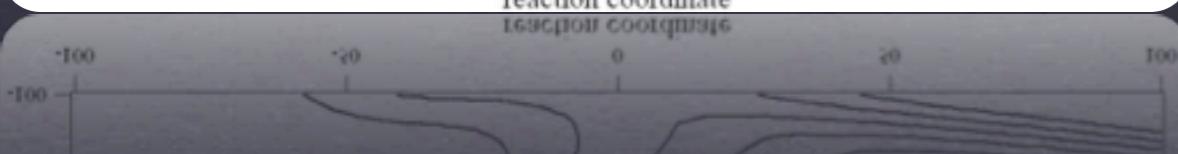
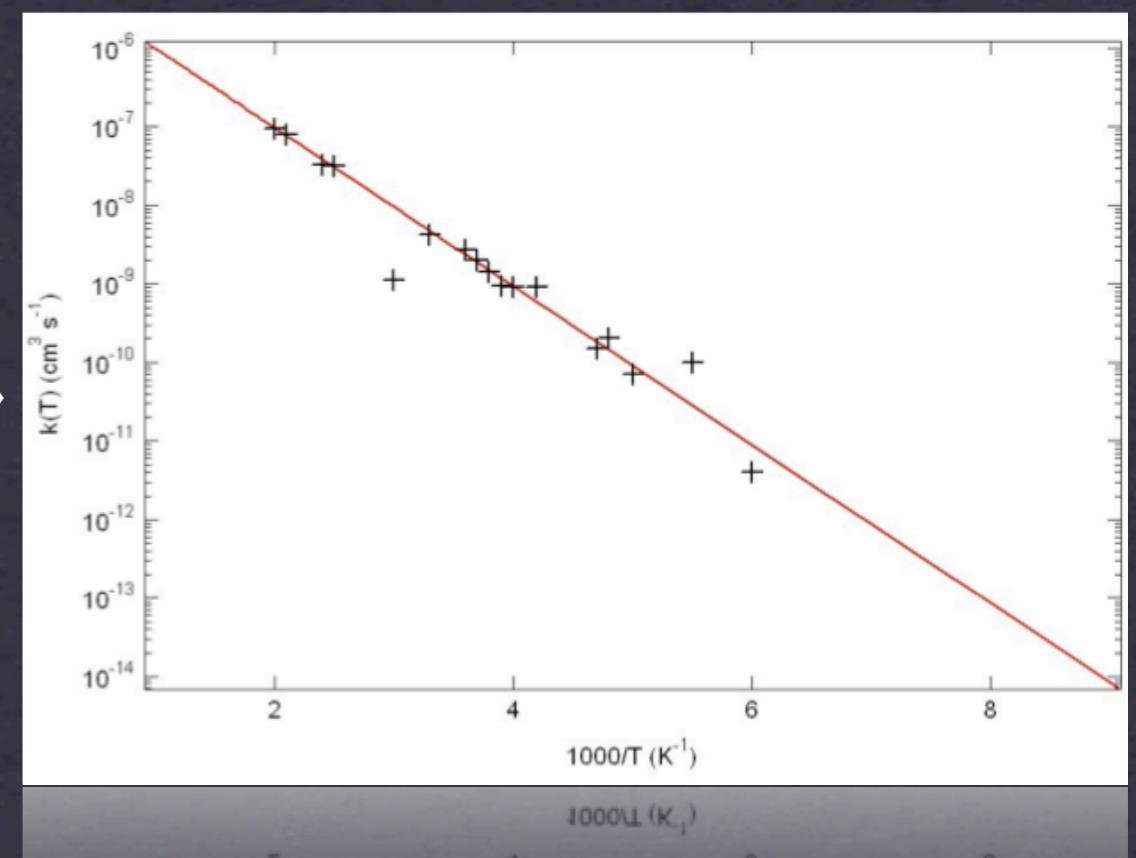
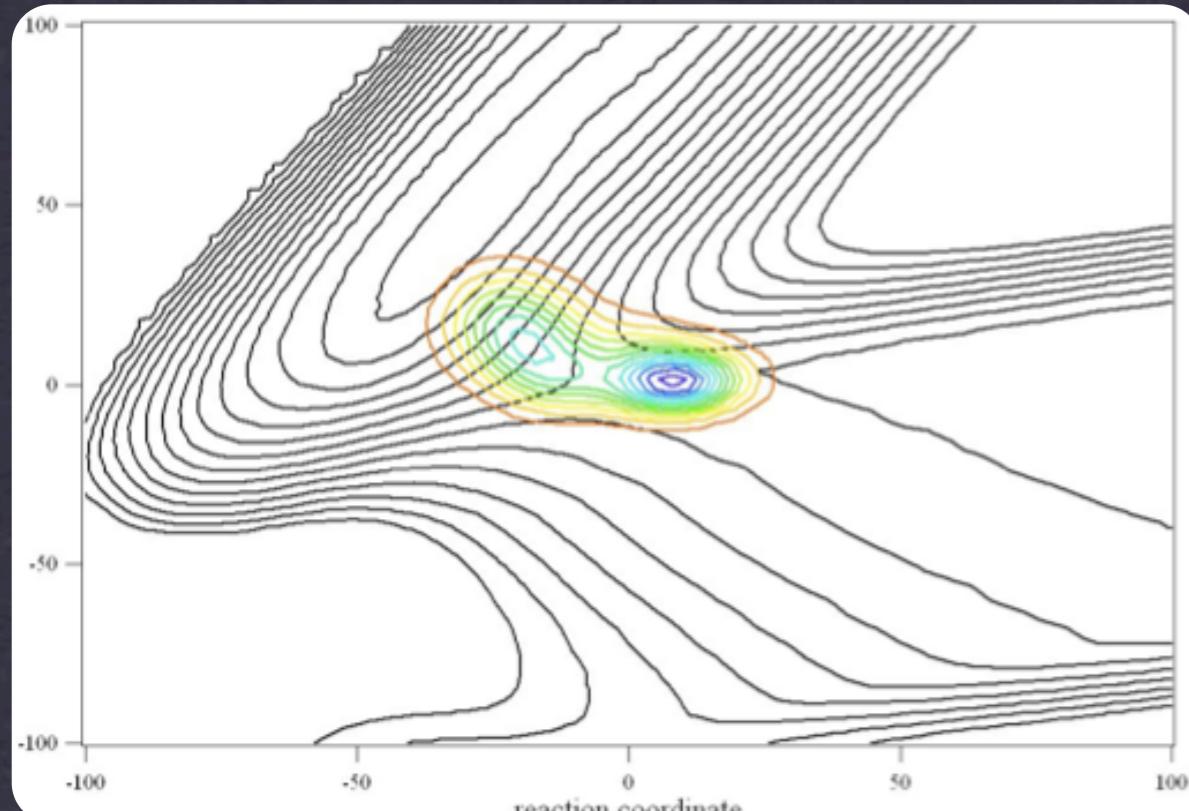


# Grid-MCTDH: quantum calculation of kinetic coefficients



# Grid-MCTDH

## Outline

- GEMS and the FLUSS/MCTDH module
- Computational scheme
- Test case:  $N + N_2$
- New tools
- Structure of the MCTDH wfn
- Conclusions & Outlook

# GEMS

## Workflow

Quantum

Time independent QD

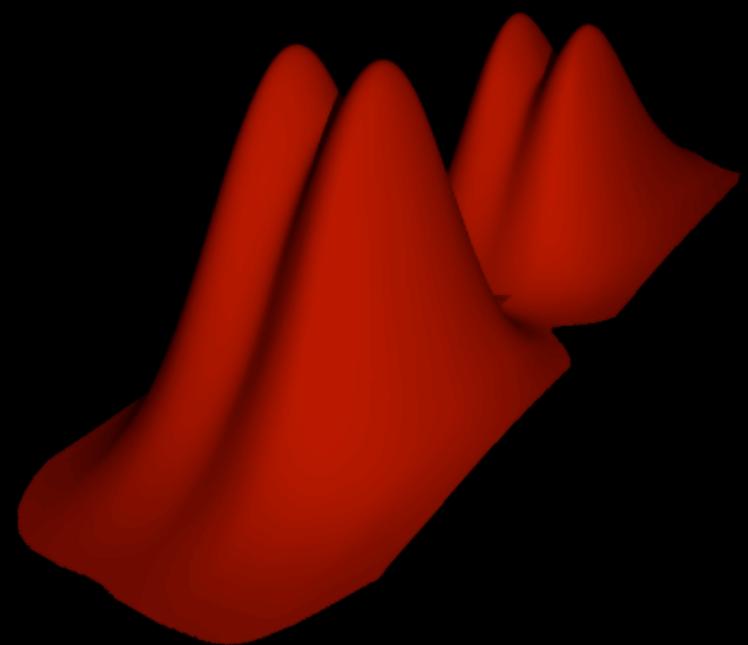
**ABC**

Time dependent QD

**RWAVEPR**

**FLUSS**  
**MCTDH**

# Multiconfigurational time-dependent Hartree



- Expression of the wave function in time-dependent basis functions.
- Multidimensional simulations.
- Short simulation times.
- Applications:
  - H + CH<sub>4</sub> (12D)
  - pyrazine spectrum (24D)
  - electron transfer model systems (100D)

# Multiconfigurational time-dependent Hartree Approach

## Standard WP approach

$$\Psi(x_1, \dots, x_f, t) = \sum_{i_1}^{N_1} \cdots \sum_{i_f}^{N_f} c_{i_1 \dots i_f}(t) \cdot \chi_{i_1}(x_1) \cdots \chi_{i_f}(x_f)$$

→ Linear equations of motion

$$\hat{H}\Psi = -i\hbar \frac{\delta}{\delta t} \Psi \rightarrow \langle \Psi | \hat{V} | \Psi \rangle \quad N_1 \times \cdots \times N_f$$

- Stationary basis ⇒ Huge V matrix
- Present limit of WP: f=9?

