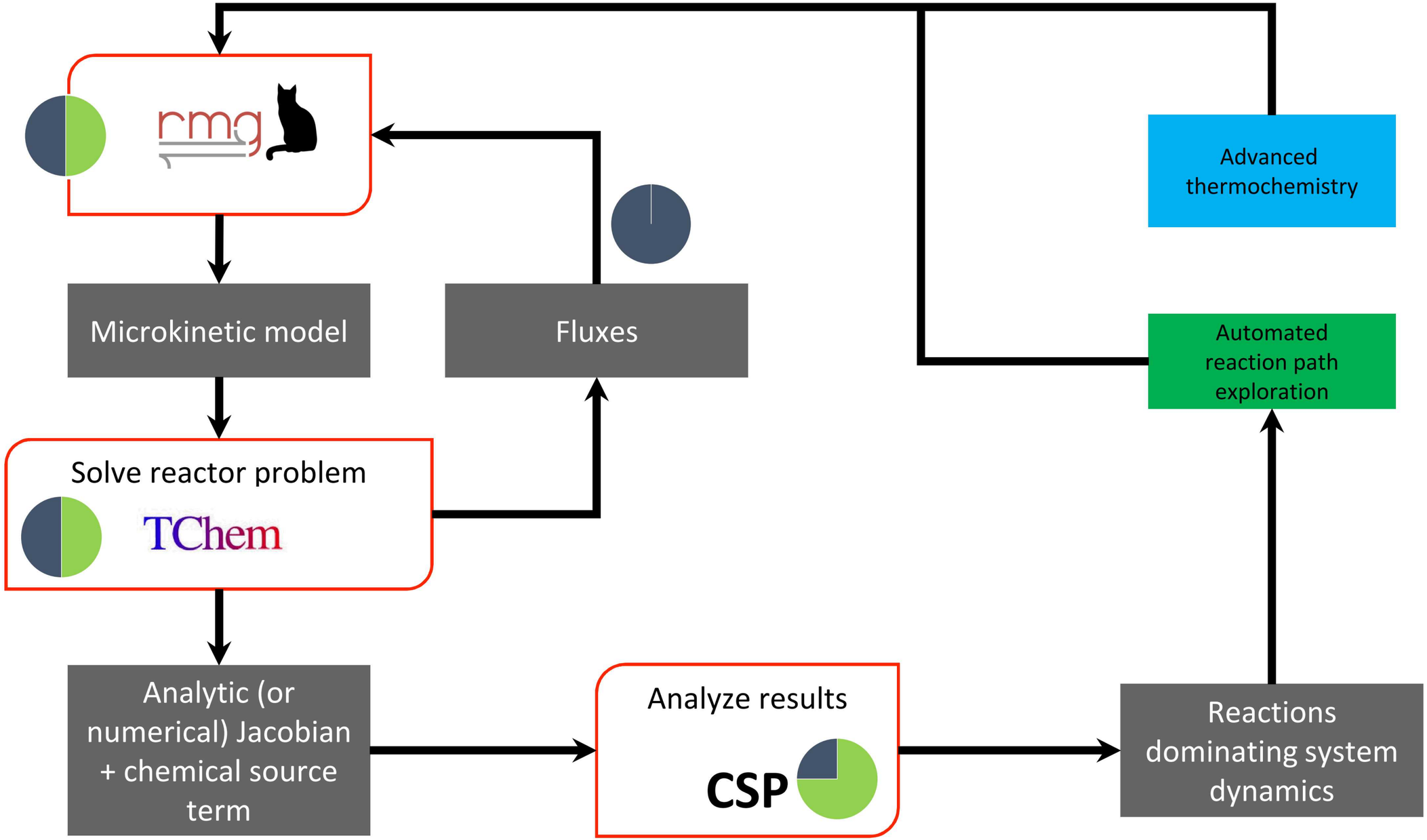
- **Developed GPU batched eigensolver** software using Kokkos P
  - Demonstrated 28x speedup provided by batching on 54x54 size matrices on NVIDIA V100
  - Comparable Kokkos versus native MKL batched eigensolver performance on Intel hardware
- Solver improvements in terms of accuracy and scaling on larger systems are in progress F



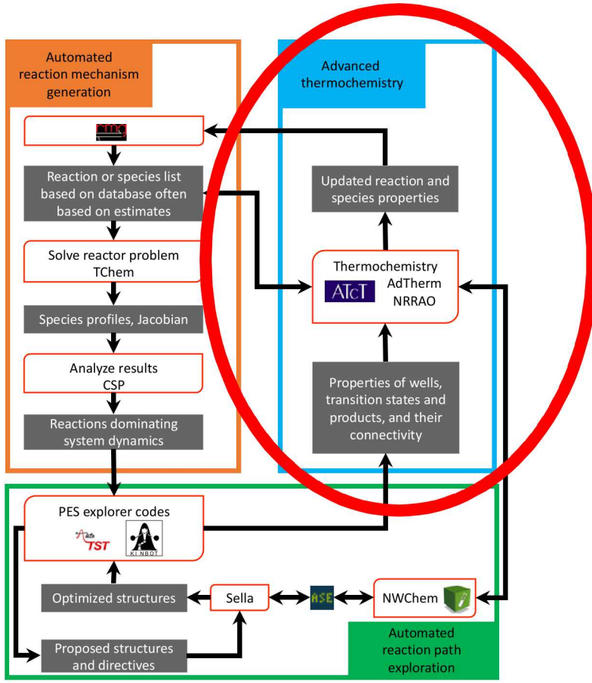
Performance of batched Kokkos (KK) eigensolver on NVIDIA V100 GPU, as well as Intel KNL and SKX hardware. Also included are the Intel MKL batched eigensolver performance, and the CUDA unbatched eigensolver for reference.

Najm, Rob, Kim

Automated reaction mechanism generation



Advanced thermochemistry



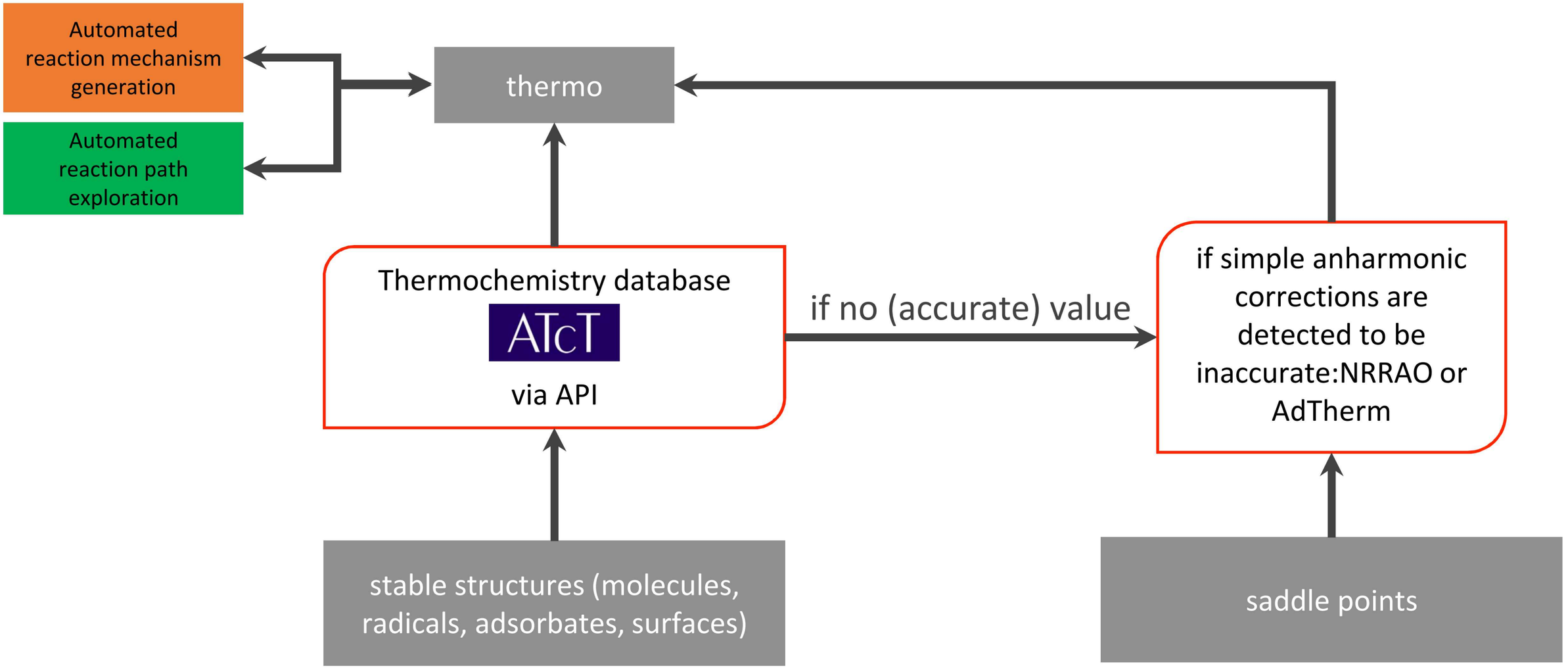
Advanced thermochemistry

Developing open databases for adsorbates and improving the accuracy of entropy and enthalpy increments for gas-phase species and adsorbates.

