A priori modeling of chemical reactions on a Grid based virtual laboratory

Towards standard representations of data for molecular chemistry

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A + BC reactions

qGEMS, the wflow

Data models

H + H_2, testcase

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The $N + N_2$ thermal rate coefficients

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Modeling chemistry

Simulating processes on a molecular basis

- modeling natural phenomena
- designing new materials
- mastering new technologies

. . . requires

- assembling various pieces of software
- converging different competences
- a world spread virtual laboratory

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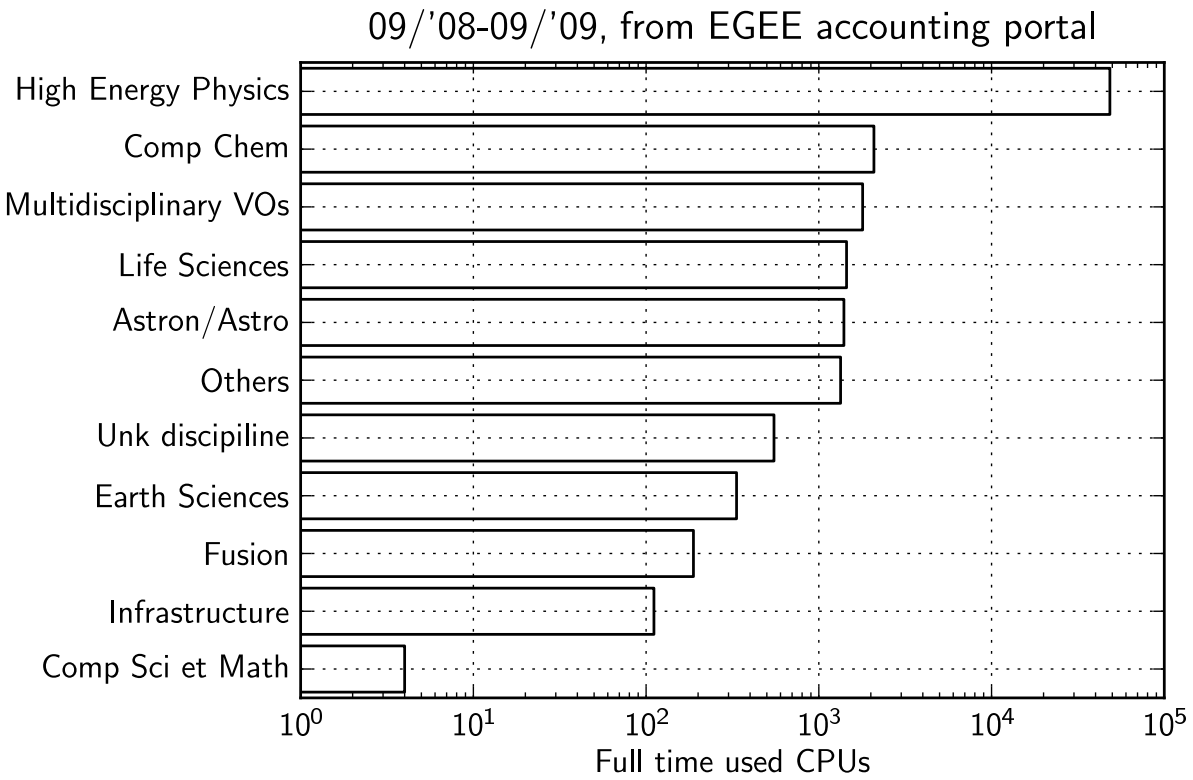
. . . on the Grid:

A self-introducing picture



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The Grid Enabled Molecular Simulator

GEMS is

A grid based realistic simulator that can act as a molecular science engine in complex multiscale chemical contexts.

The recipe

- software: a suite of codes
- interoperability: standards and tools
- a director: workflow management
- a factory: Grid, the modern paradigm of HTC

Let's start with a few atoms...

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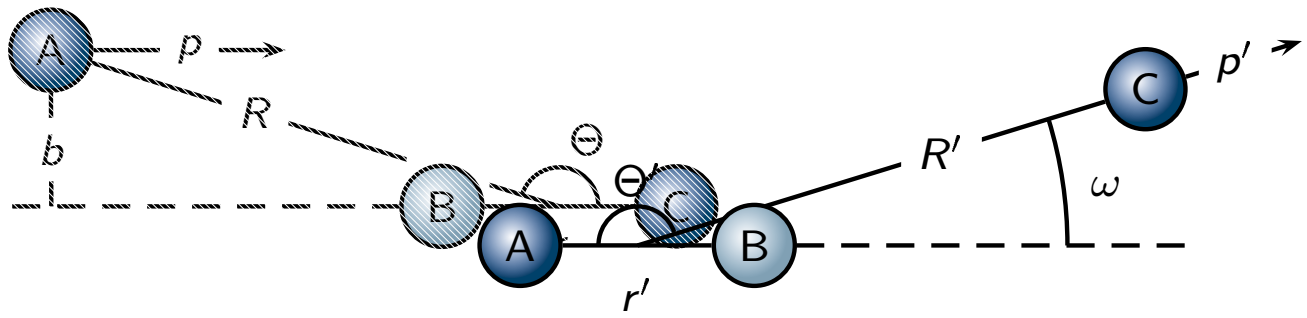
A + BC, the quantum view