# Multiconfigurational time-dependent Hartree Approach

## MCTDH

$$\Psi(x_1, \dots, x_f, t) = \sum_{j_1}^{n_1} \cdots \sum_{j_f}^{n_f} A_{j_1 \dots j_f}(t) \cdot \phi_{j_1}(x_1, t) \cdots \phi_{j_f}(x_f, t)$$

- *Dynamic basis*: basis fns evolve with the system
- Much smaller size of the V-matrix:  $n_i \ll N_i$
- Equations of motion become non-linear
- Loses efficiency as  $t \rightarrow \infty$

# MCTDH Applications

Electron transfer spin boson model: (> 1000 dofs)

H. Wang, M. Thoss, JCP 2003 (119) 1289

Photoabsorption spectrum of pyrazine: ( 24 dofs)

T. Gerdts, U. Manthe, CPL 1998 (295) 167

Raab, Worth, Meyer, Cederbaum, JCP 1999 (110) 936

Vibrational dynamics of water clusters: ( >15 dofs)

O. Vendrell, F. Gatti, H-D. Meyer, JCP 2007 (127) Art. 184303

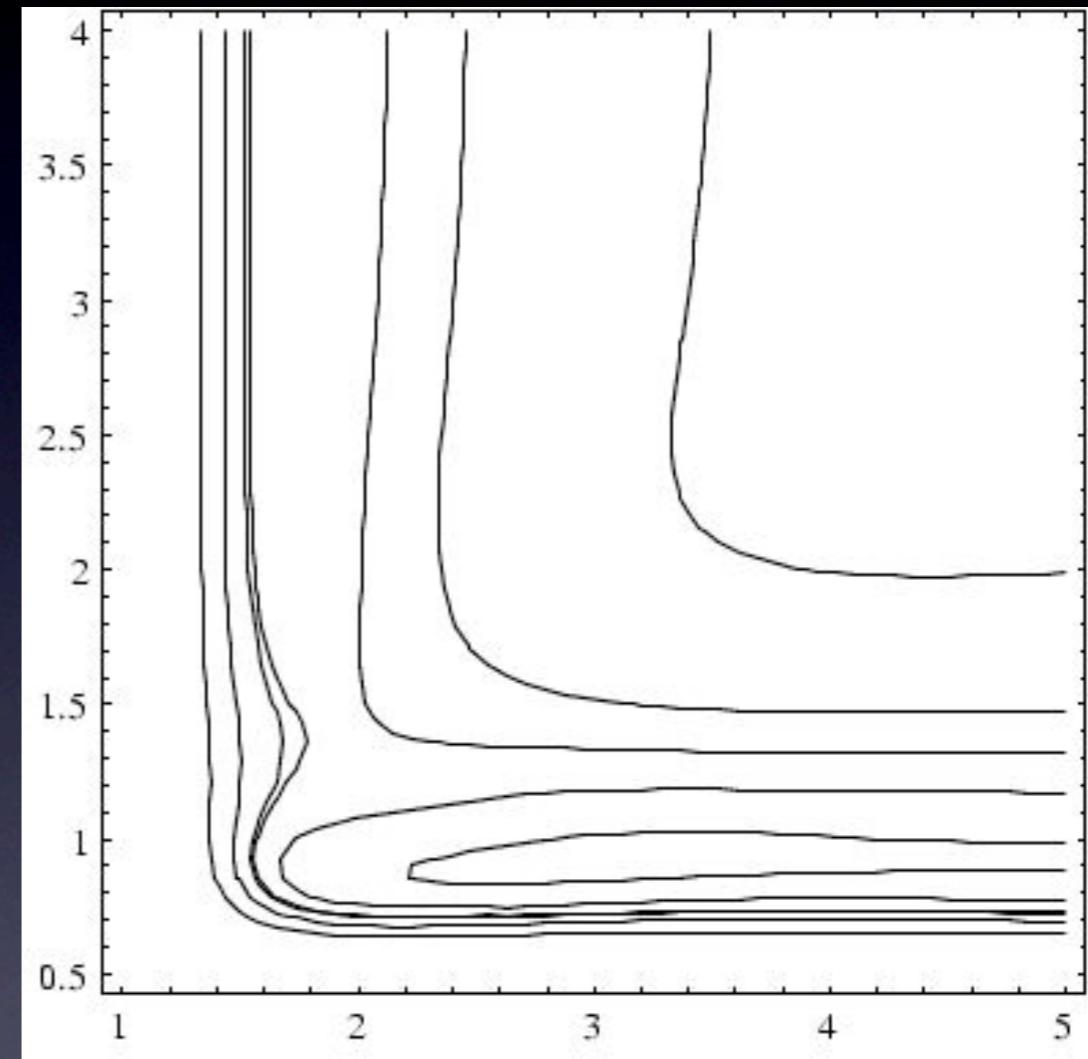
Accurate calculation of thermal reaction rates:

F. Huarte-Larrañaga, U. Manthe, JCP 2000 (113) 5115

T. Wu, H-J. Werner, U. Manthe, Science 2004 (306) 2227

Coming up...

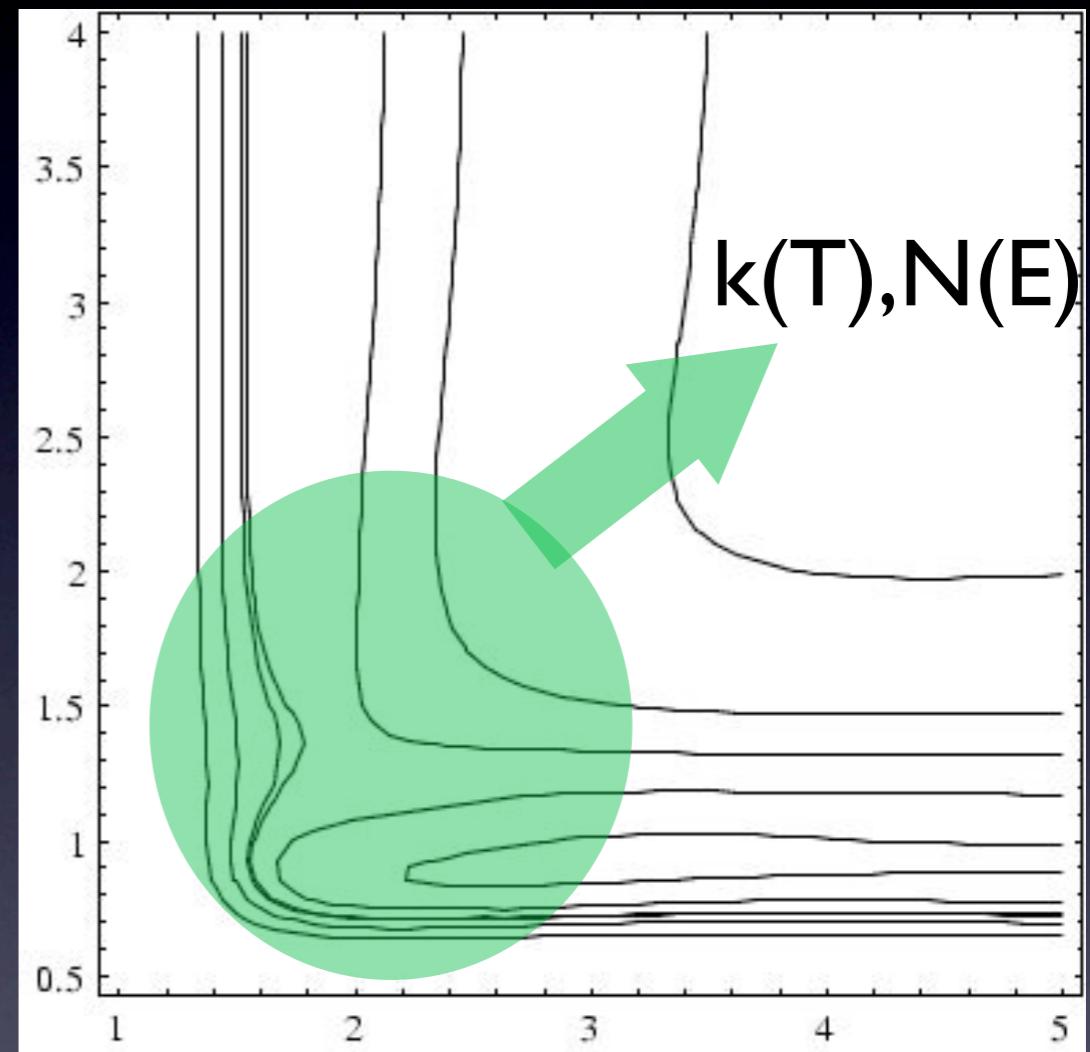
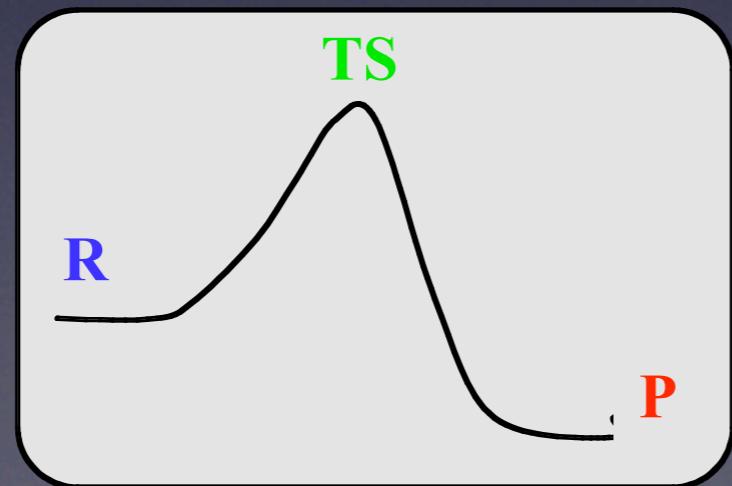
# FLUSS: $k(T)$ from first principles simulations



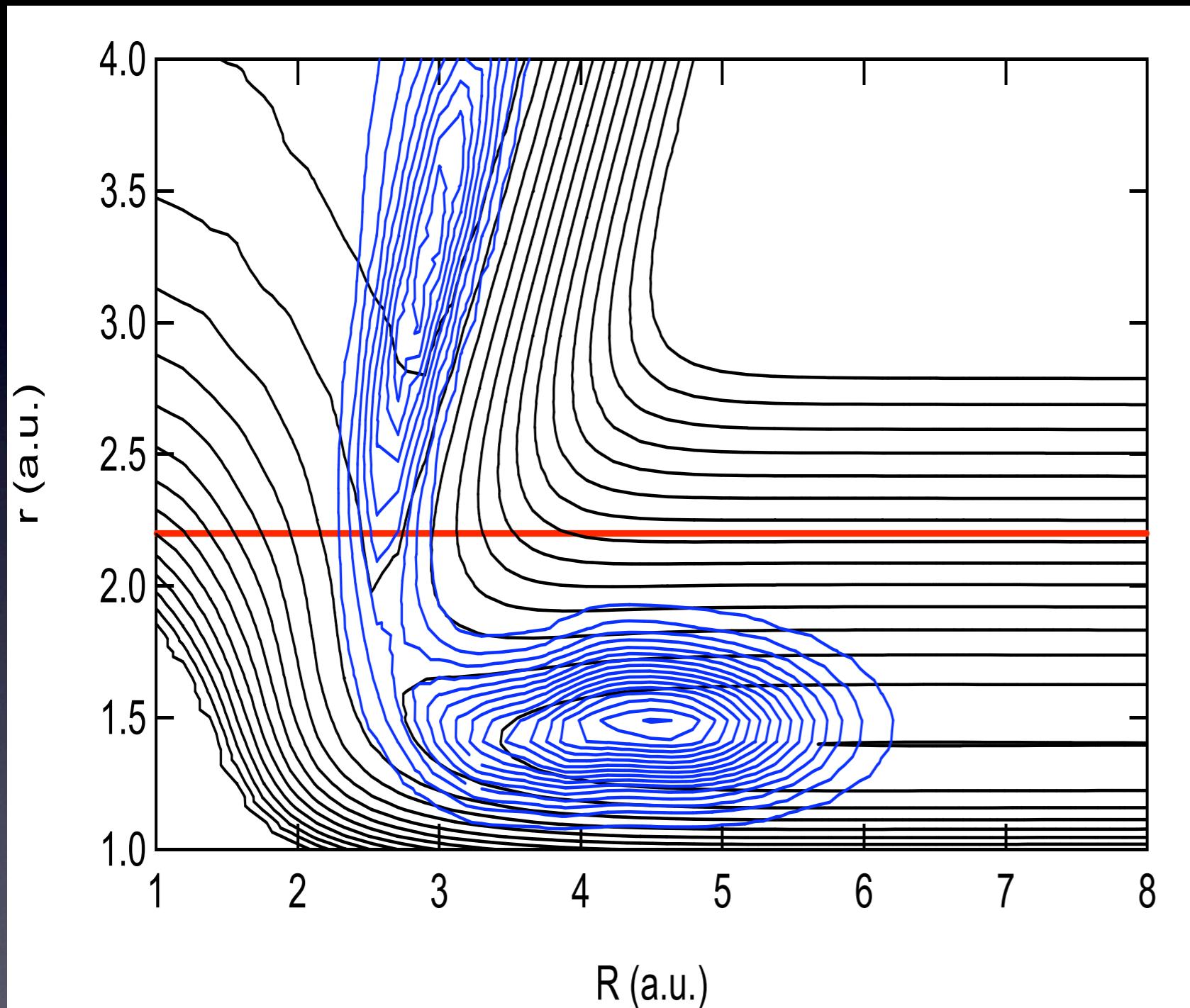
# FLUSS: $k(T)$ from first principles simulations

Obtain  $k(T)$  from a dynamics simulation exclusively in the region around the reaction barrier.