- Develop ATcT into a public and interactive database while preserving a strict control over accuracy, and incorporate access for automated chemical mechanism calculations
- Enable the routine inclusion of certain anharmonic effects, crucial for accurate entropy, and provide a code to do that
- Create AdTherm, a suite of methods implemented into ASE to compute the partition function for the coupled, anharmonic motion of adsorbates relative to the catalyst surface

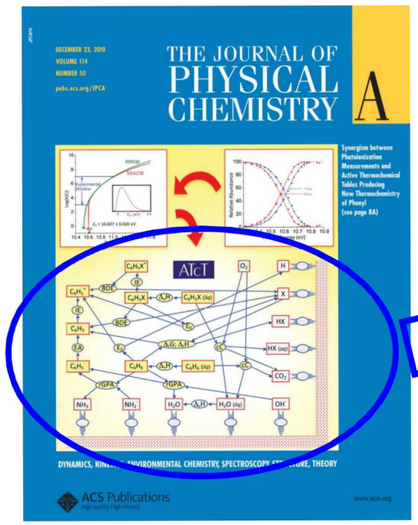
Bross, Ruscic, Goldsmith, Phipps

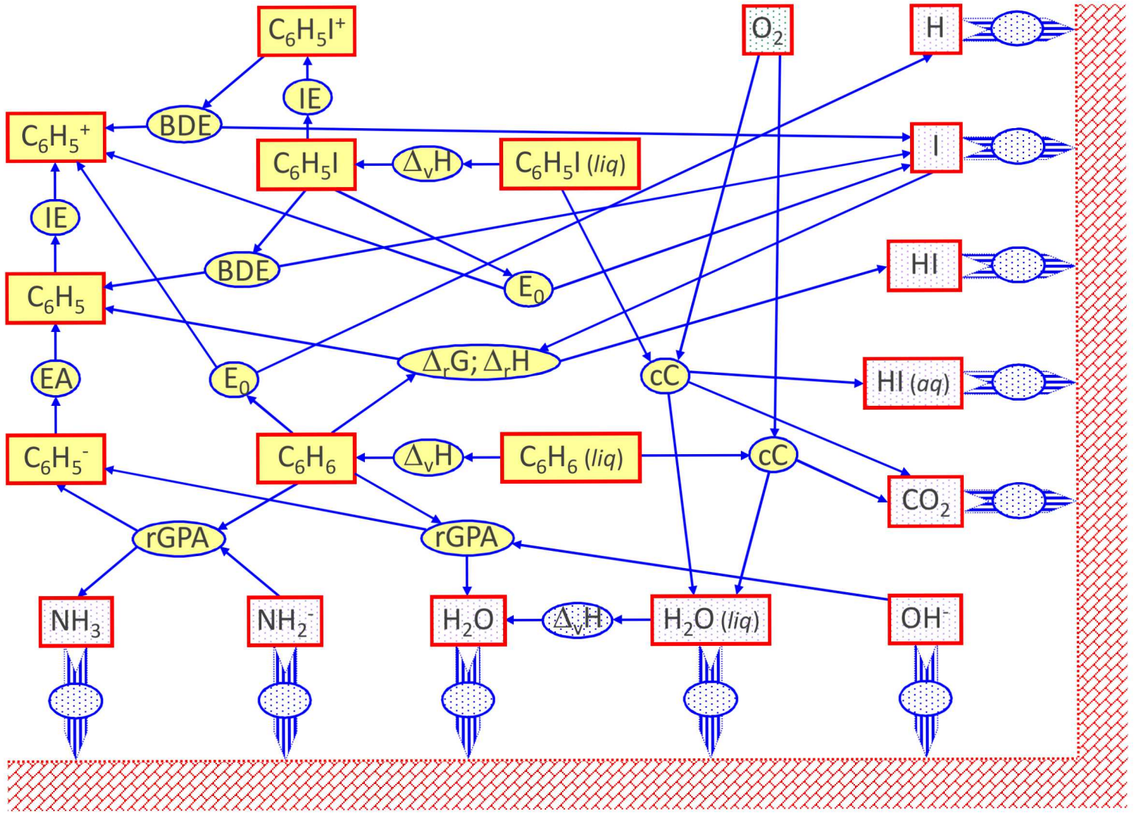
Advanced thermochemistry



Active Thermochemical Tables

- As opposed to conventional sequential thermochemistry (A begets B, B begets C), **ATcT** are based on the **Thermochemical Network (TN)** approach, producing **accurate, reliable, robust, and internally consistent** thermochemical values





