Enabling Grids for E-science in Europe

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Grid implemented quantum versus semiclassical evaluation of thermal rate coefficients

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Summary

- Thermal rate coefficient
- Quantum and Semiclassical approach
- Grid implementation of the codes and results
- Conclusions

Thermal rate coefficient

The computation of thermal rate values can be of great use in several realistic multiscale simulations of complex systems.

By definition the thermal rate coefficient k(T) can be formulated as the thermal average of the cumulative reaction probability, N(E):

$$k(T) = \frac{1}{hQ_r(T)} \int_{-\infty}^{\infty} \mathrm{d}E e^{-E/k_B T} N(E)$$

1-Quantum approach

The direct evaluation of k(T) is based on the following formulation of thermal rate coefficients

$$k(T) = \frac{1}{hQ_r(T)} \int_0^\infty dt C_f(t)$$

C_f (t) is the flux correlation function that can be calculated in terms of the flux operator F and of the Hamiltonian operator $\hat{H}$ as follows

$$C_f(t) = tr[\hat{F} e^{i(\hat{H}t + i\beta\hat{H}/2)} \hat{F} e^{-i(\hat{H}t + i\beta\hat{H}/2)}]$$

C_f (t) allows a direct calculation of the cumulative reaction probability, N(E)

Quantum approach

The quantum mechanical code is articulated in a sequence of consecutive steps

-Step 1 (Grid-FLUSS)

Diagonalization of the thermal flux operator, F
Krylov basis functions generations

-Step 2 (Grid-MultiConfigurationalTimeDependentHartree)

propagation in time of Krylov basis functions

-Step 3

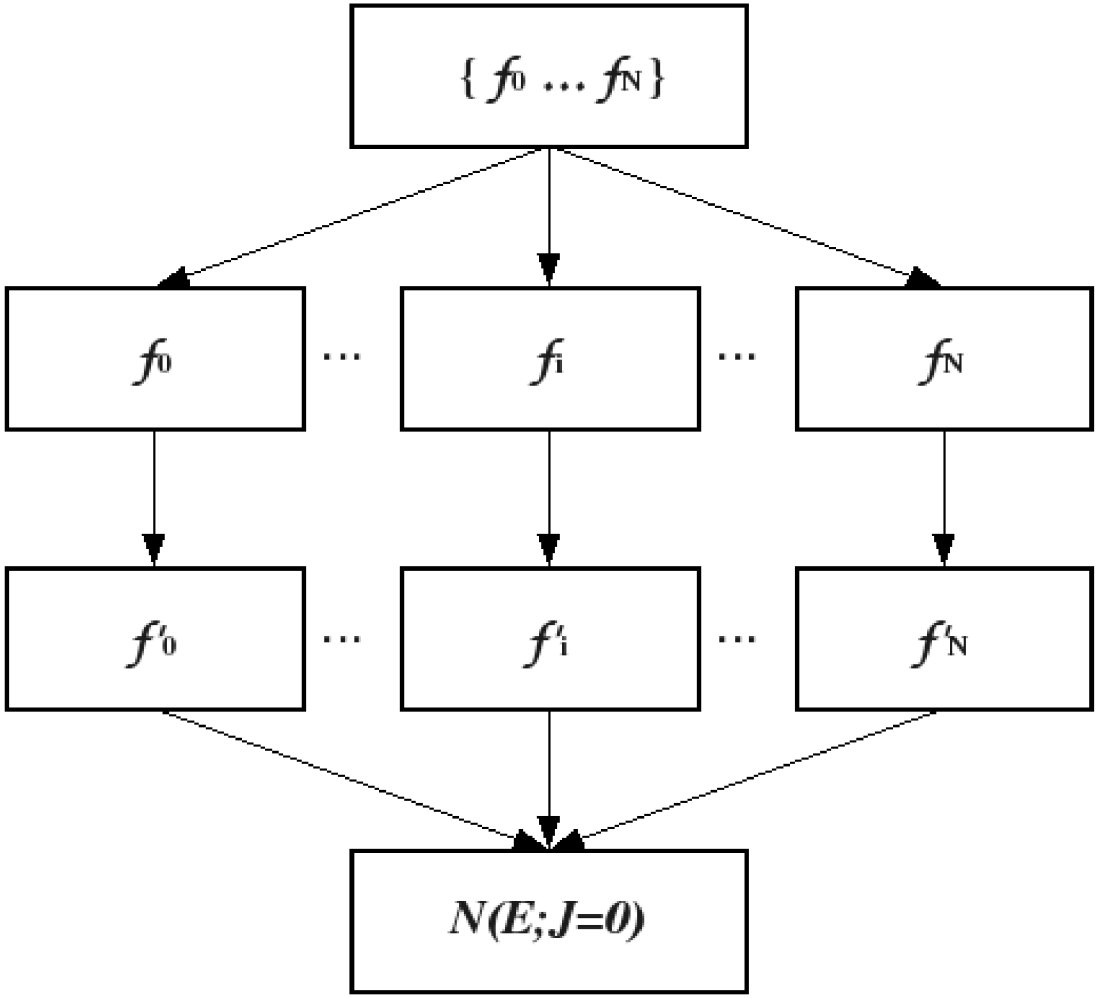
calculation of cumulative reaction probability, N(E)