- Rigorous and intuitive
- Computationally efficient
- Formally applicable to condensed phase
- Efficiency intrinsically bound to direct reaction profiles.



# Computation of N(E) & k(T)



I. Definition of dividing surface and flux operator.

II. Flux operator diagonalization.

$$\hat{F}_m = \sum_m^{NL} |f_m\rangle f_m \langle f_m|$$

III. Eigenstates propagation

$$|f_\ell(t + \Delta t)\rangle = e^{-i\hat{H}t/\hbar} |f_\ell(t)\rangle$$

# Computation of $N(E)$ & $k(T)$

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III. Eigenstates propagation

$$N(E) = \sum_{i=1}^{N_f} F_i(E)$$

$$|f_\ell(t + \Delta t)\rangle = e^{-i\hat{H}t/\hbar} |f_\ell(t)\rangle$$

# The Tools

- Reactivity decomposed as a sum of contributions of the activated complex (flux states).

**Grid-Fluss**



- ... however overall efficiency is determined by the WP propagation.

**Grid-MCTDH**



# Grid-MCTDH

## Outline

- GEMS and the FLUSS/MCTDH module
- Computational scheme
- Test case:  $N + N_2$
- New tools
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- Conclusions & Outlook

# QM calculation of $k(T)$ : *Gridification*

$J=0$

Flux diagonalization

$\{f_0, \dots, f_N\}$

F-states propagation

Calculation of  
magnitudes

# QM calculation of $k(T)$ : *Gridification*

$J=0$

Flux diagonalization

$$\{f_0, \dots, f_N\}$$

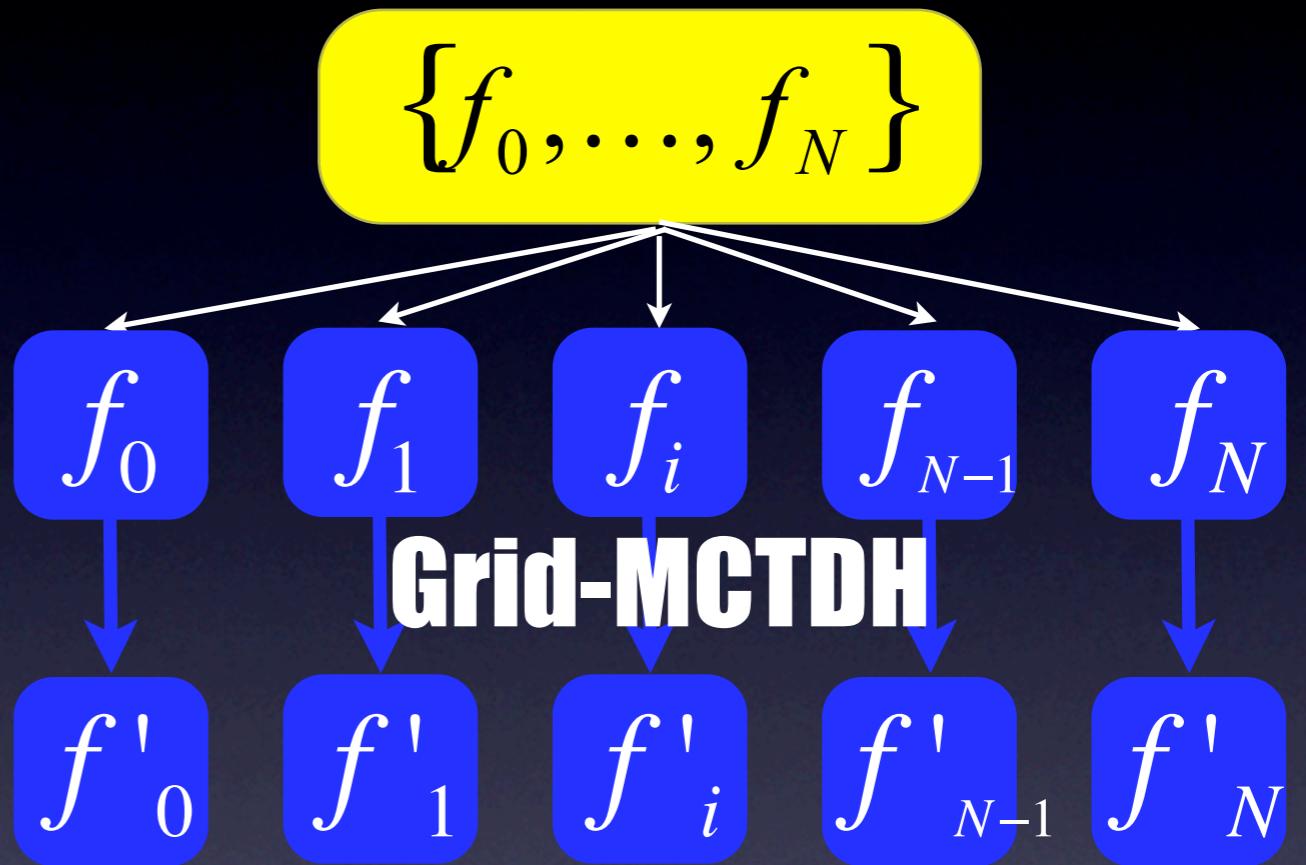
Iterative process: one single  
submission to the Grid