A reactive collision

$$A + BC\ (v,j) \rightarrow AB\ (v',j') + C$$



The B-O "equation of motion"

$$i\hbar\frac{\partial\psi(\boldsymbol{\xi},t)}{\partial t} = \left[\hat{T}_{\boldsymbol{\xi}} + V(\boldsymbol{\xi})\right]\psi(\boldsymbol{\xi},t)$$

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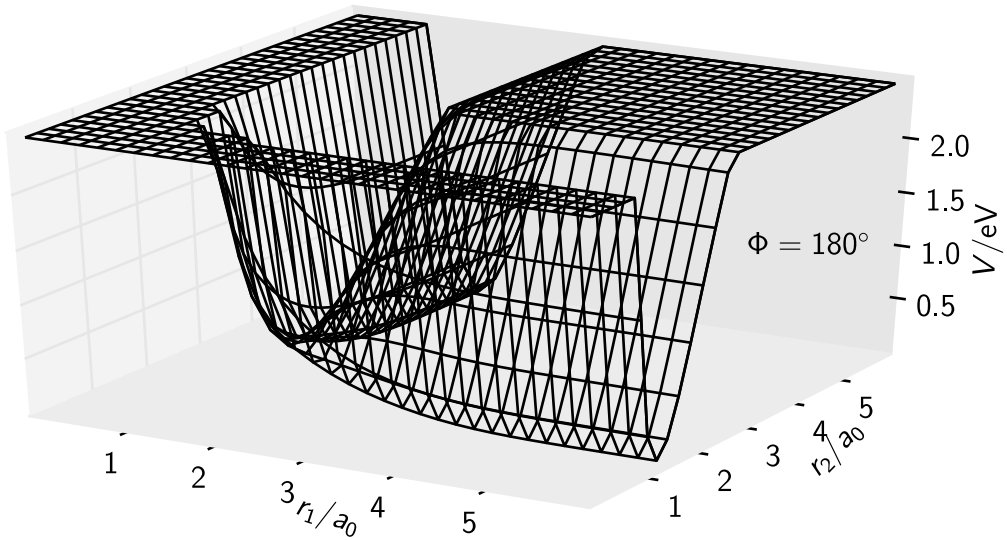
A + BC, potential energy surface

$$V(\boldsymbol{\xi}) = f(\boldsymbol{\xi}; \mathbf{c})$$

$\mathbf{c}$, a set of parameters

determined by fitting a set of ab initio energies



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A + BC, solution methods

If $\hat{H} \neq f(t)$, then either (TD methods)

$$\psi(\boldsymbol{\xi}, t+\tau) = e^{-\frac{i\hat{H}\tau}{\hbar}}\psi(\boldsymbol{\xi}, t)$$

Or simply (TI methods)

$$\hat{H}\psi(\boldsymbol{\xi}) = E\psi(\boldsymbol{\xi})$$

From an analysis on ψ

The detailed scattering matrix elements $S^{J}_{cv'j'k',avjk}(E)$

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Relevant quantities

From the state to state **S** elements

- detailed reaction probabilities
- state to state differential cross sections
- integral cross sections

Further elaborating...

- branching ratios
- product internal energy distributions
- microscopic branching
- reaction rates

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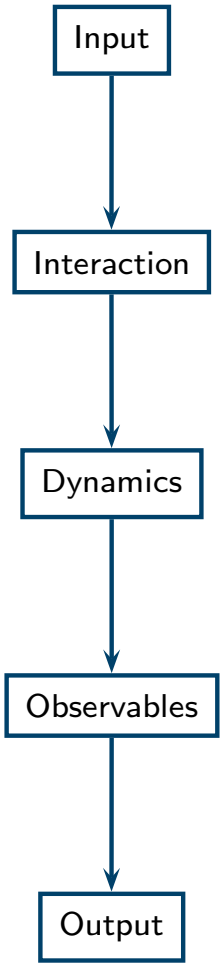