X Ruscic Bross

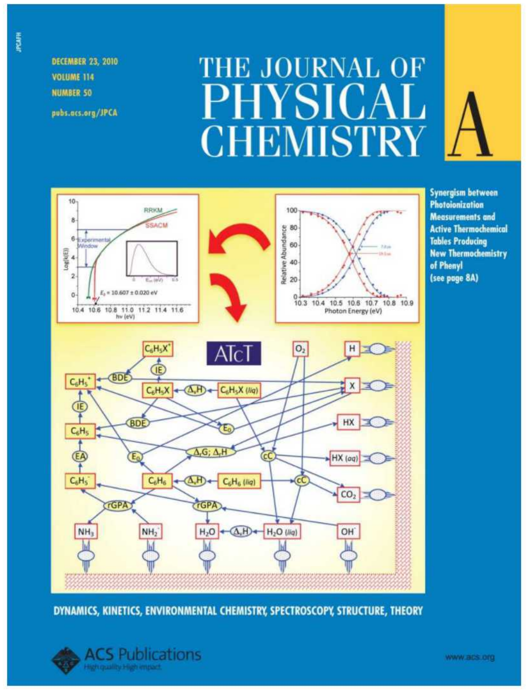
Active Thermochemical Tables

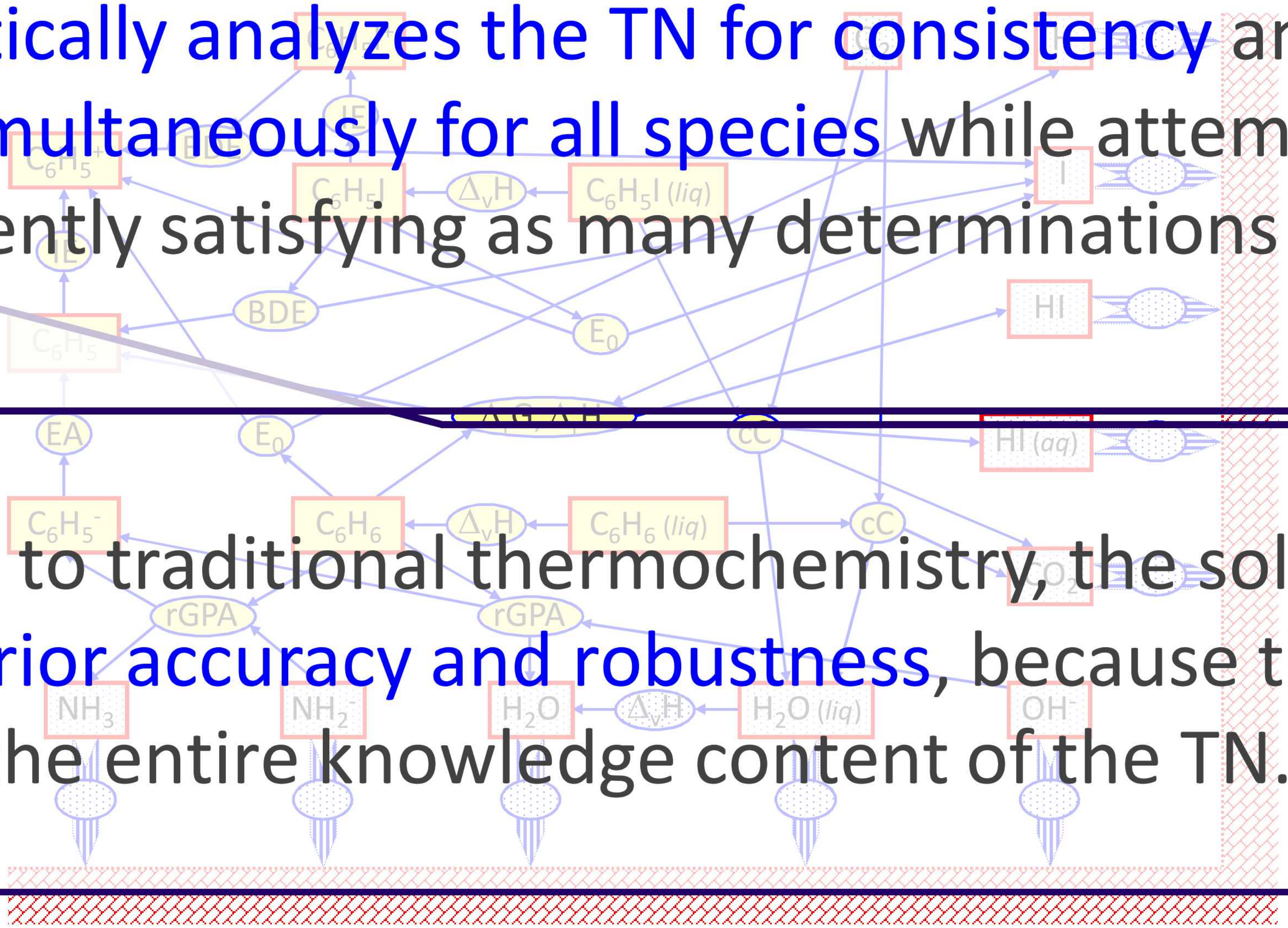
- As opposed to conventional sequential thermochemistry (A begets B, B begets C), **ATcT** are based on the Thermochemical Network (TN) approach, producing **accurate, reliable, robust, and internally consistent** thermochemical values

ATcT constructs the TN from available determinations ($\Delta_r H°$, K_{eq}, BDE_T, TAE_0, IE_a, AE_0, EA_a, …)

ATcT statistically analyzes the TN for consistency and solves it simultaneously for all species while attempting to concurrently satisfying as many determinations as possible

Compared to traditional thermochemistry, the solutions have superior accuracy and robustness, because they are based on the entire knowledge content of the TN.





X
Ruscic
Bross

ATcT API has been created, enabling access by codes including ours, e.g., TChem, RMG https://atct.anl.gov/api/

- JSON access to current public database that accepts common queries including:
  - CASRN, species name, SMILES, InChI, ATcTID
- Easy programmatic access through scripts:

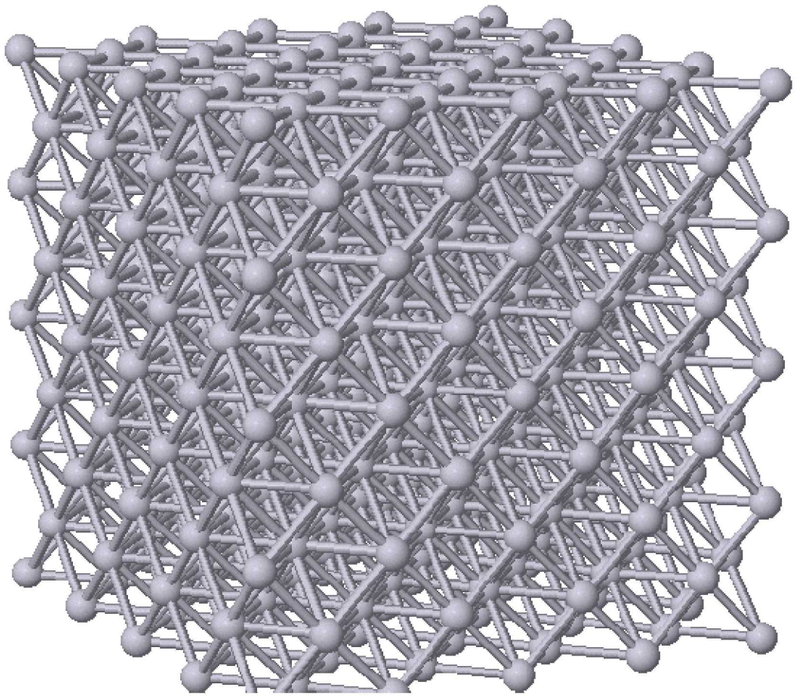
```
def CASRNsearch(inputCASRN):
    from requests import get
    import urllib.parse
    r = get('https://atct.anl.gov/api/?casrn='+urllib.parse.quote(str(inputCASRN)))
    import json
    try:
        json=json.loads(r.text)
    except json.decoder.JSONDecodeError:
        print('No records found')
        return
    return(json)
```

```
Name                    Formula         Delta_Hf_0K     Delta_Hf_298K       uncertainty
Methane                 CH4  (g)        -66.557         -74.526             ±0.056
```

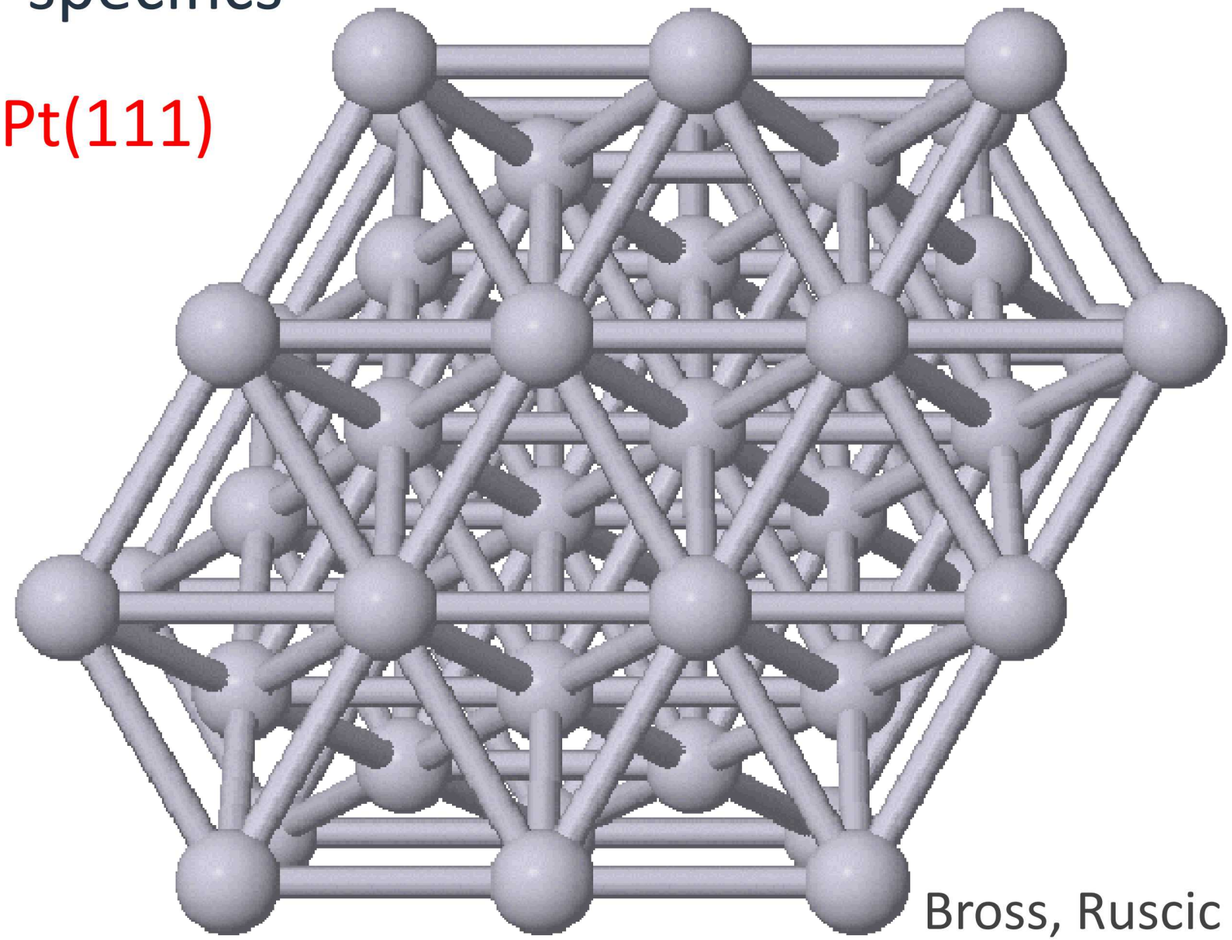
Adsorbates Thermochemistry

- Adsorbate species systematics must distinguish not only the adsorbed species, but also the catalyst, the surface (facet), the coverage density (concentration), orientation, and other specifics