**Grid-FLUSS**

# Grid-FLUSS: computational scheme

J=0

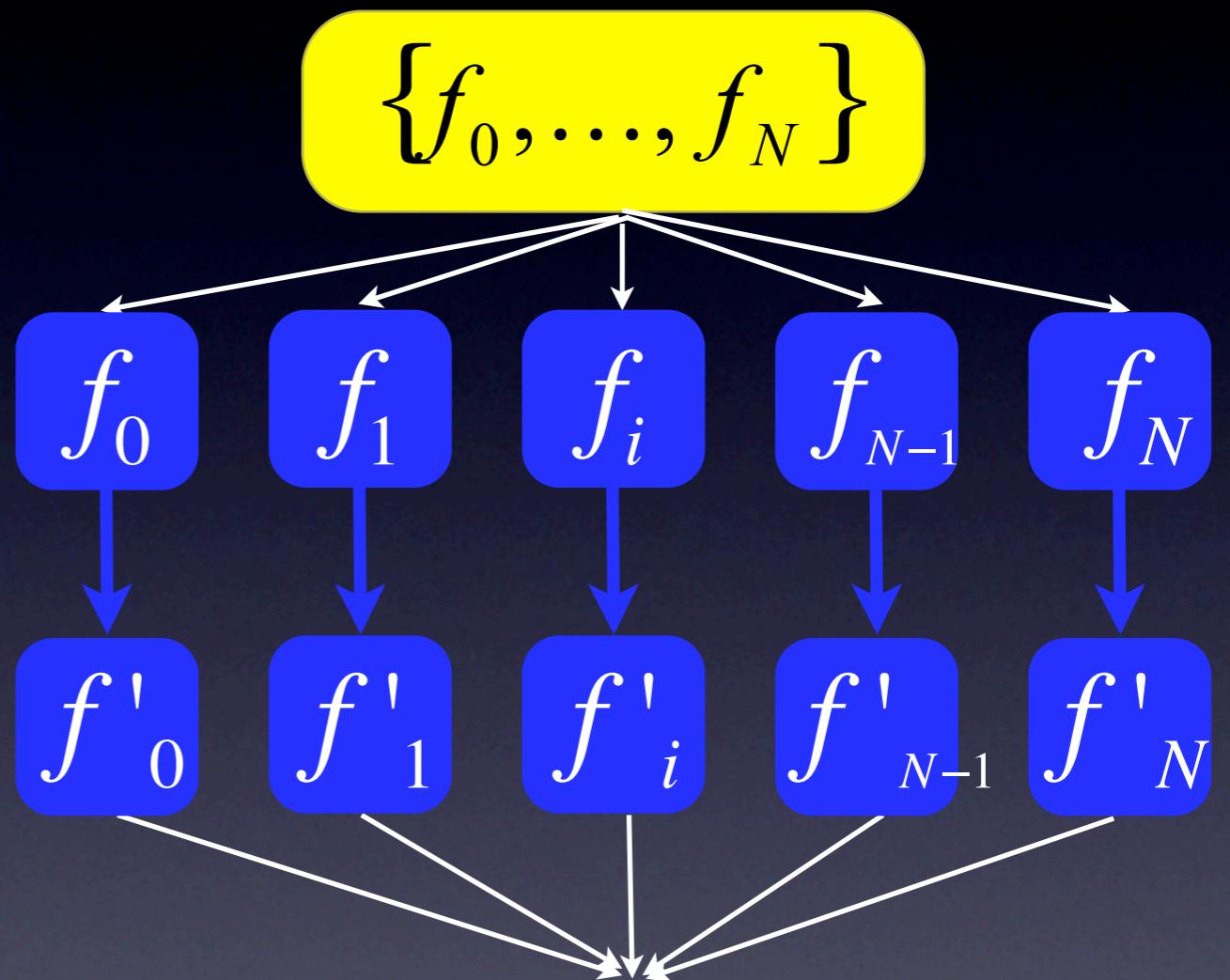
F-states propagation



Independent simultaneous  
propagations: multiple  
submissions one prop x CE

# QM calculation of $k(T)$ : computational scheme

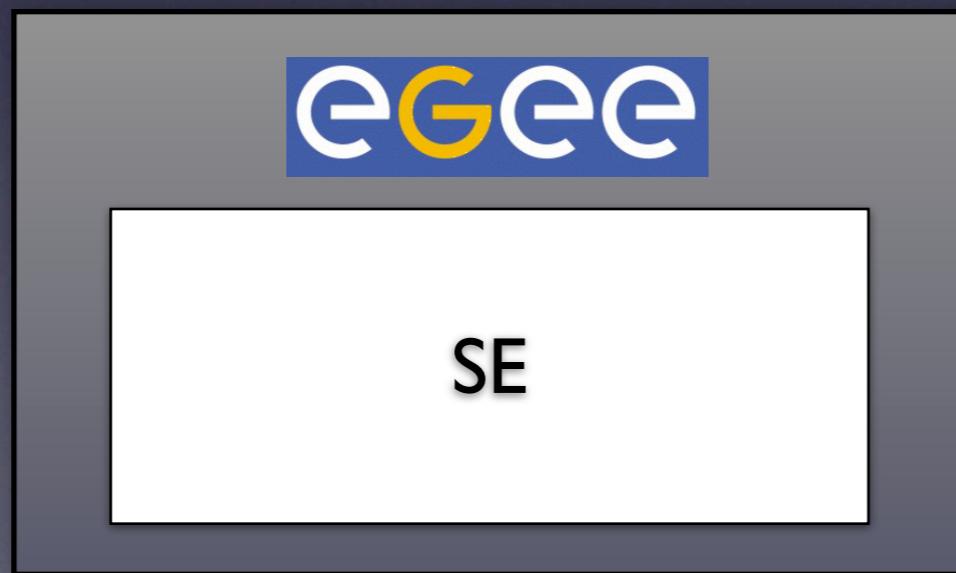
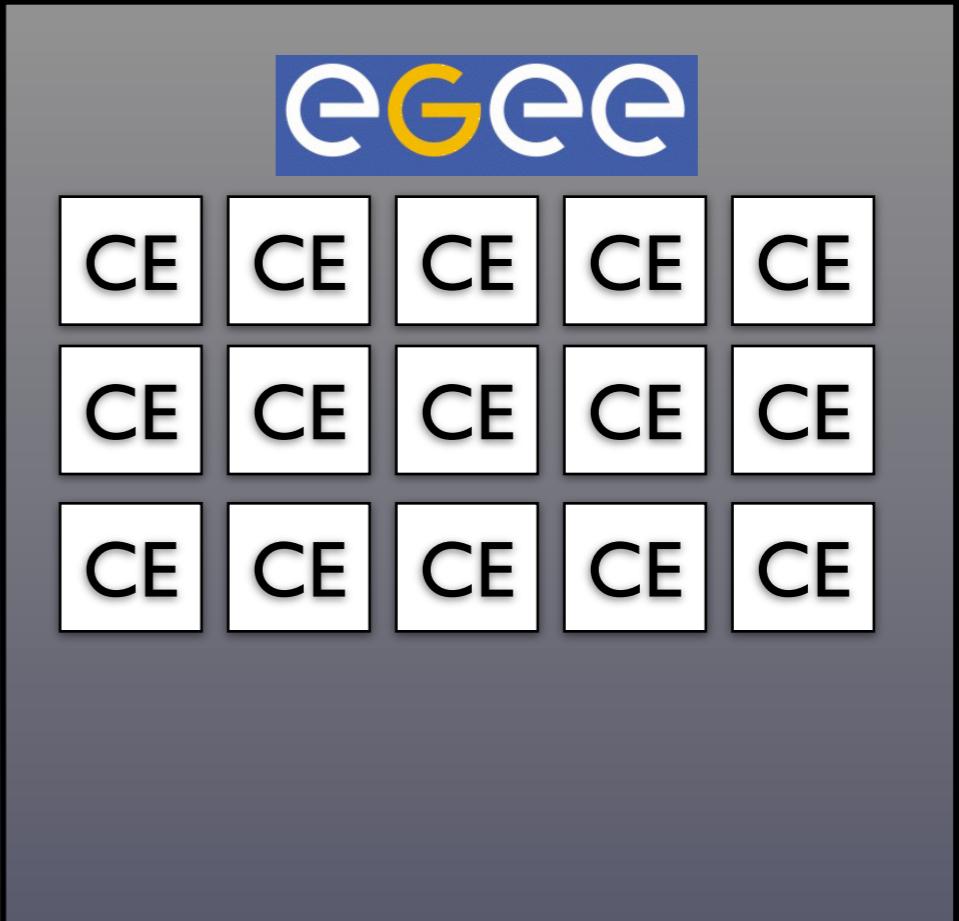
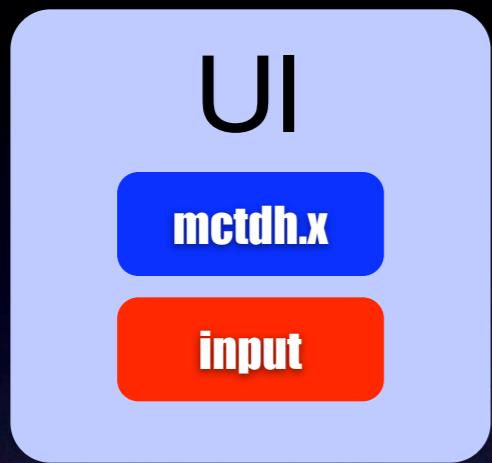
$J=0$



Calculation of  
magnitudes

Collect data: single calculation  
of observables

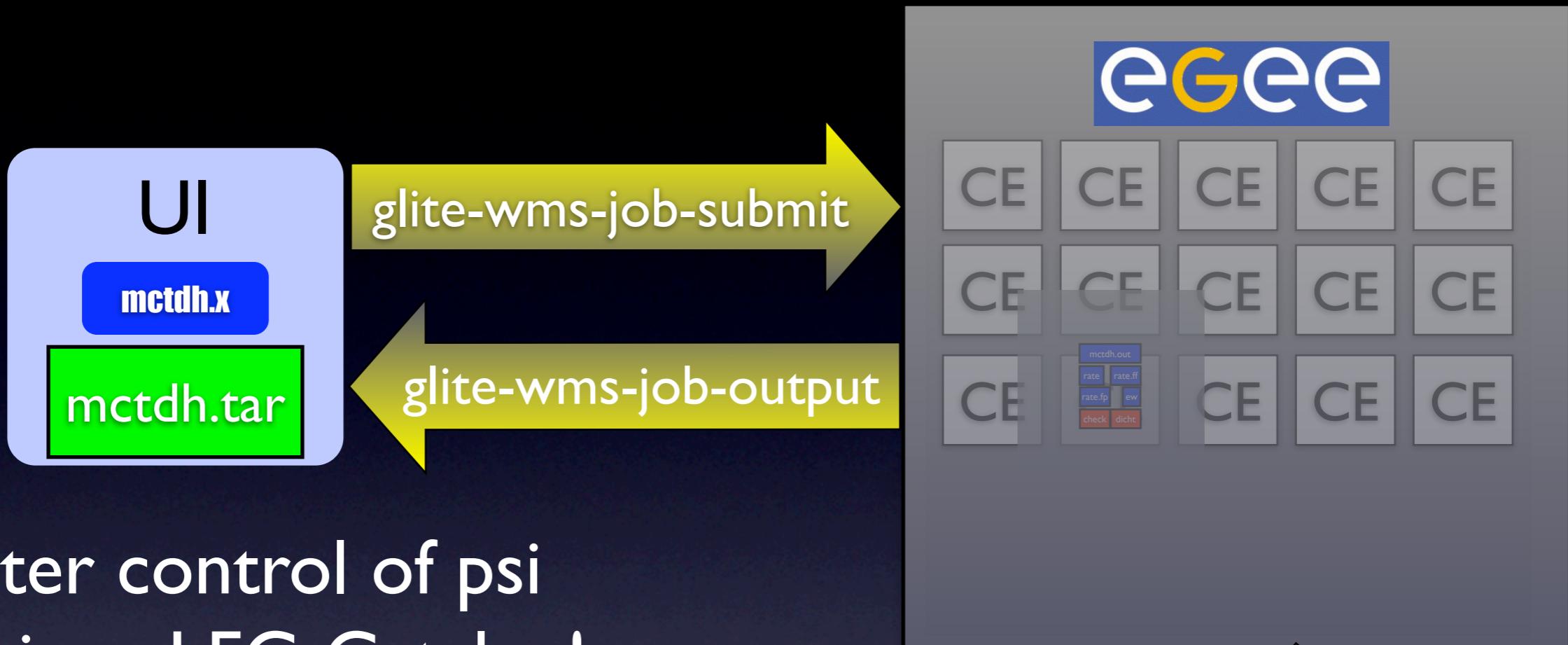
# Management of the *psi* file: use of Storage Elements



**skip**

[se.grid.unipg.it](http://se.grid.unipg.it)

# Management of the *psi* file: use of Storage Elements



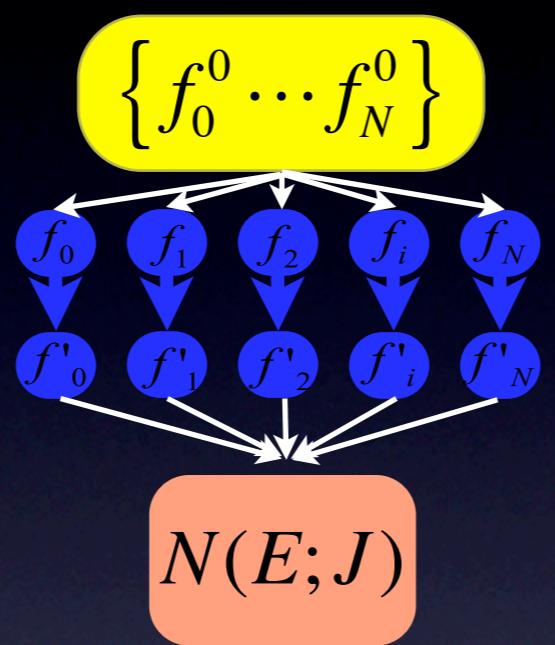
Greater control of psi  
files since LFC-Catalog!



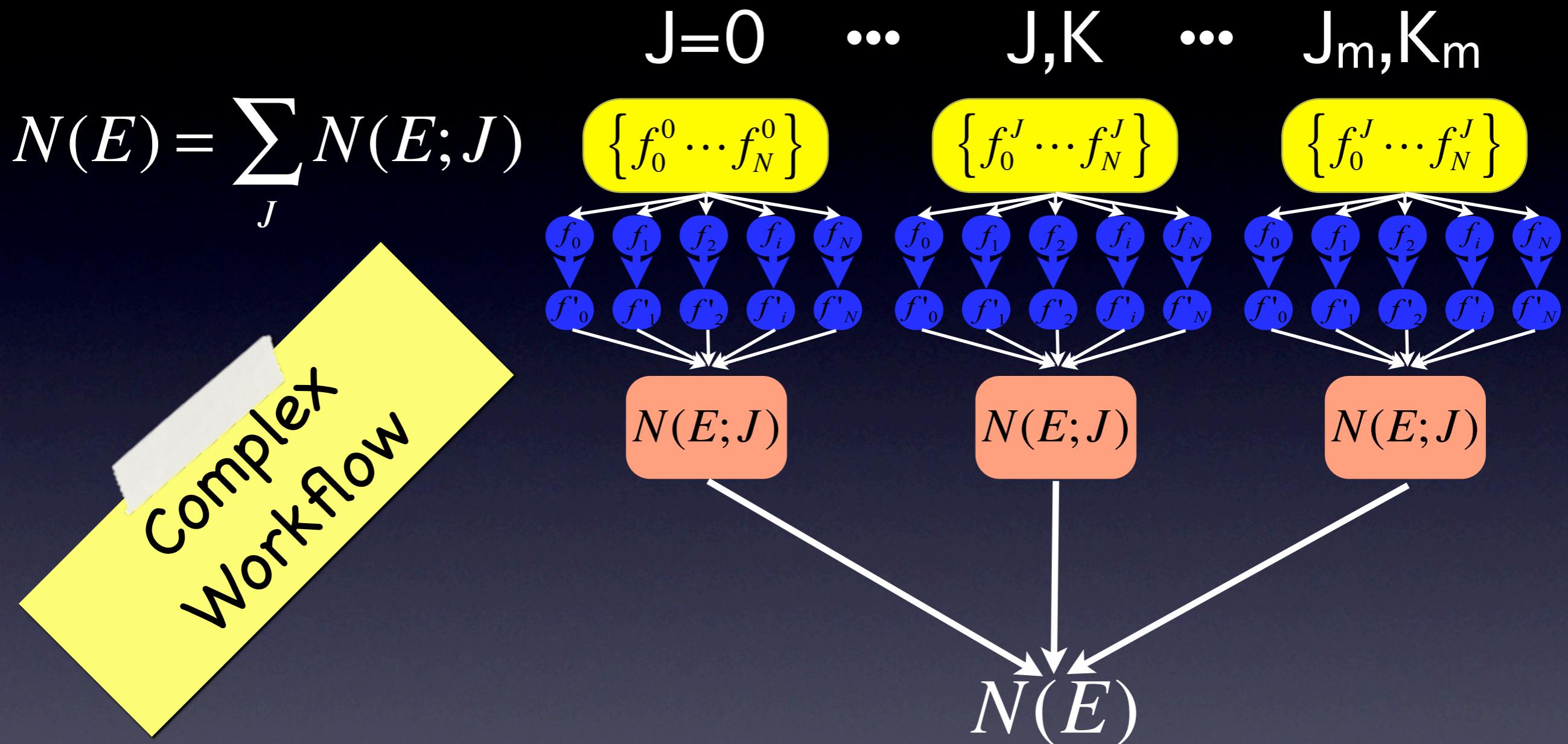
$J>0$ : Complete Computational scheme!