Interaction

- evaluate $V(\xi)$

Dynamics

- solve the equation of motion

Observables

- average and get observable properties

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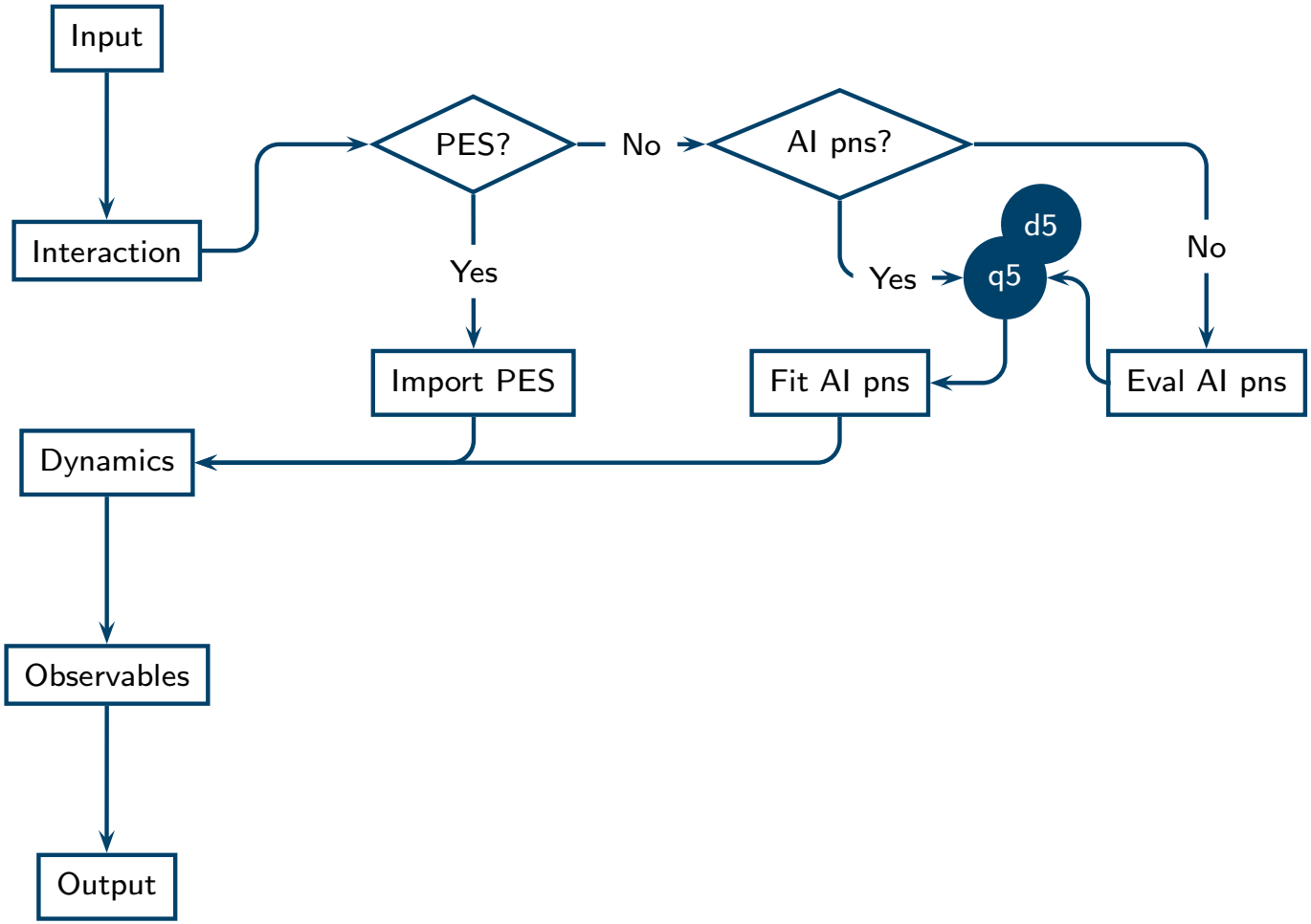
qGEMS, Interaction