Quantum approach

Step 1

Step 2

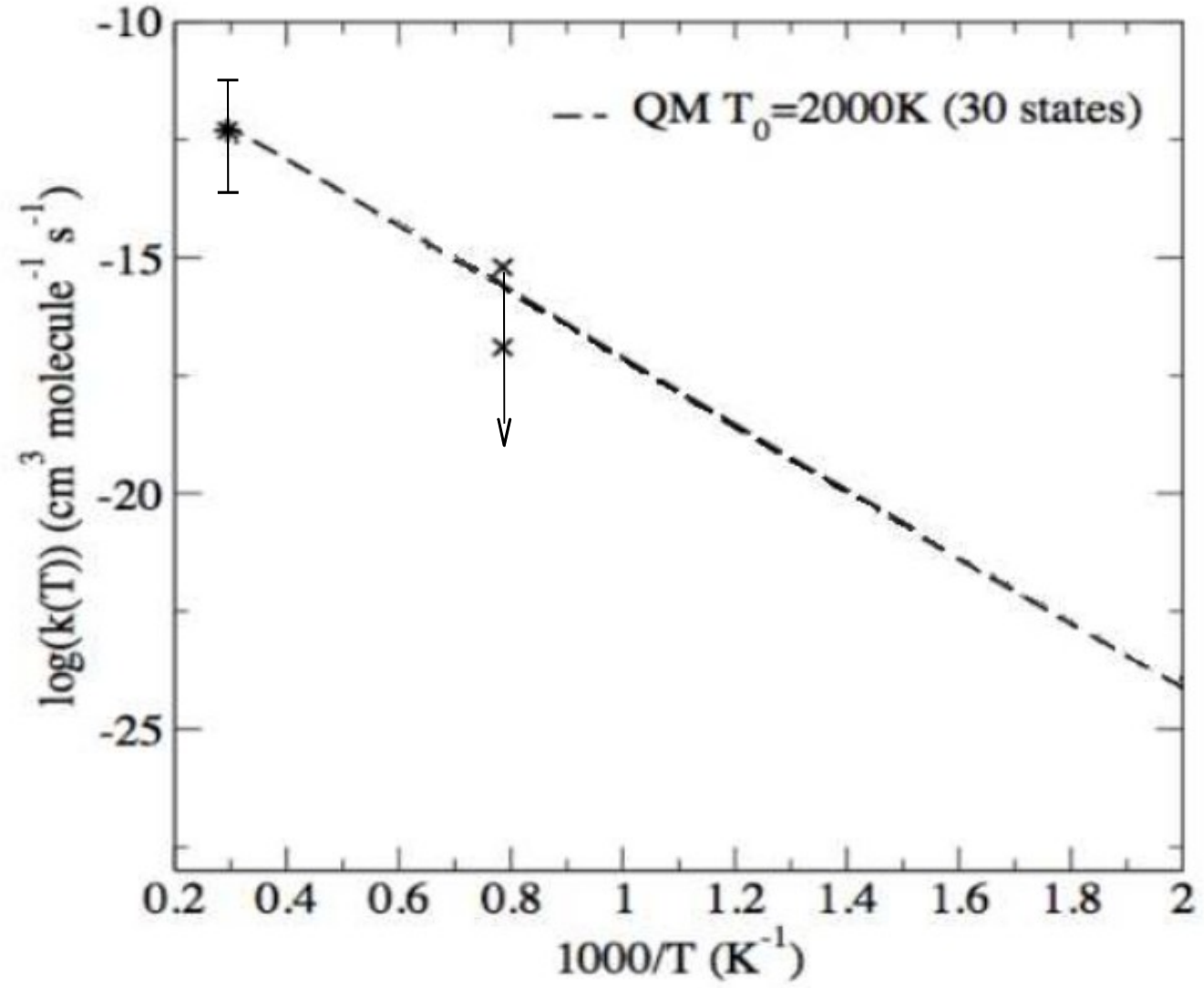
Step 3



Grid-Fluss

Grid-MCTHD

Results ($N+N_2$ reaction)