$J=0$

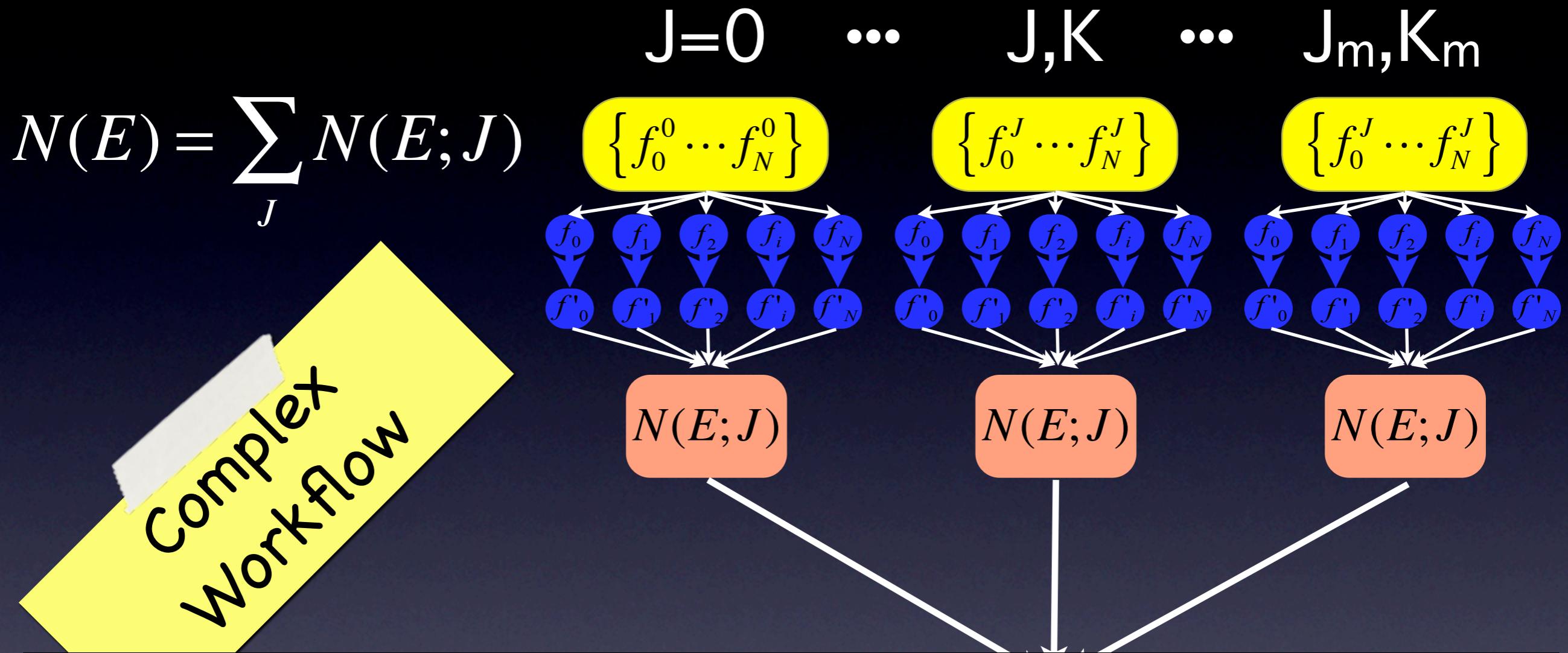
$$N(E) = \sum_J N(E; J)$$



# $J > 0$ : Complete Computational scheme!



# $J > 0$ : Complete Computational scheme!



- Use of advanced JDL: DAG jobs / parametric jobs ✗
- Advanced job control php scripts ✓
- Use of available tools: Dirac, Superscalar ... ?

# Towards a control of the workflow

## jobmask.dat file

JOBNAME	ISTAT	ILAN	TYPE	JOBID	STATUS	CE
Basis1	I	-I	I	https://...	9	ce2.egee.cesga.es
Basis2	I	-I	I	https://...	2	cex.grid.unipg.it
Basis1	I	I	2	https://...	2	ce2.egee.cesga.es
Basis1	...	...	...	...	...	...
Basis1	...	...	...	...	...	...
Basis0	2	10	3	https://...	5	...

create\_job.php / send\_job.php / check\_status.php

# MCTDH Simulations using the Grid

## Outline

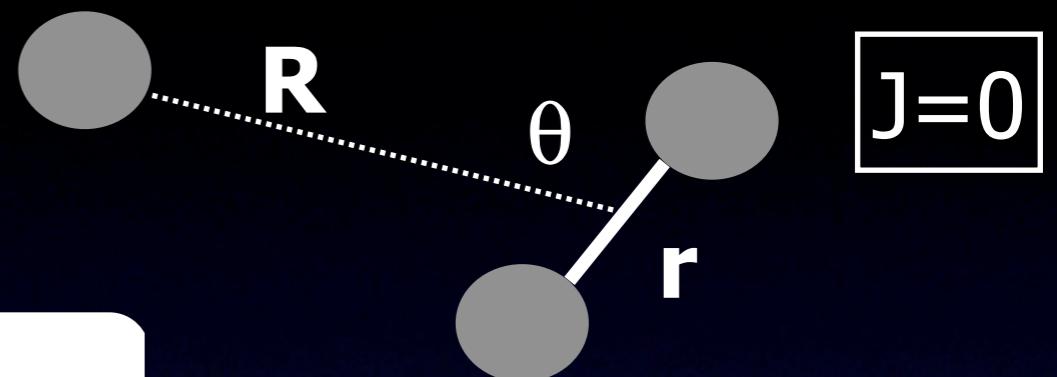
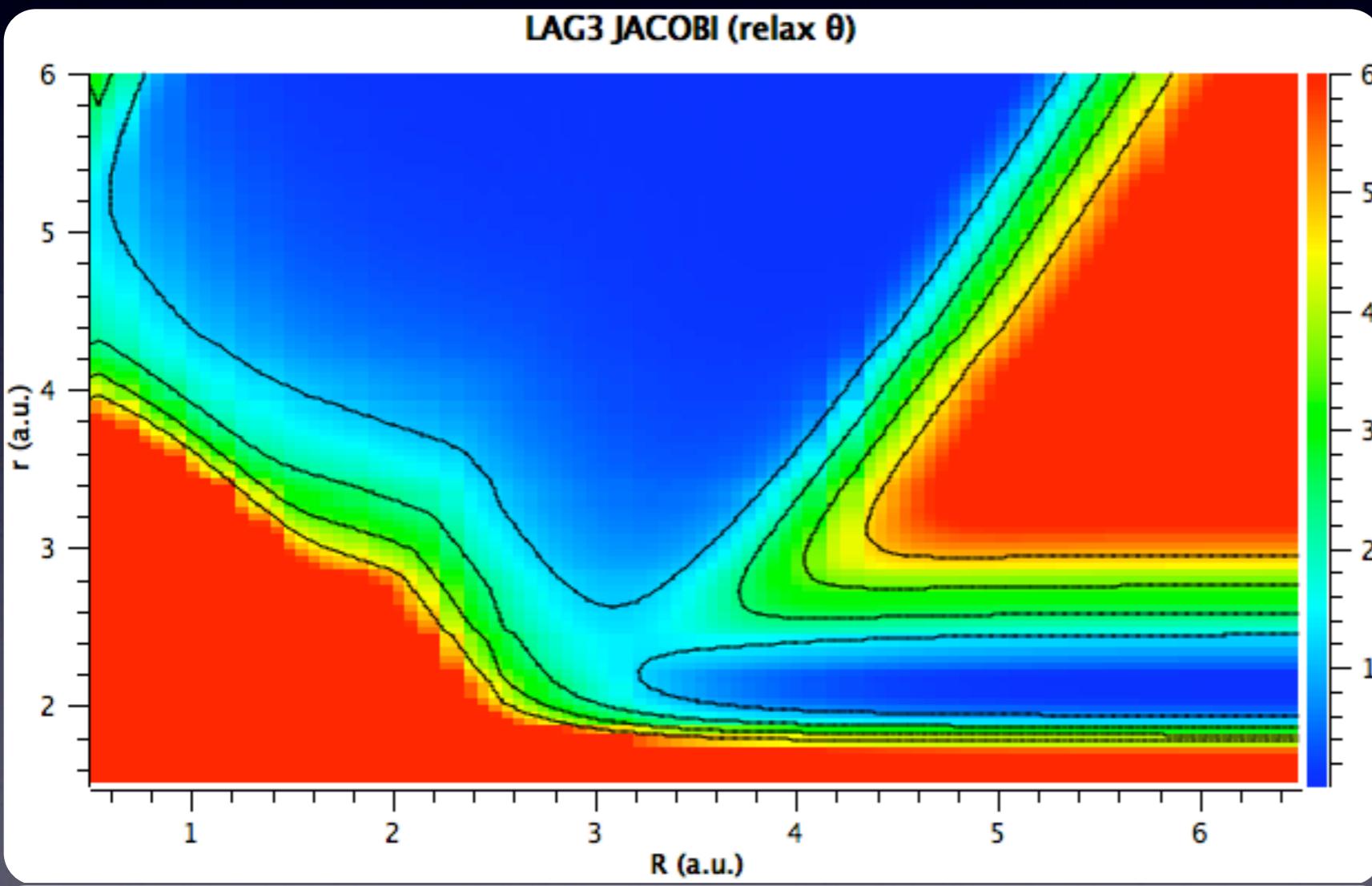
- GEMS and the FLUSS/MCTDH module
- Computational scheme
- Test case: N + N<sub>2</sub>
- New tools
- Structure of the MCTDH wfn
- Conclusions & Outlook

# Atmospheric Reaction Dynamics in the Grid



SEP-LAG3 (Perugia)

LAG3 JACOBI (relax  $\theta$ )