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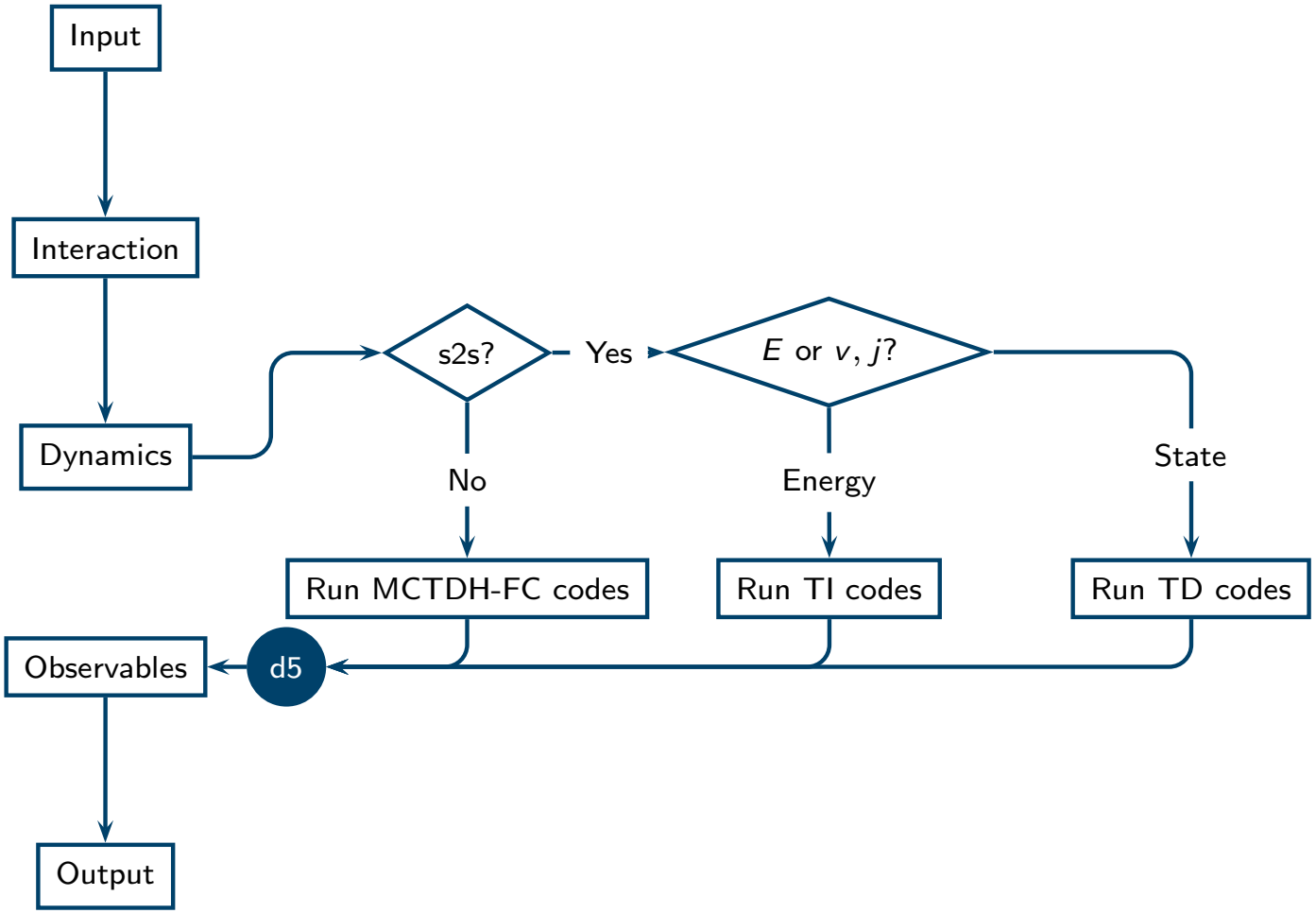
qGEMS, Dynamics



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A standard for Quantum Chemistry

QC formats so far

- legacy formats (GAMESS, DALTON, etc)
- CMLComp (?)
- Q5Cost

Q5Cost, both a library and a data model

- data compression (HDF5)
- portability
- Fortran binding
- partial access

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Q5Cost, library

Overview

- conceived as a high level tool for quantum chemists
- based on HDF5 technology
- provides r/w access to .q5 files

Structure

- Q5Cost: API "speaking" chemistry
- Q5Core: wrapping facilities for HDF5 routines
- Q5Error: error handling