Grid implementation

-The porting of the quantum codes onto the Grid environment performed by making use of the User Interface (UI) machine available in COMPCHEM

-provide standalone library-independent F77 version

Problems

-large binary file containing the thermal flux eigenfunctions

-distribution of the eigenstates (eigenfunctions) for time propagation

-manage the database generated by the two codes

Grid implementation

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Solutions

-Use the SE available for COMPCHEM via lcg- commands
-not impose limitations on the size of the file

- Developed SPLIT to distribute the eigenstates (eigenfunctions) for time propagation

- Developed a set of PHP scripts to manage the database

Grid implementation

JOBNAME: name of directory containing the input files.
JOBTYPE: "1" for `Grid-FLUSS` and "2" for `Grid-MCTDH`.
LAN: eigenfunction being propagated (only applies if JOBTYPE=2).
ISTAT: Seed of the random number generator.
JOBID: JobID provided by the WMS.
JOBSTATUS: integer number defining the Job Status.
CE: Computing Element where the Job is executed.

Jobname	Jobtype	Lan	Istat	JobID	Jobstatus	CE
Basis1	1	1	3	https://prod-lb-01.pd.infn.it:9000/rzqSizfh_Th-e23pGAyfqQ	4	egceaix.frascati.enea.it:2119/jobmanager-lsf-egeeaixshort

Performance

		ns		
		10	20	30
CLUSTER B 1 CPU	flux	0.17	0.31	0.48
	t-prop	13.07	26.20	35.52
EGEE n_s CPU	flux	0.16	0.35	0.5
	⟨t-prop⟩	6.27	5.89	6.15

Time in hours

CLUSTER B: AMD64 Opteron 1,86Ghz, 8GB memory, Cache 1 MB

2-Semiclassical approach

In the semiclassical (SC) approach the flux correlation function is factorized in terms of a "static" C_f (0) and a "dynamical" R_f (t) factor as follows:

$$k(T) = \frac{1}{hQ_r(T)} C_f(0) \int_0^\infty dt R_f(t)$$

Semiclassical approach

$$C_f(0) = \frac{32}{(\hbar\beta)^2}(Q_{rrpp} - Q_{rprp})$$

Q_{rrpp} and Q_{rprp} (where r stands for reactants and p stands for products) are the constrained partition functions

$$R_f(t) \sim \left\langle \frac{\langle \mathbf{q}'_t\mathbf{p}'_t \mid \hat{F}(\beta/2) \| \mathbf{q}_t\mathbf{p}_t \rangle}{\langle \mathbf{q}'_0\mathbf{p}'_0 \mid \hat{F}(\beta/2) \mid \mathbf{q}_0\mathbf{p}_0 \rangle} C_t(\mathbf{q}_0\mathbf{p}_0) C_t^*(\mathbf{q}'_0\mathbf{p}'_0) e^{i[S_t(\mathbf{q}_0\mathbf{p}_0) - S_t(\mathbf{q}'_0\mathbf{p}'_0)]/\hbar} \right\rangle_W$$

$\langle \mathbf{q}'_0\mathbf{p}'_0 \mid \hat{F}(\beta/2) \mid \mathbf{q}_0\mathbf{p}_0 \rangle$ terms are the elements of coherent-state matrix (CSM) of the Boltzmannized (thermal) flux operator

Semiclassical approach

The semiclassical code is articulated in a sequence of consecutive steps

-Step 1

calculation of the Coherent State Matrix elements of the Boltzmannized flux operator

-Step 2

generation of the initial states ($\mathbf{q}_0\ \mathbf{p}_0$; $\mathbf{q}_0'\ \mathbf{p}_0'$) of the pairs of considered trajectories