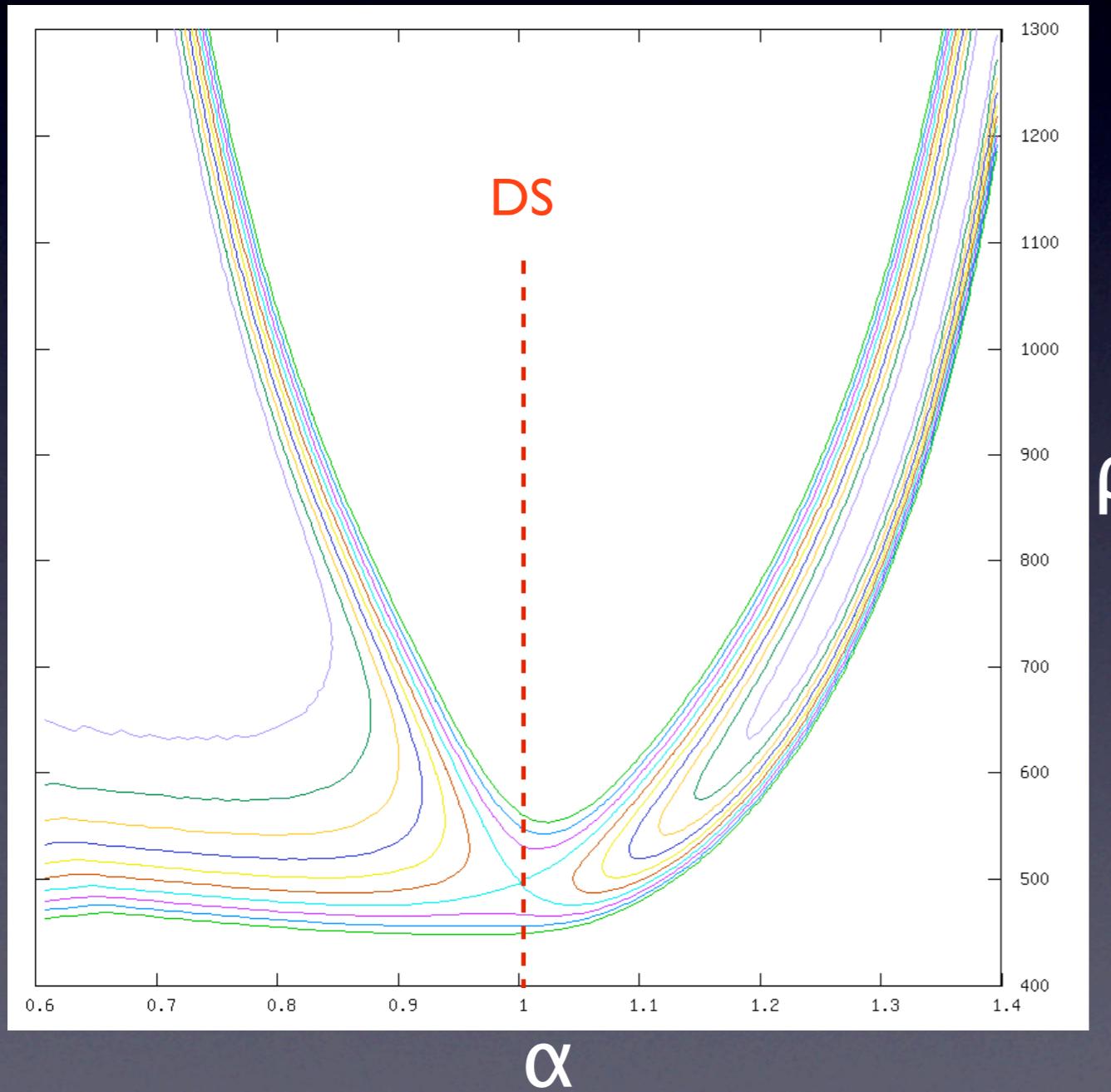


- LAGROBO Functional fit
- Bent TS geometry
- 1.4eV reaction barrier

# Q-dynamics simulation: computational details

Hyperspherical coordinates based on Jacobi

$$\rho = \sqrt{\tilde{R}^2 + \tilde{r}^2} \quad \tan \alpha = \frac{\tilde{r}}{\tilde{R}} \quad \theta$$

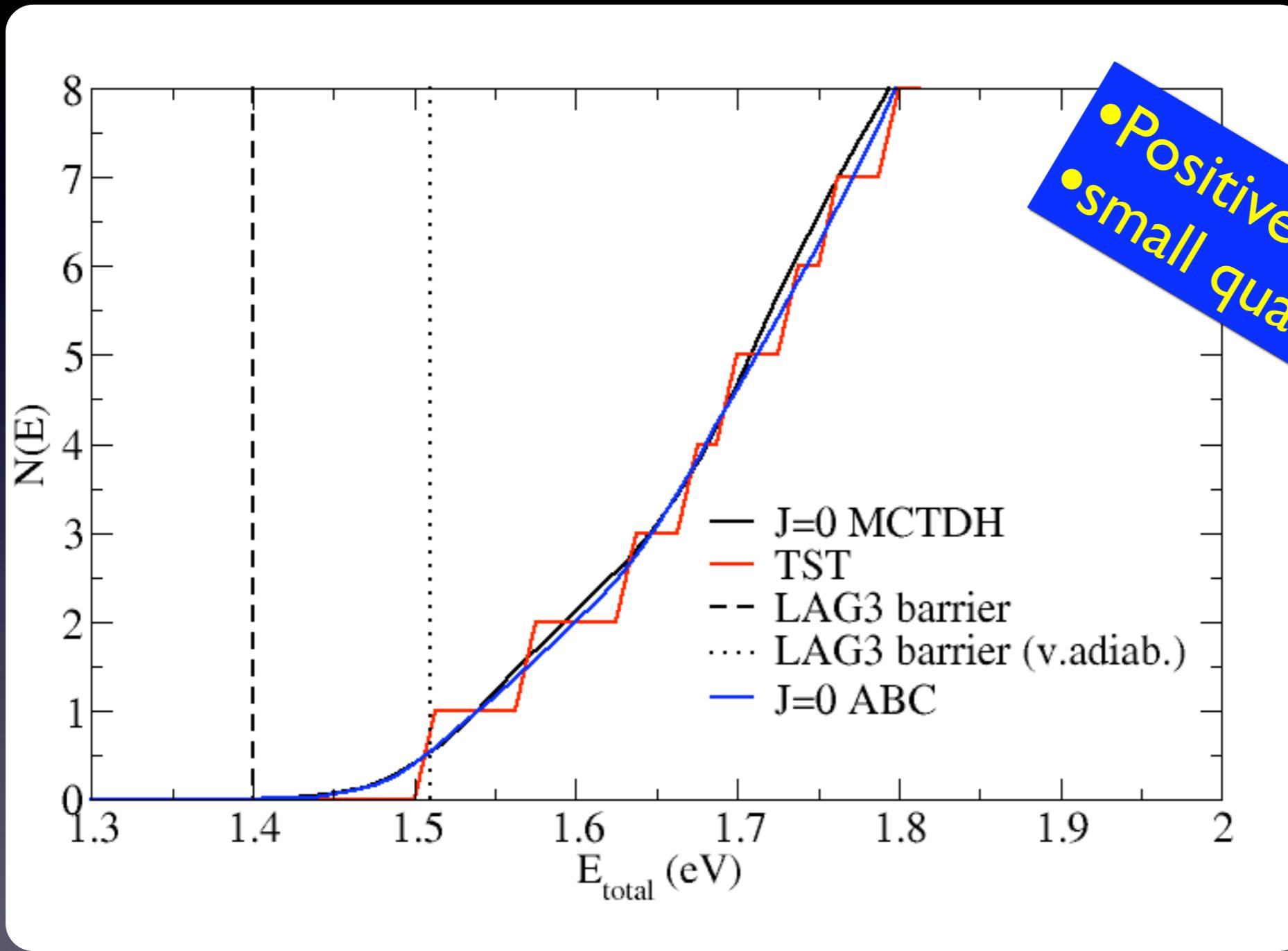


Simulation details:

- $J=0-80, |K| \leq 20 \rightarrow 2901$  states
- over 30.000 MCTDH confs
- 60 flux eigenstates
- time propagation: 40 fs