Pt(cr)



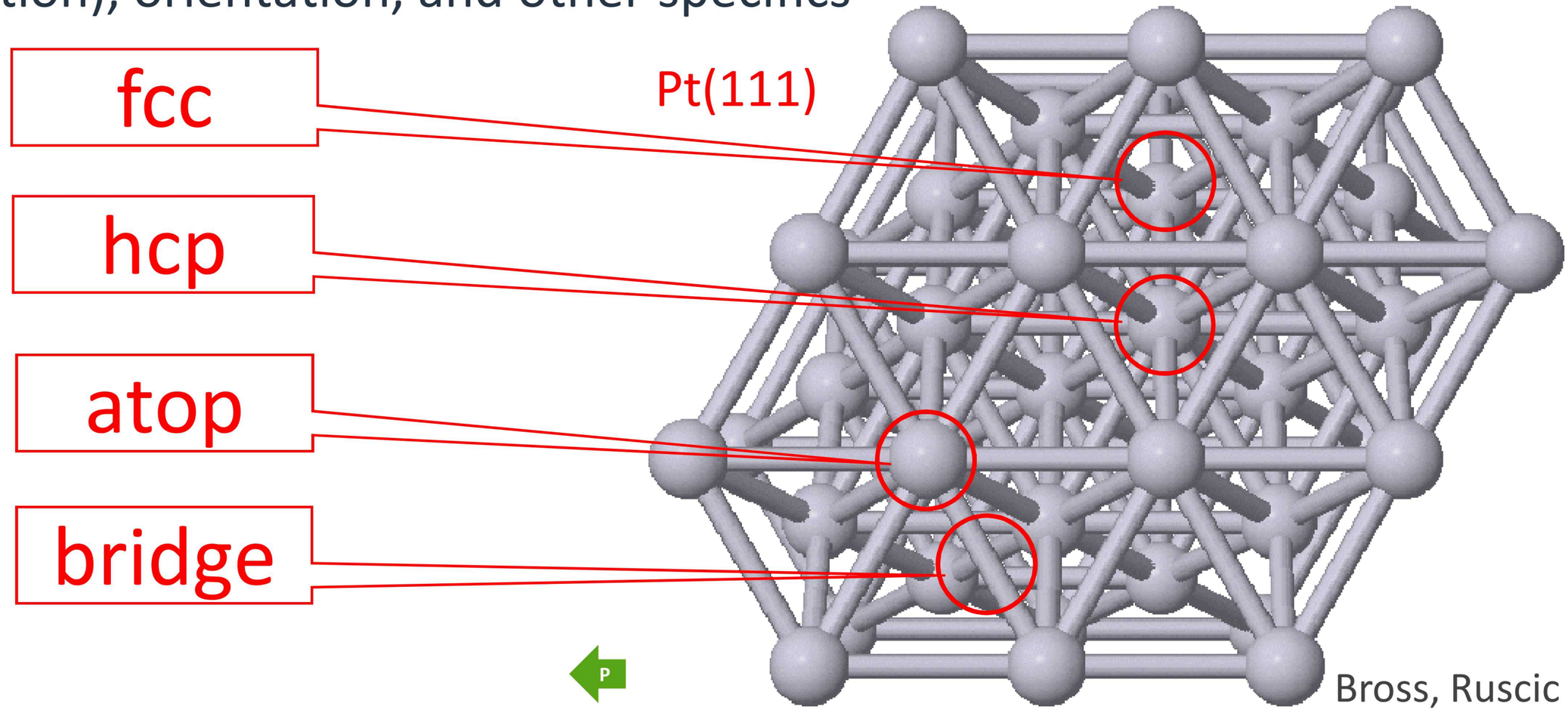
Pt(111)



Bross, Ruscic

Adsorbates Thermochemistry

- Adsorbate species systematics must distinguish not only the adsorbed species, but also the catalyst, the surface (facet), the coverage density (concentration), orientation, and other specifics

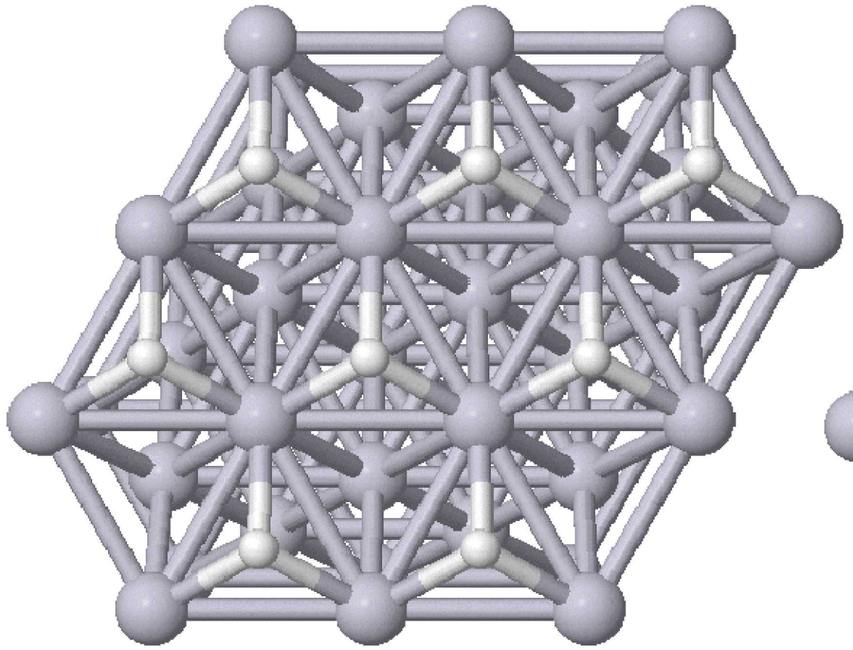


Bross, Ruscic

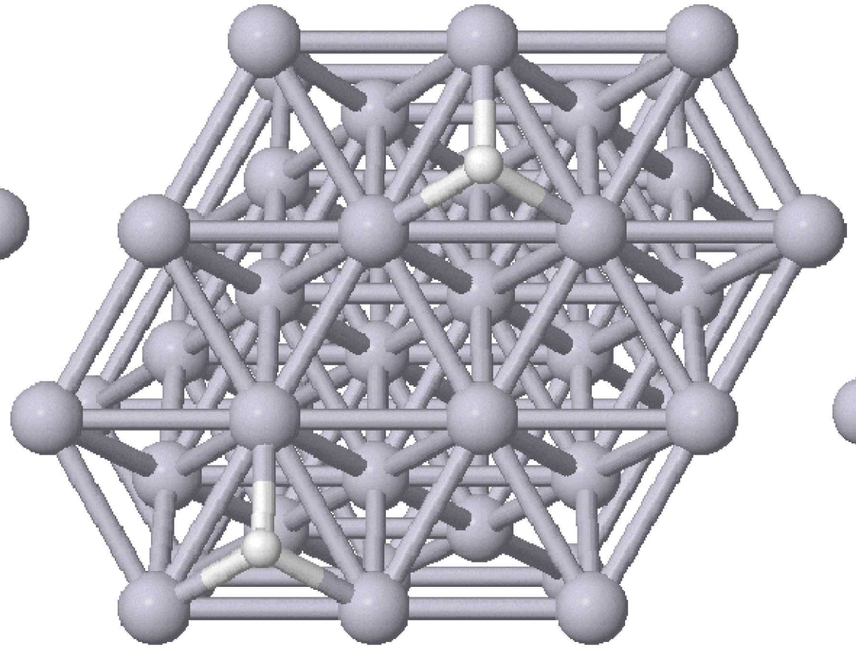
Adsorbates Thermochemistry

- ATcT systematics for adsorbates follows, with additional expansion, previously successfully validated logistics of aqueous thermochemistry:

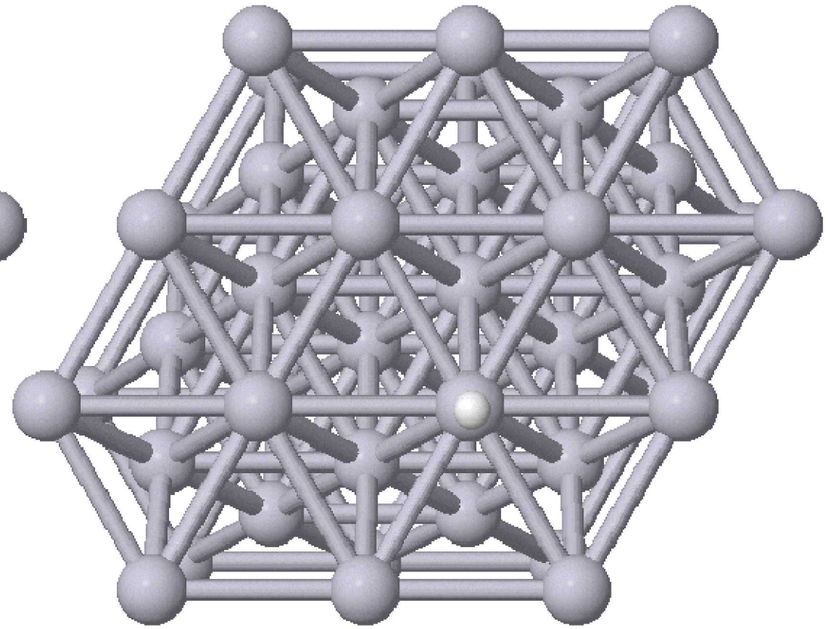
12385-13-6*1001001
H (ad, 1 Pt(111) fcc)
H-atom on Pt(111) fcc, 1:1



12385-13-6*1001004
H (ad, 4 Pt(111) fcc)
H-atom on Pt(111) fcc, 1:4



12385-13-6*1002000
H (ad, Pt(111) atop)
H-atom on Pt(111) atop, 1:inf.



etc.

Bross, Ruscic

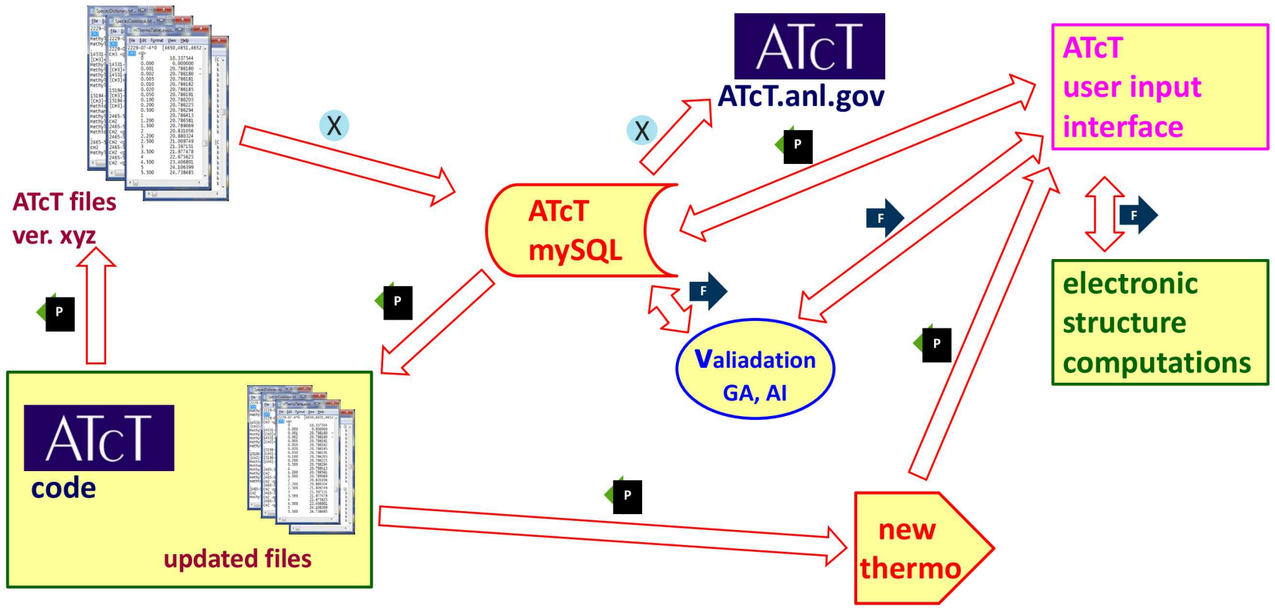
Adsorbates Thermochemistry

- A test TN for Pt and H (ad, x Pt(111) yyy) has been constructed, statistically analyzed, and solved as a local network (22 species, 75 reactions, 3 terminators).
- Once the new ATcT adsorbate systematics, the H (ad, Pt(111)) TN, and the assigned partition functions were successfully tested, they were added to the main ATcT TN

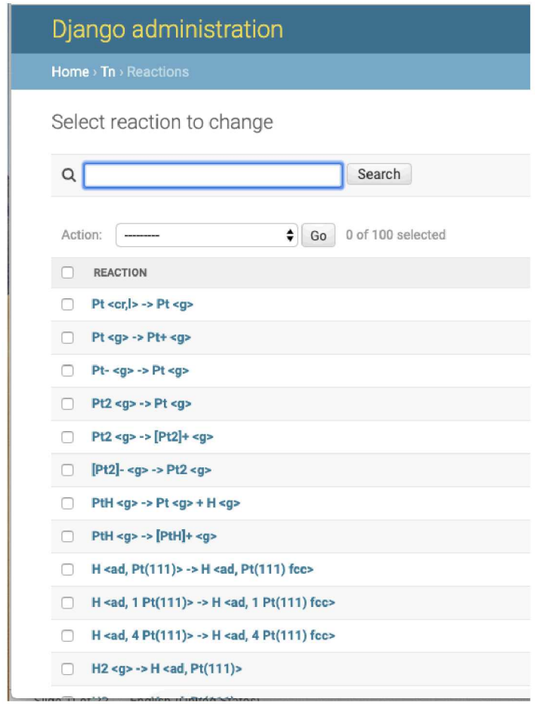
							0.000070	6*1002004
Hydrogen atom	H (ad, 1 Pt(111) fcc)	H	-22.2	-25.5	± 1.6	kJ/mol	1.007940 ± 0.000070	12385-13-6*1001001
Hydrogen atom	H (ad, 4 Pt(111) fcc)	H	-33.3	-36.6	± 1.6	kJ/mol	1.007940 ± 0.000070	12385-13-6*1001004
Hydrogen atom	H (ad, 1 Pt(111) hcp)	H	-16.9	-20.1	± 5.3	kJ/mol	1.007940 ± 0.000070	12385-13-6*1003001
Hydrogen atom	H (ad, 1 Pt(111) bridge)	H	-14.0	-16.9	± 8.8	kJ/mol	1.007940 ± 0.000070	12385-13-6*1004001
Hydrogen atom	H (ad, 4 Pt(111) hcp)	H	-30.2	-33.3	± 7.4	kJ/mol	1.007940 ± 0.000070	12385-13-6*1003004
Hydrogen atom	H (ad, 4 Pt(111) bridge)	H	-28.2	-31.0	± 7.9	kJ/mol	1.007940 ± 0.000070	12385-13-6*1004004
Hydrogen atom	H (ad, Pt(111))	H	-36.9	-38.6	± 1.2	kJ/mol	1.007940 ± 0.000070	12385-13-6*1000000
Hydrogen atom	H (ad, 1 Pt(111))	H	-22.2	-23.9	± 1.6	kJ/mol	1.007940 ± 0.000070	12385-13-6*1000001
Hydrogen atom	H (ad, 4 Pt(111))	H	-33.3	-35.0	± 1.6	kJ/mol	1.007940 ± 0.000070	12385-13-6*1000004
Hydrogen atom	H (ad, Pt(111) fcc)	H	-36.9	-40.2	± 1.2	kJ/mol	1.007940 ± 0.000070	12385-13-6*1001000