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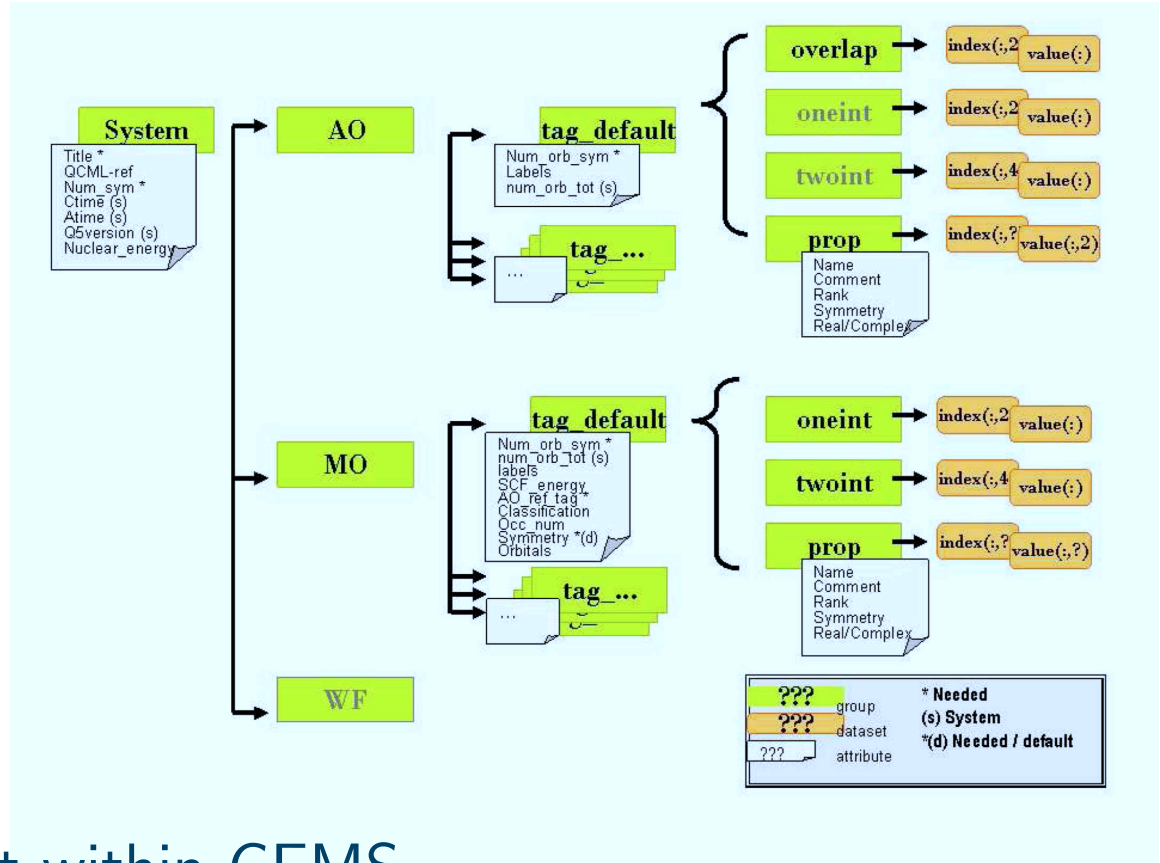
Q5Cost, data model



Q5Cost within GEMS

- a .q5 file stores all QC info, at 1 ξ
- GEMS only needs V, ∇, $\mathbf{H}$; at many ξ's, though!

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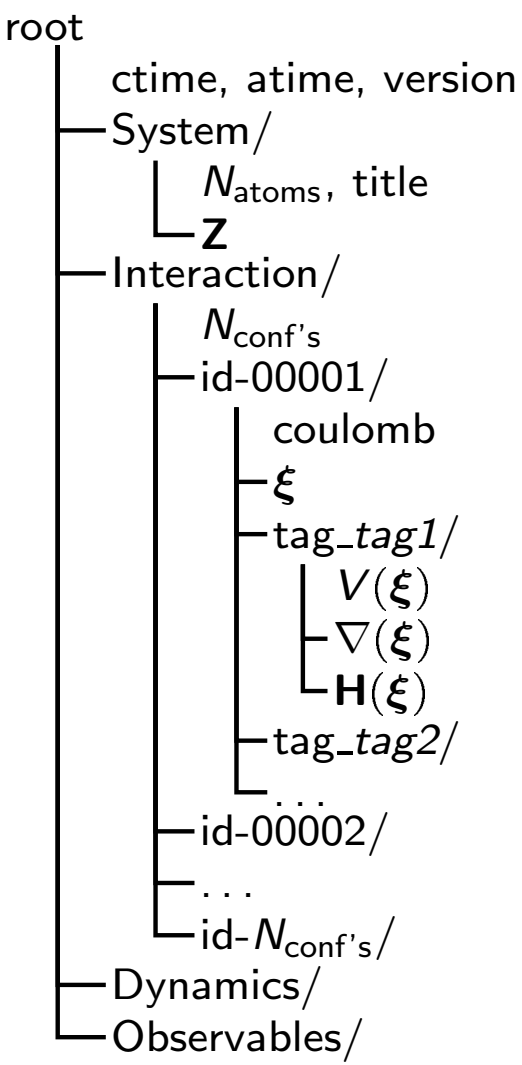
Towards D5Cost



Data model

- only System and Interaction defined at present
- abstracts from 3-body systems

Library

- D5Cost built on top of Q5Core and Q5Error
- provide r/w access to .d5 files

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$H + H_2$, computing details

AI runs (DALTON)