# Q-dynamics Results

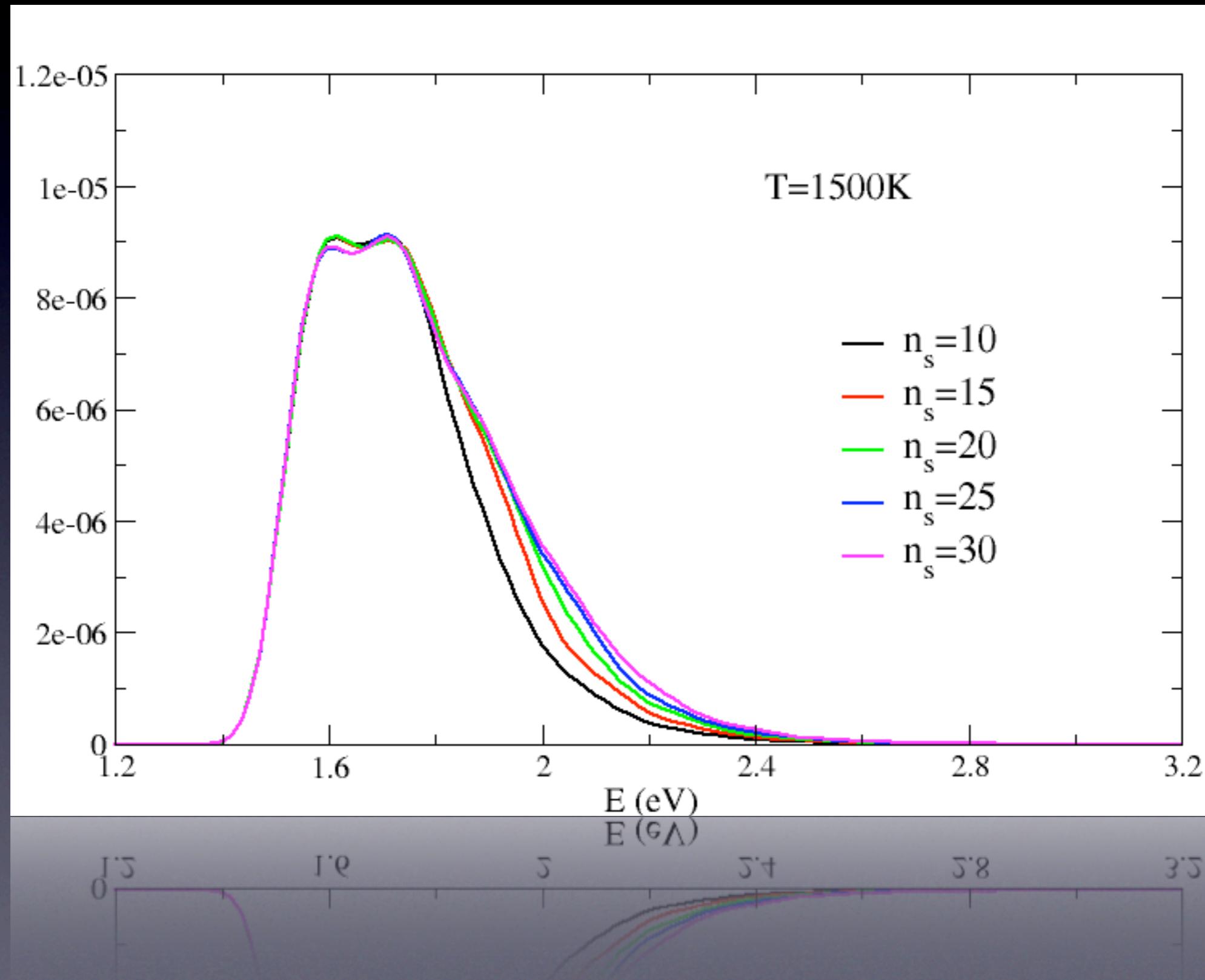
## J=0 Cumulative reaction probability



# Q-dyn @ high T: number of -states

$$N_T(E) = N(E) \cdot e^{-E/kT}$$

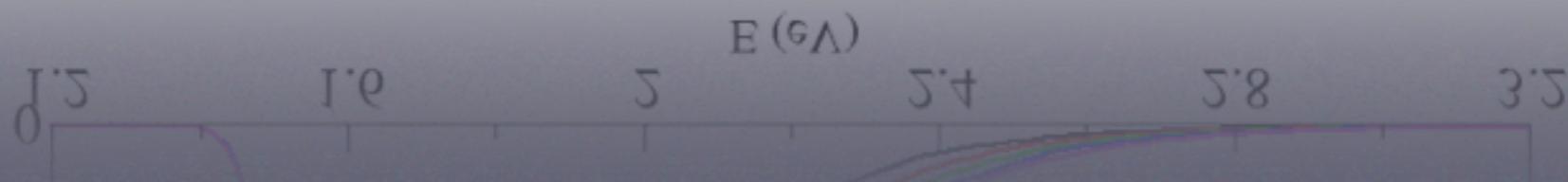
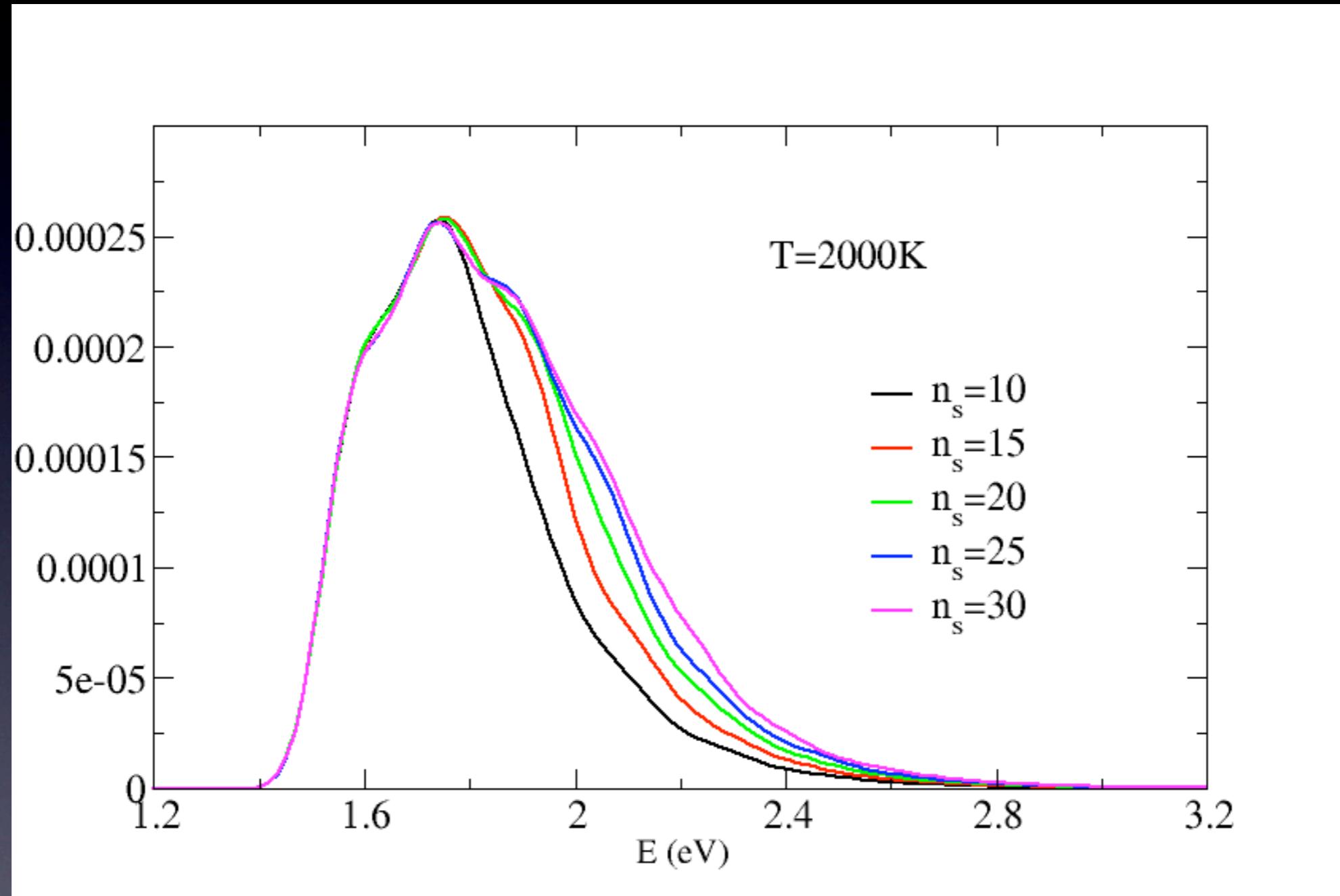
$$k(T)\alpha \int N_T(E)dE$$



# Q-dyn @ high T: number of -states

$$N_T(E) = N(E) \cdot e^{-E/kT}$$

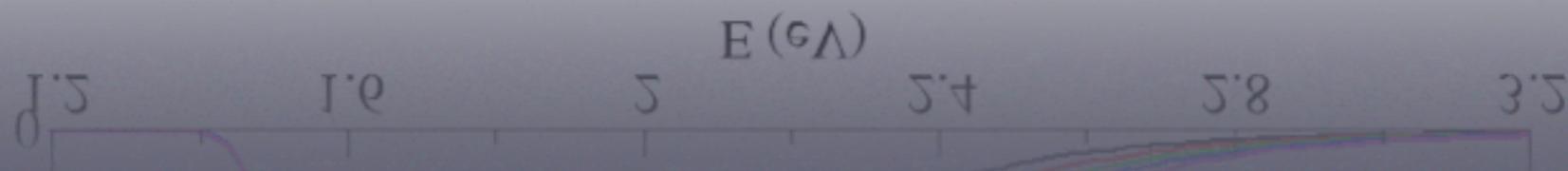
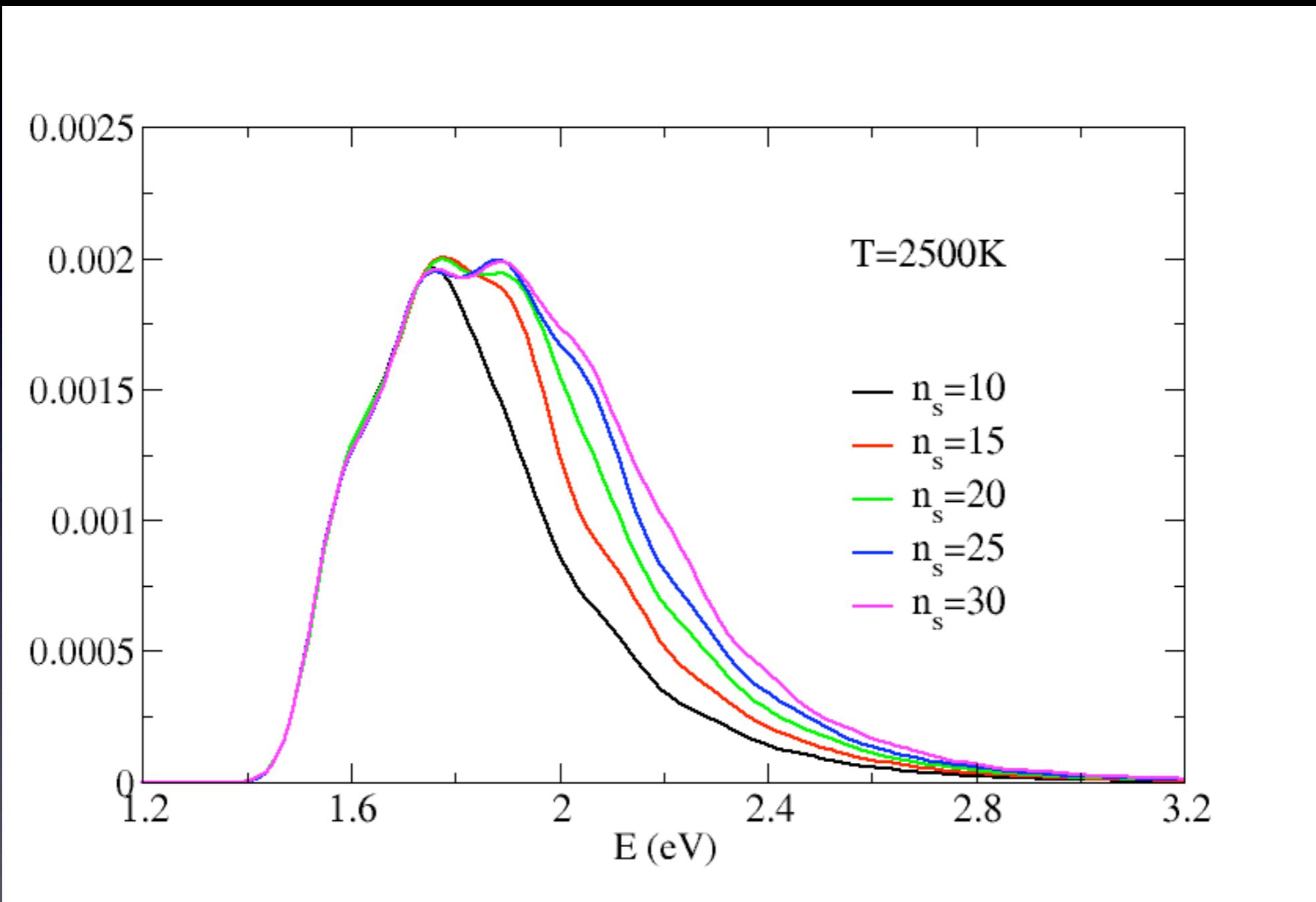
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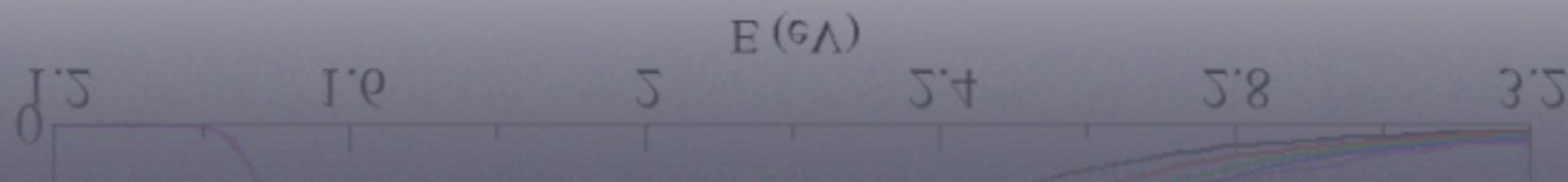
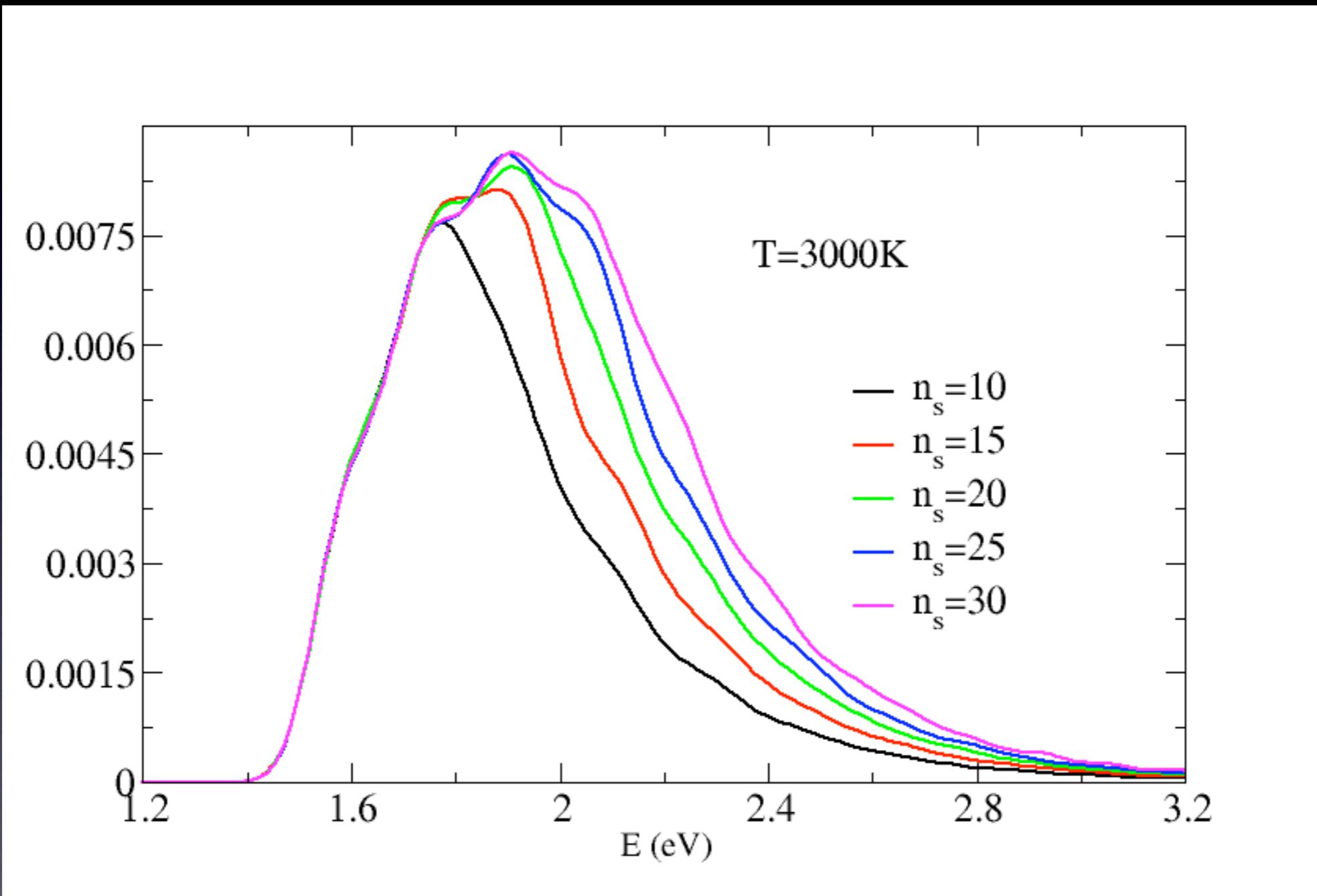
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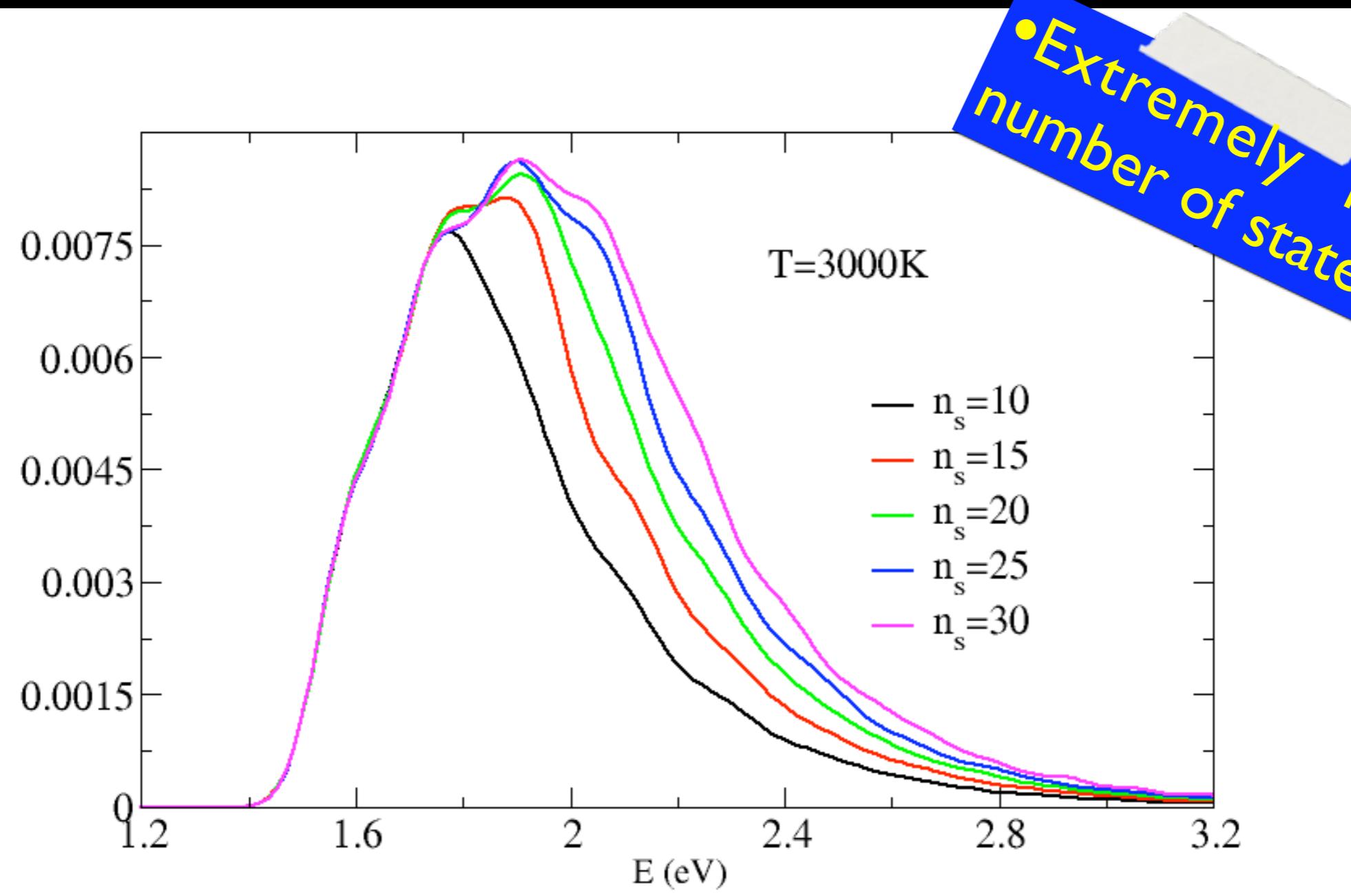
$$k(T)\alpha \int N_T(E)dE$$