- Future Work: Include remaining adsorbates on Pt(111)

Opening ATcT to contributions from the world



Beta Django interface:
https://atct.anl.gov/thermo_ecc_review/admin/
username
DOE_Reviewer2019,
password
ECC_Reviewer_September

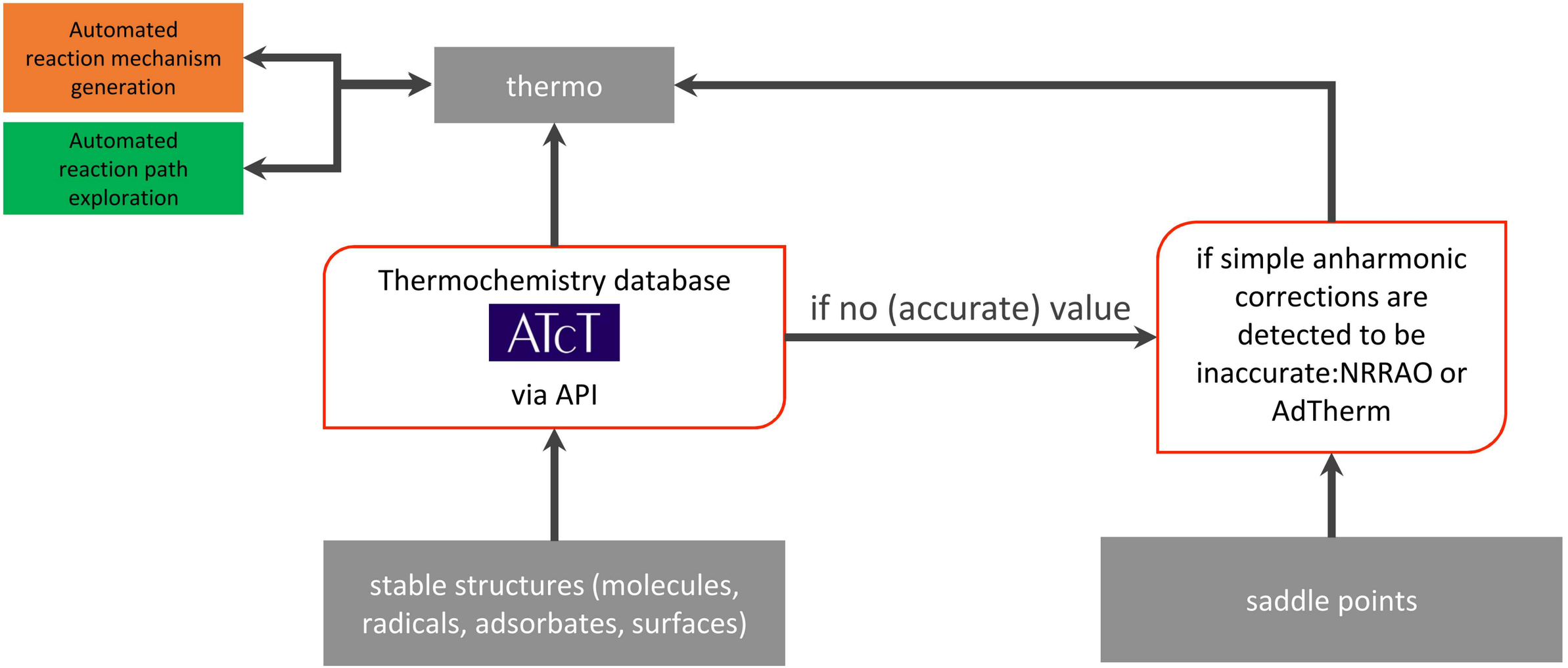


- We developed a Django Interface that allows selecting an ATcT version and species.
- A version can then be modified as desired
- It can then be run through ATcT to get new thermochemistry

Currently works through server scripts that directly interface with the Django sever. In the remainder of the award period we will work to refine this interface, create tools that guide users through interactive experience, and help validate data.

Bross, Ruscic

Advanced thermochemistry



Motivation for improving partition functions in ATcT by including anharmonic terms

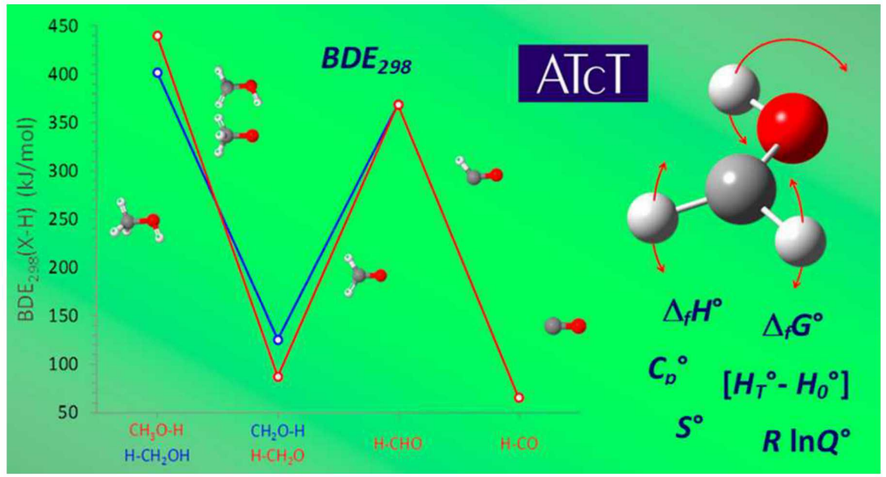
- ATcT publicly released database (1.122e) contains 1604 species.
- Most of these do not have anharmonic Q
- Anharmonic effects are a major source of potential errors where comparing data across a wide range of temperatures, and can have especially large impacts on entropies, causing disagreements between computed and experimental results.

Large Amplitude Motions

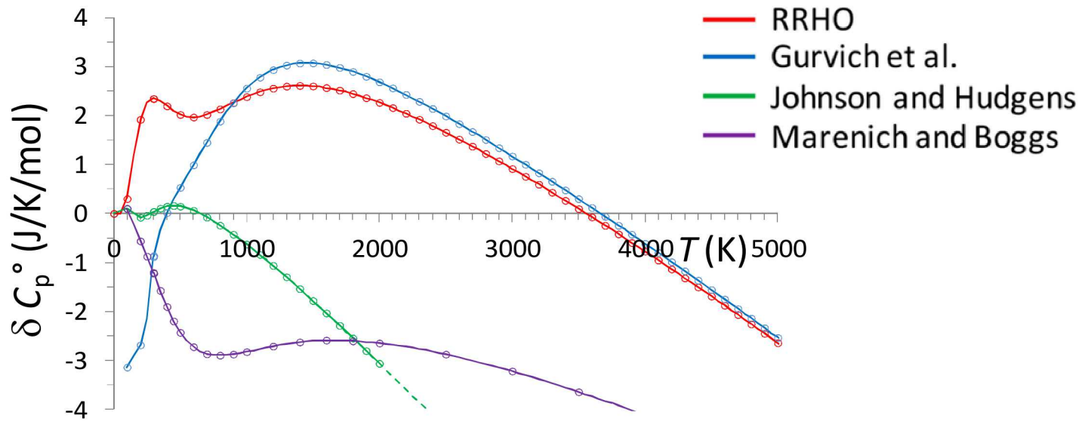
Goal

Develop an approach that enables routinely going beyond RRHO by computing partition functions that include anharmonic effects, crucial for accurate thermochemistry.