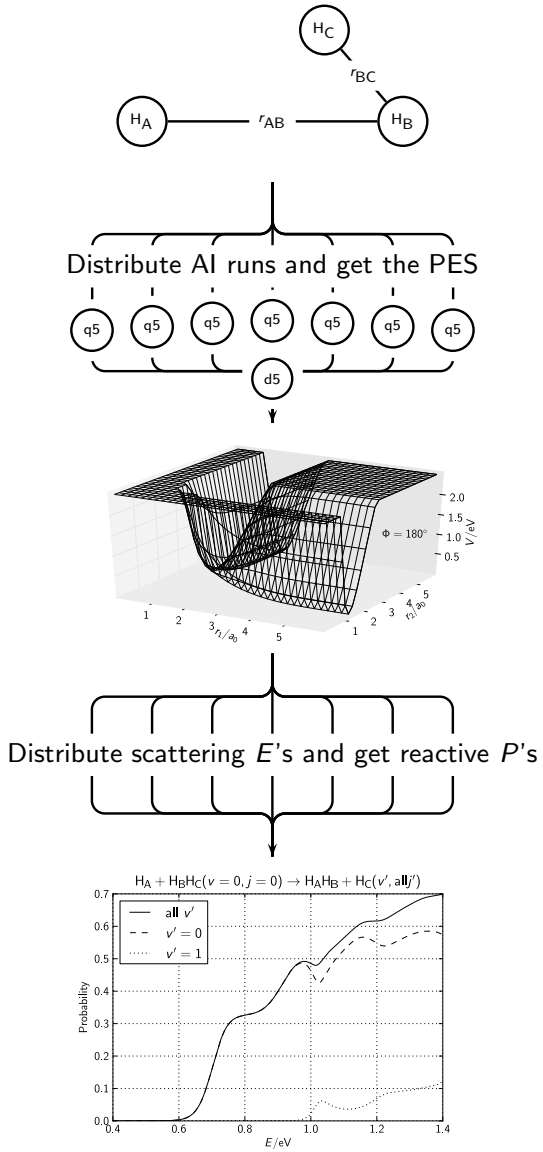
- 23 H_2 and 270 H_3 ξ's
- NEVPT2/cc-pV5Z

Fitting routine (GFIT3C)

- 3C polynomial fit, degree 10
- rms, 0.19 kcal/mol

TI dynamics (ABC)

- 1000 null-J fixed-E runs
- 100 E's per 10 CE's



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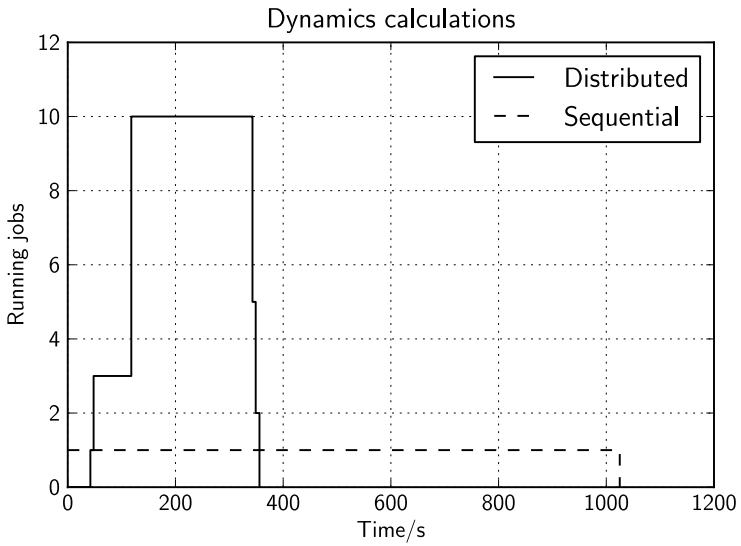
H + H_2, performances

The dynamics: execution time



Heavier systems

- the solid box grows upward
- the dashed box flattens rightward

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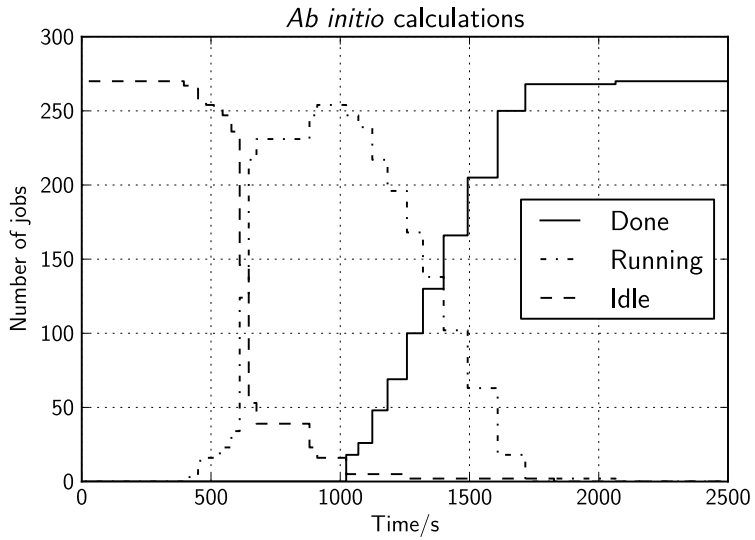
AI runs: over in about 2000 s



Remarks

- sequential execution time over 30000 s !
- besides, computation grain still fine