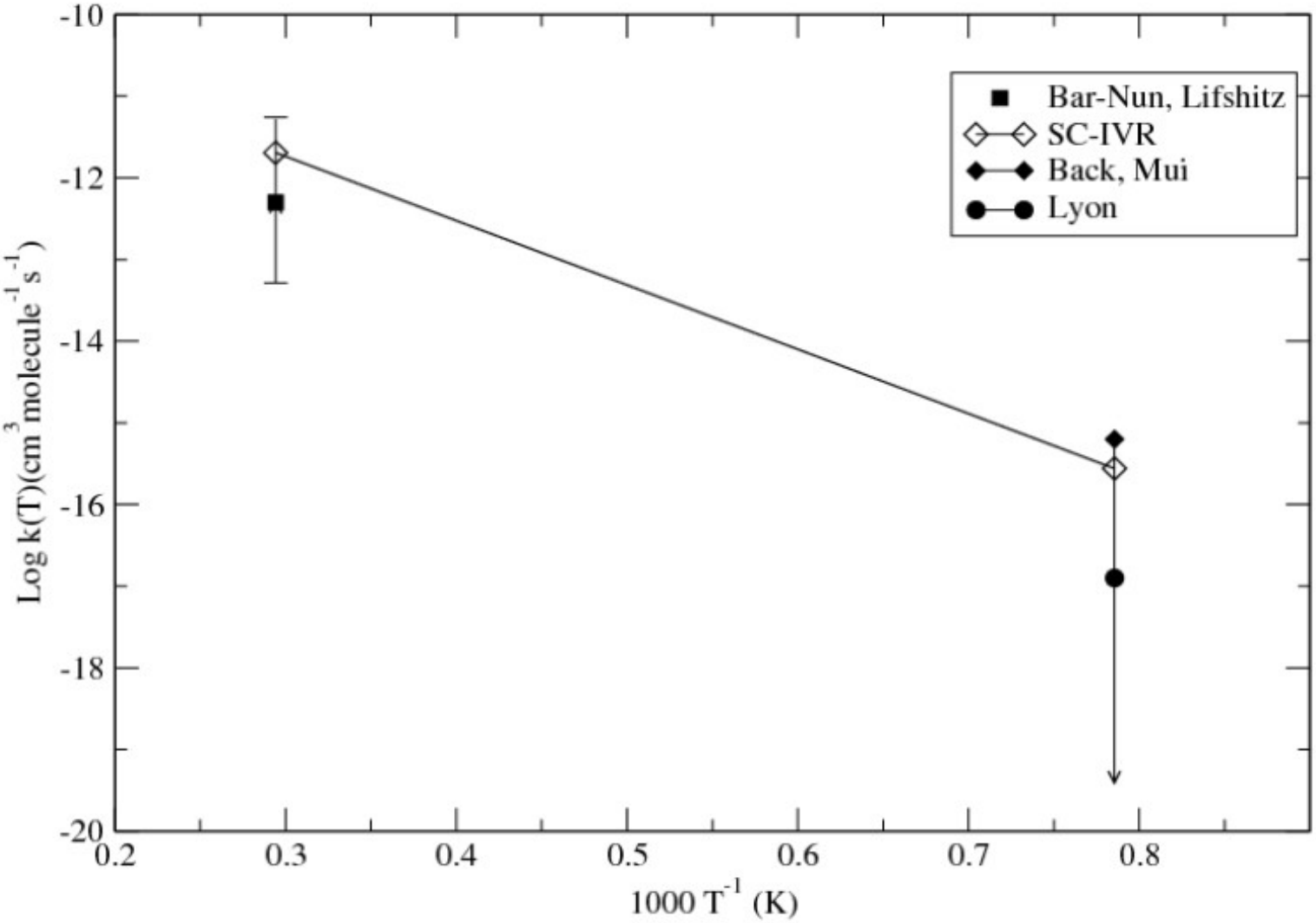
-Step 3

evaluation of the Static factor C_f (0)

-Step 4

calculation of the normalized flux-flux correlation function R_f by performing the integration of a suitable set of trajectories

Results ($N+N_2$ reaction)



Grid implementation

-The porting of the semiclassical code onto the Grid environment performed by making use of the User Interface (UI) machine available in COMPCHEM

Problems

-dependency of the calculation from the dynamic libraries

-support of the Message Passing Interface (MPI) libraries and in particular of the *shared memory* version

Grid implementation

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Solutions

- code compiled in a totally static fashion
  -strictly architecture dependent

This was made possible by the homogeneity of the software and the adoption of the gLite middleware

Performance

	Elapsed time		
	CLUSTER A 1 CPU	Grid 1 CPU	Grid 2 CPU
initial_states	70.09	72.25	31.19
dynamics	8.00	9.00	6.87

CLUSTER A: Compaq AlphaServer ES40, CPU EV68, 0.8GHz, 4GB RAM/node, cache L1 64KB/L2 8MB

Conclusions

- EGEE Grid Platform suitable for Computational Chemistry calculations (Quantum and Semiclassical)
- Perform concurrent calculations
  - Distributed and parallel fashion
  - Sensible reduction of time execution
- (Against) The user must to learn how to submit jobs onto the grid environment
  - Effort coadiuvated by the COMPCHEM User support