- We are creating reference *Q* for 60 small molecules, based on results for CH_2OH



CH_2OH, difference between our partition function and prior work



We are using Woolley's VPT2 method

CH_2OH: Bross, D. H.; Yu, H.-G.;Harding L. B.; Ruscic, B.; *J. Phys. Chem. A* **2019**.
set of 60 ongoing: Bross, Ruscic, Stanton, Phipps, Harding, and Changala

Plan: Use similar approaches for the calculation of partition functions of **adsorbates on surfaces**

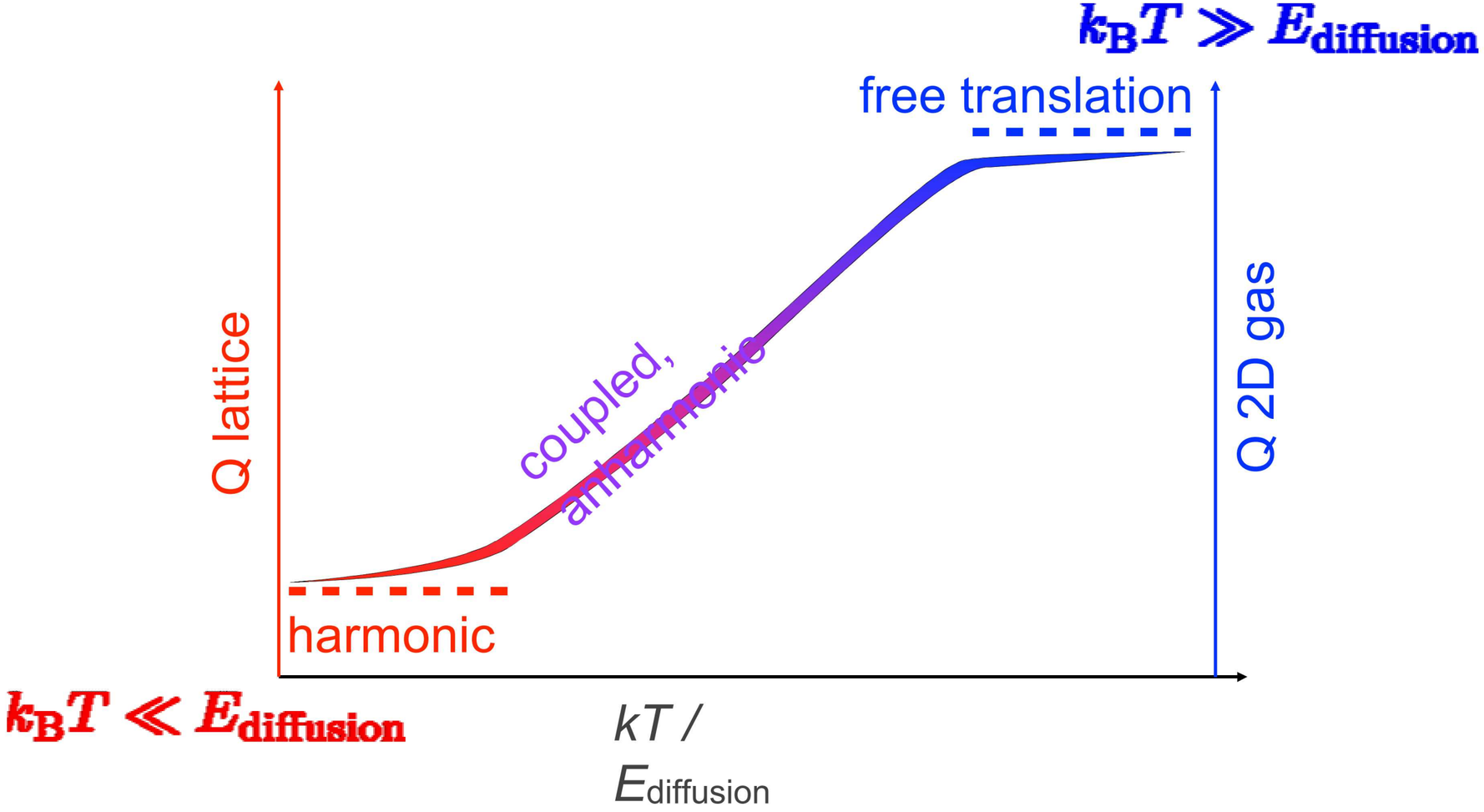
Bross, Ruscic, Phipps

Large Amplitude Motions

- Accomplishments P
  - We have developed approaches to include anharmonic effects based on Woolley's VPT2 method.
  - Using reduced dimensionality approaches for Large Amplitude Motion vibrations we quantitatively reproduced full QM result.

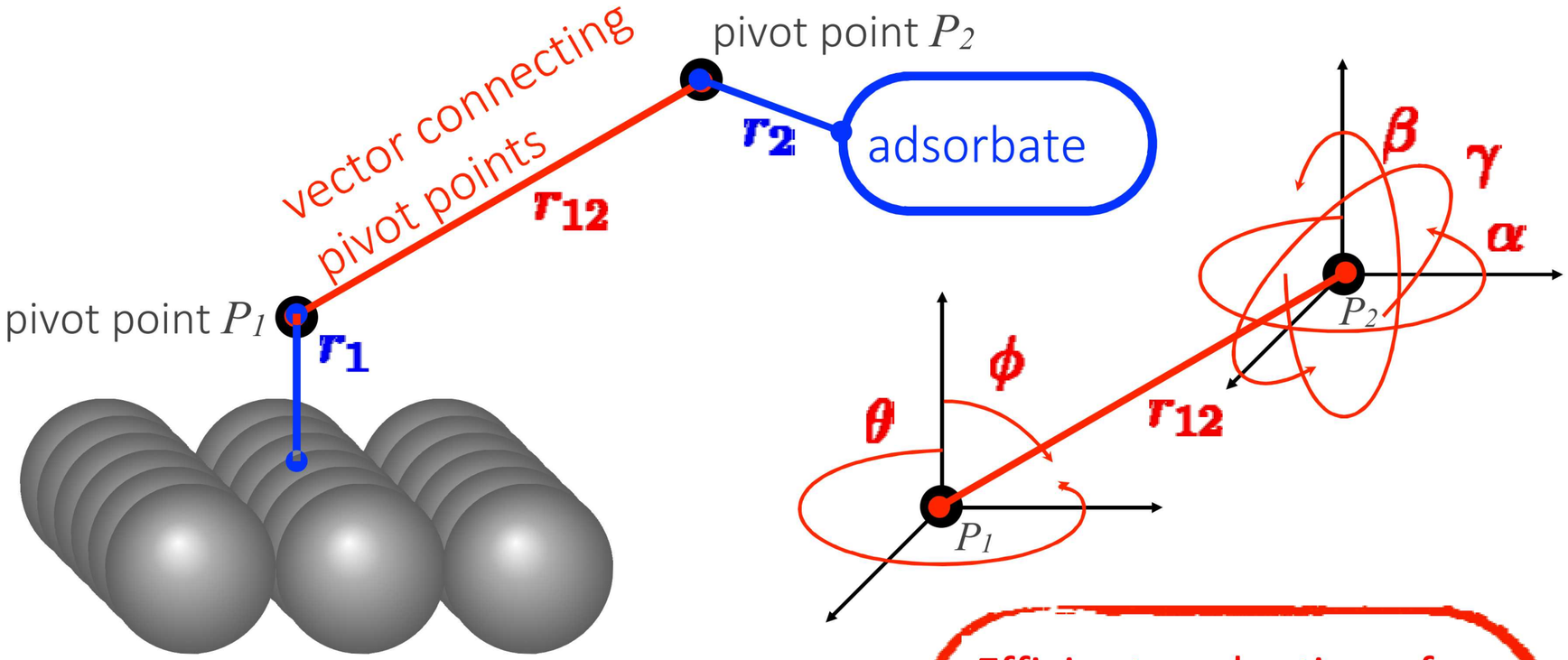
- Ongoing and Future Work F
  - Finish testing and release our code called NRRAO
  - Develop and use analogous approaches to benchmark AdTherm approach to adsorbate partition functions.