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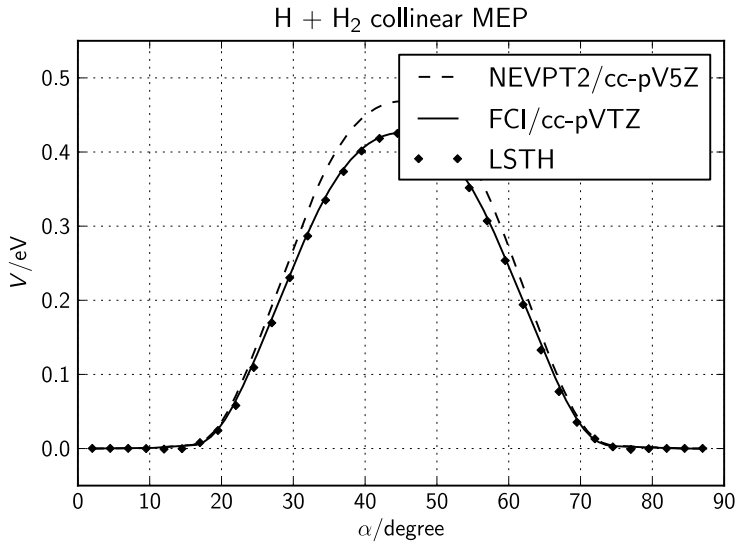
$H + H_2$, accuracy

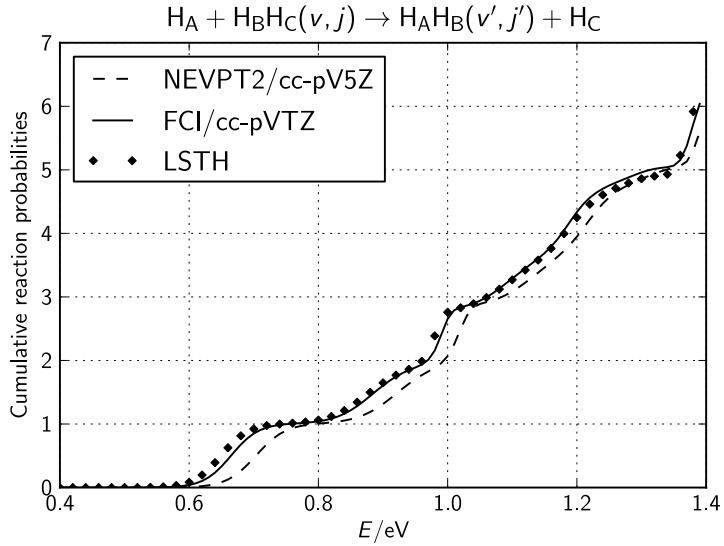
vs accurate LSTH

- same MEP shape
- but shallow VdW's

Global reactivity: $P^{J=0}_{\mathrm{all}v'j',\mathrm{all}vj}$

- same CRP's shape
- — matches ◆'s





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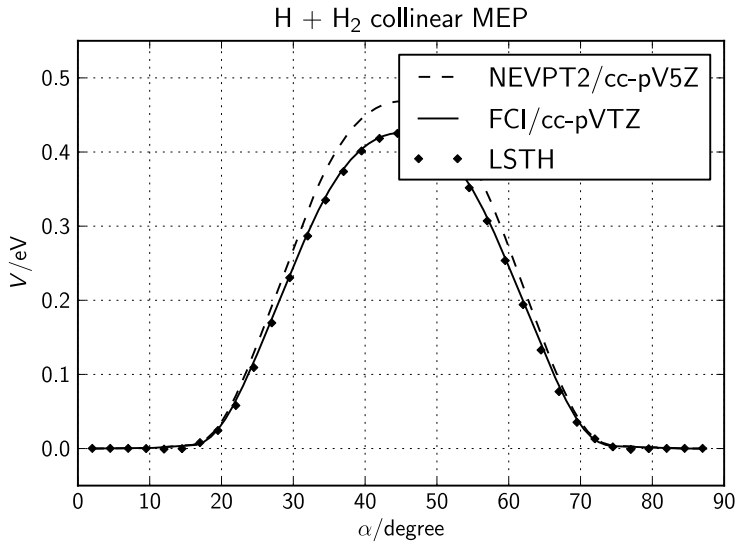
$H + H_2$, accuracy