Most current mechanisms use one of two limits for adsorbate partition functions



Goldsmith

AdTherm: We will use Monte Carlo Phase Space integrals for the motion of the adsorbate relative to the surface



$$q\,(T,) \approx q_{\text{internal}}\,(T)\,q_{\text{relative}}\,(T)$$

$$q_{\text{relative}}\,(T) = \frac{1}{h^6}\iint e^{-\mathbf{H}(\mathbf{p},\mathbf{q})/kT}\,d\mathbf{p}\,d\mathbf{q}$$

$$\propto \int_{R^-}^{R^+}\int_0^{\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} e^{-V(\mathbf{q})/kT} r^2 \sin\phi\,d\theta\,d\phi\,d\alpha\,d\beta\,d\gamma\,dr$$

Efficient evaluation of integral requires machine learning

AdTherm

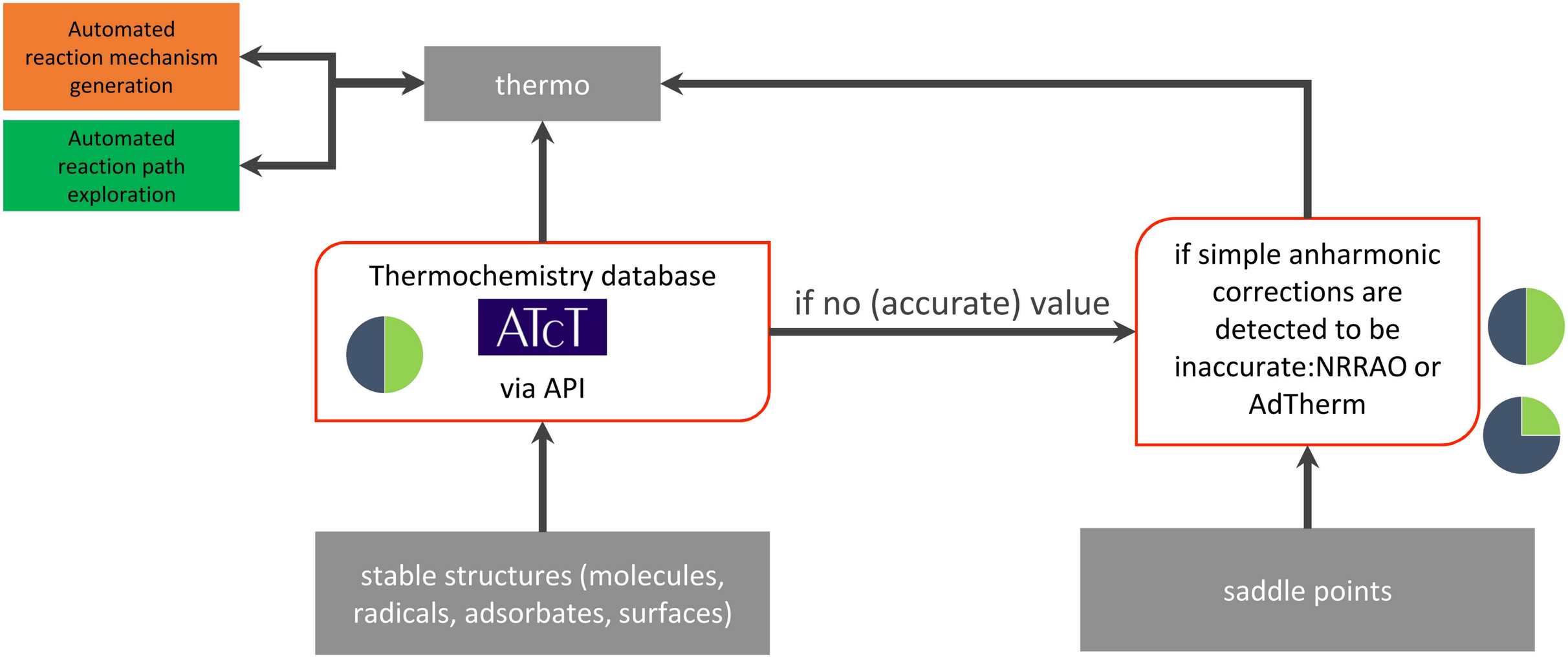
Ongoing work:

1. Testing the system for simple analytical potentials
2. Set up Sobol sequence for training data
3. Interfacing with Amp for training neural network

Future work:

1. Test the full method with DFT
2. Compare with other anharmonic methods
3. Implement in ASE
4. Update thermo database

Advanced thermochemistry



Software inventory

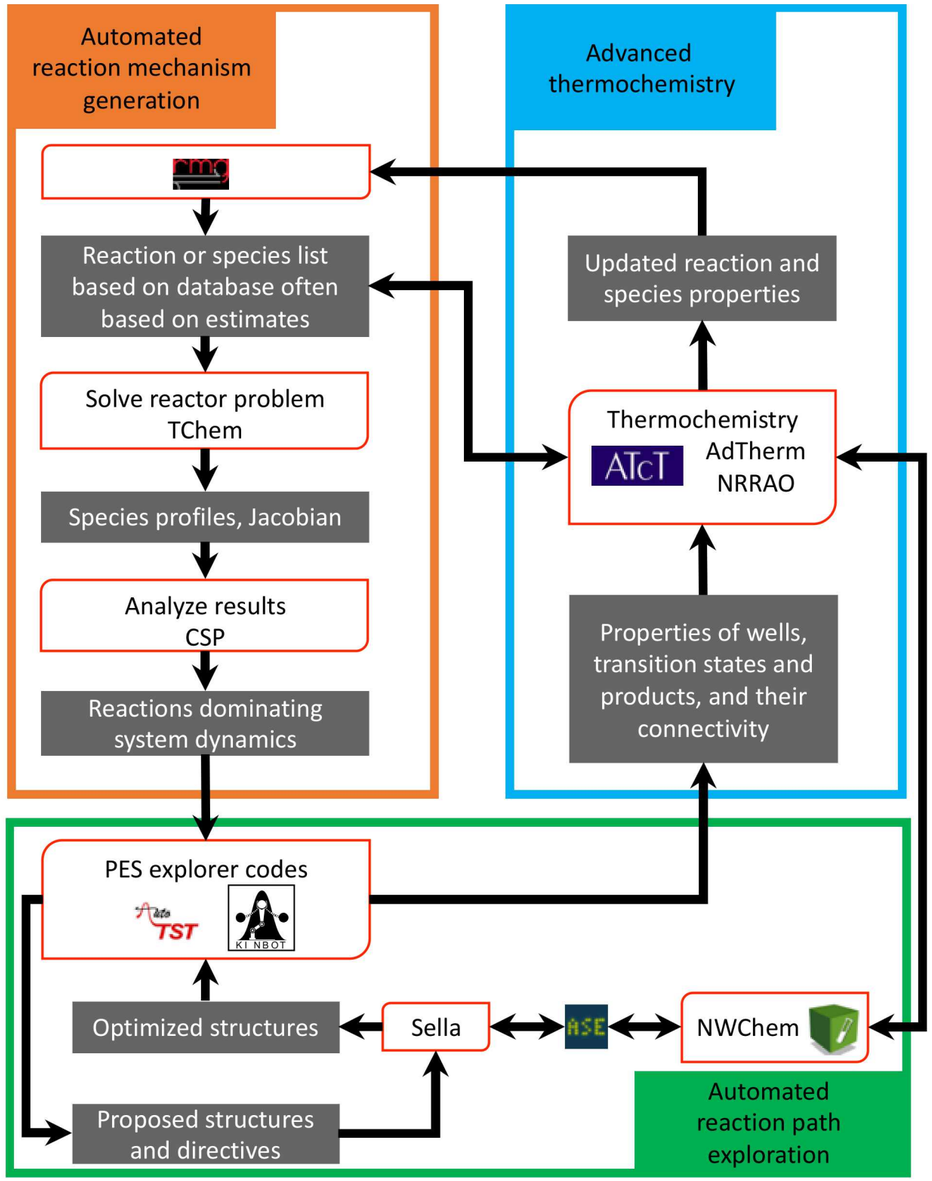
KinBot
AutoTST
Sella
NWChem
Arrows

RMG
TChem
CSP

ATcT
NRRAO
AdTherm

see also at https://ccs-psi.org/awards

Summary



On track to achieve our integrated goal:
Generate microkinetic models automatically for catalytic systems with coupled gas-phase and heterogeneous chemistry.

Codes have been developed and improved, most of the **interfaces** are established, and where applicable, we have upgraded our codes for **heterogeneous many-core architectures.**

We have made good progress in including **catalysis-specific aspects** in our originally gas-phase only software.

We also adapted our **web-based technologies**, ATcT and Arrows for a broader user base and for catalysis.

We have released one completely new code under this program (Sella), others are nearing release (CSP, NRRAO), in addition to the significant additions to the existing codebase.