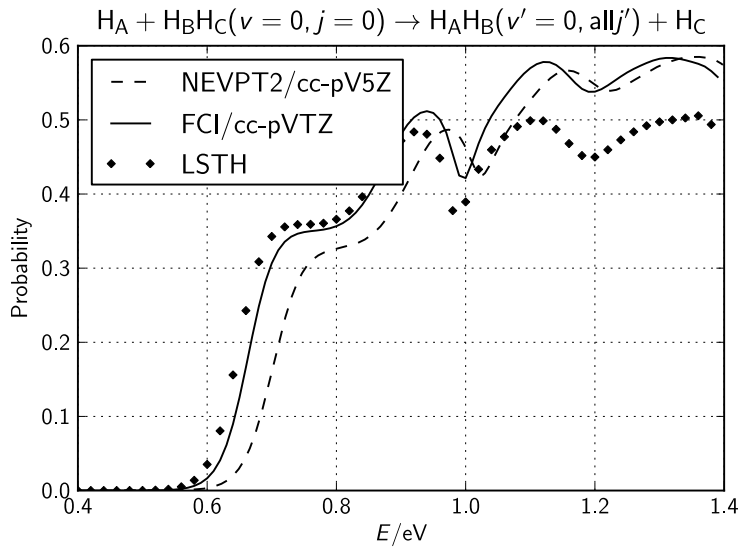
vs accurate LSTH

- same MEP shape
- but shallow VdW's

Detailed reactivity: $P^{J=0}_{0\mathrm{all}j',00}$

- non-ME paths weigh
- or VdWs?





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The ML4LJ PES

J-shifting $k(T)$'s

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The ML4LJ PES

A LAGROBO potential

$$V(\boldsymbol{\xi}) = \sum_{\tau=1}^{3} w(\Phi_\tau)\, V_\tau(\rho_\tau, \alpha_\tau, \Phi_\tau; \mathbf{c})$$

Short range

- bent (about 120°) and structured MEP
- shallow well (1.45 eV) flanked by 2 saddles (1.60 eV)

Long range

- Improved Lennard-Jones attractive tail added

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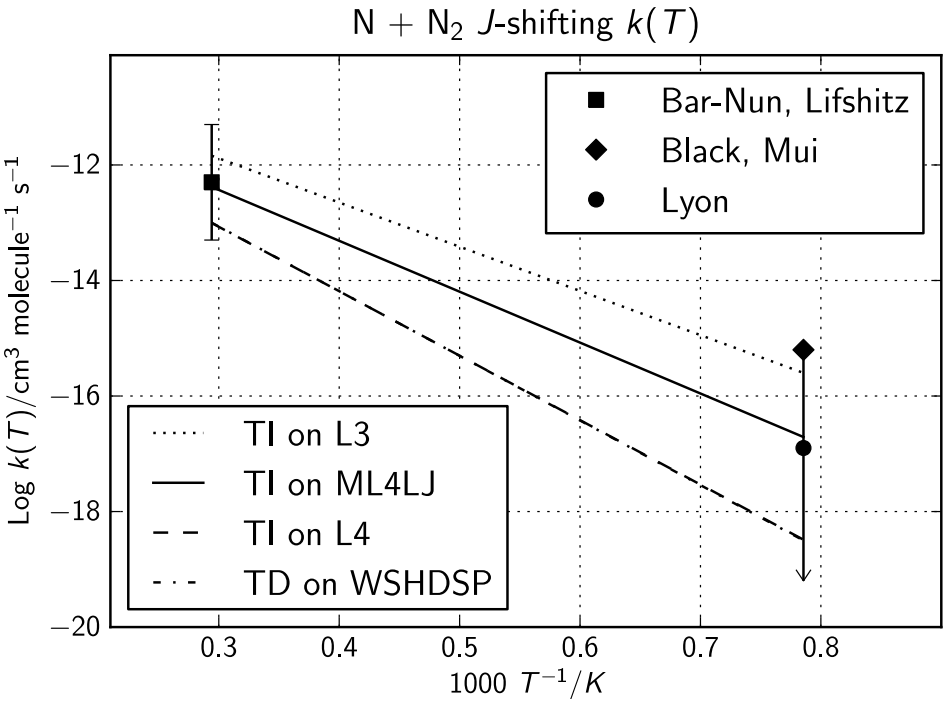

A comparison with the experiment

- best agreement with the available data
- L3, L4 and WSHDSP differ orders of magnitude

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- A Laganà
  Towards a grid based universal molecular simulator, in
  A Laganà, G Lendvay Eds "Theory of the dynamics of elementary chemical reactions", 363-380 (Kluwer, 2004)
- C Angeli, G L Bendazzoli, S Borini, R Cimiraglia, A Emeerson, S Evangelisti, D Maynau, A Monari, E Rossi, J Sanchez-Marin, P G Szalay, A Tajti
  The problem of interoperability: a common data format for Quantum Chemistry codes
  Int J Quantum Chem 107, 2082-2091 (2007)
- S Rampino, A Monari, S Evangelisti, E Rossi, K Ruud, A Laganà
  A priori modeling of chiemical reactions on a Grid based virtual laboratory
  Proceedings of the Cracow Grid Workshop CGW09 (2009)
- S Rampino, F Pirani, E Garcia, A Laganà
  A study of the impact of long range interactions on the reactivity of N + N_2 using the Grid Empowered Molecular Simulator GEMS

  Int J Web Grid Serv, in press (2010)