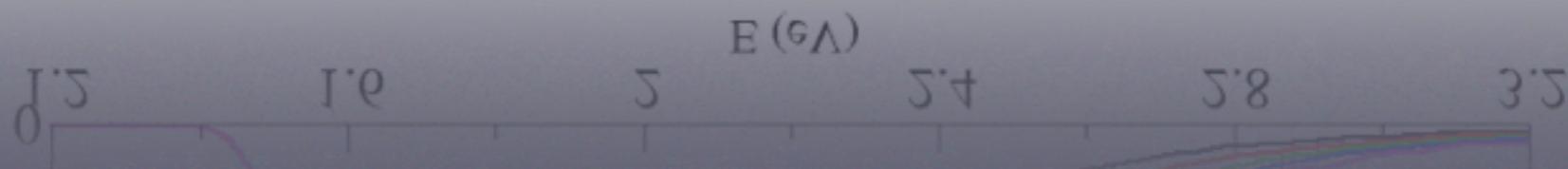
# Q-dyn @ high T: number of -states

$$N_T(E) = N(E) \cdot e^{-E/kT}$$

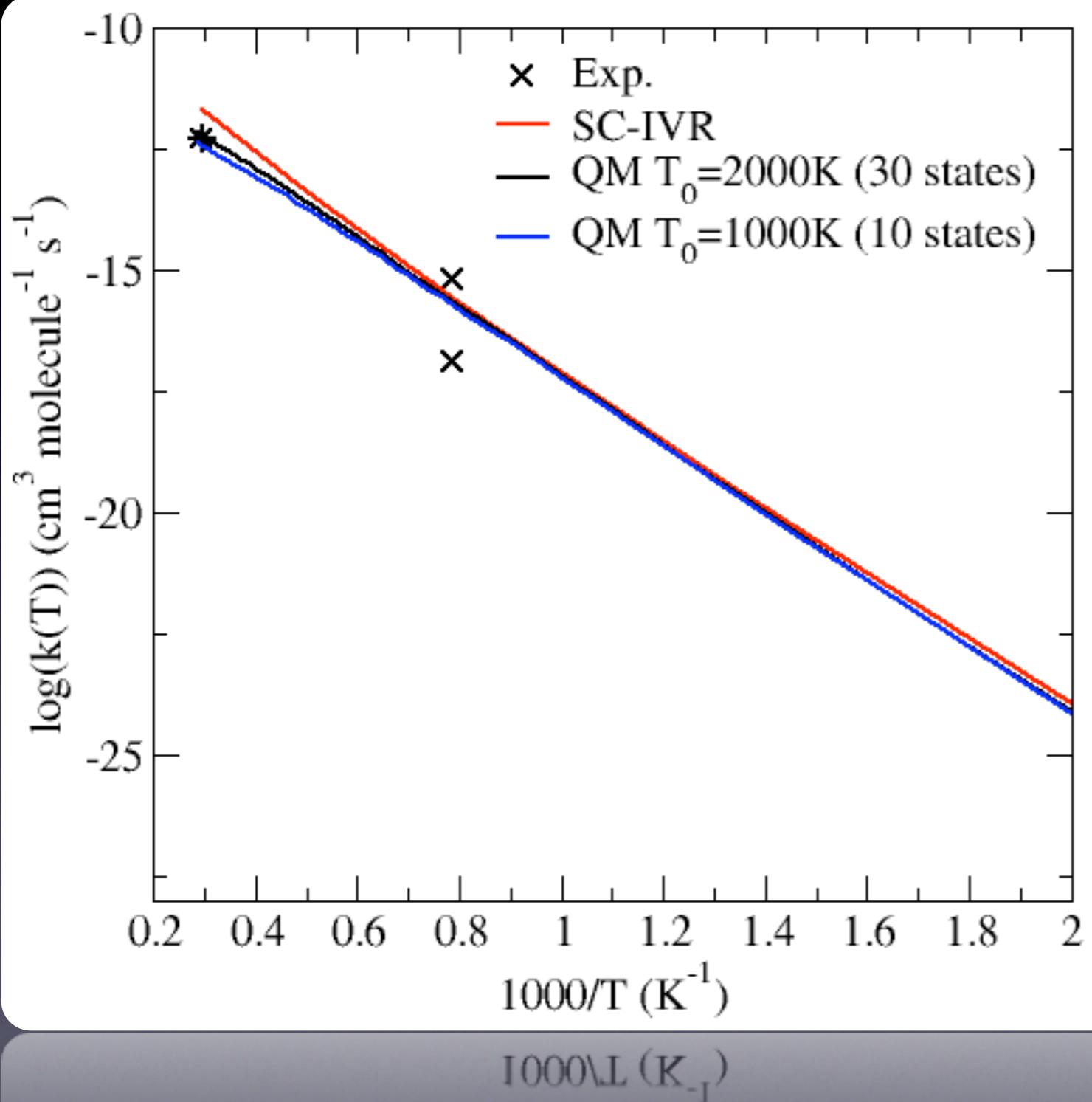
$$k(T)\alpha \int N_T(E)dE$$



•Extremely large  
number of states!!



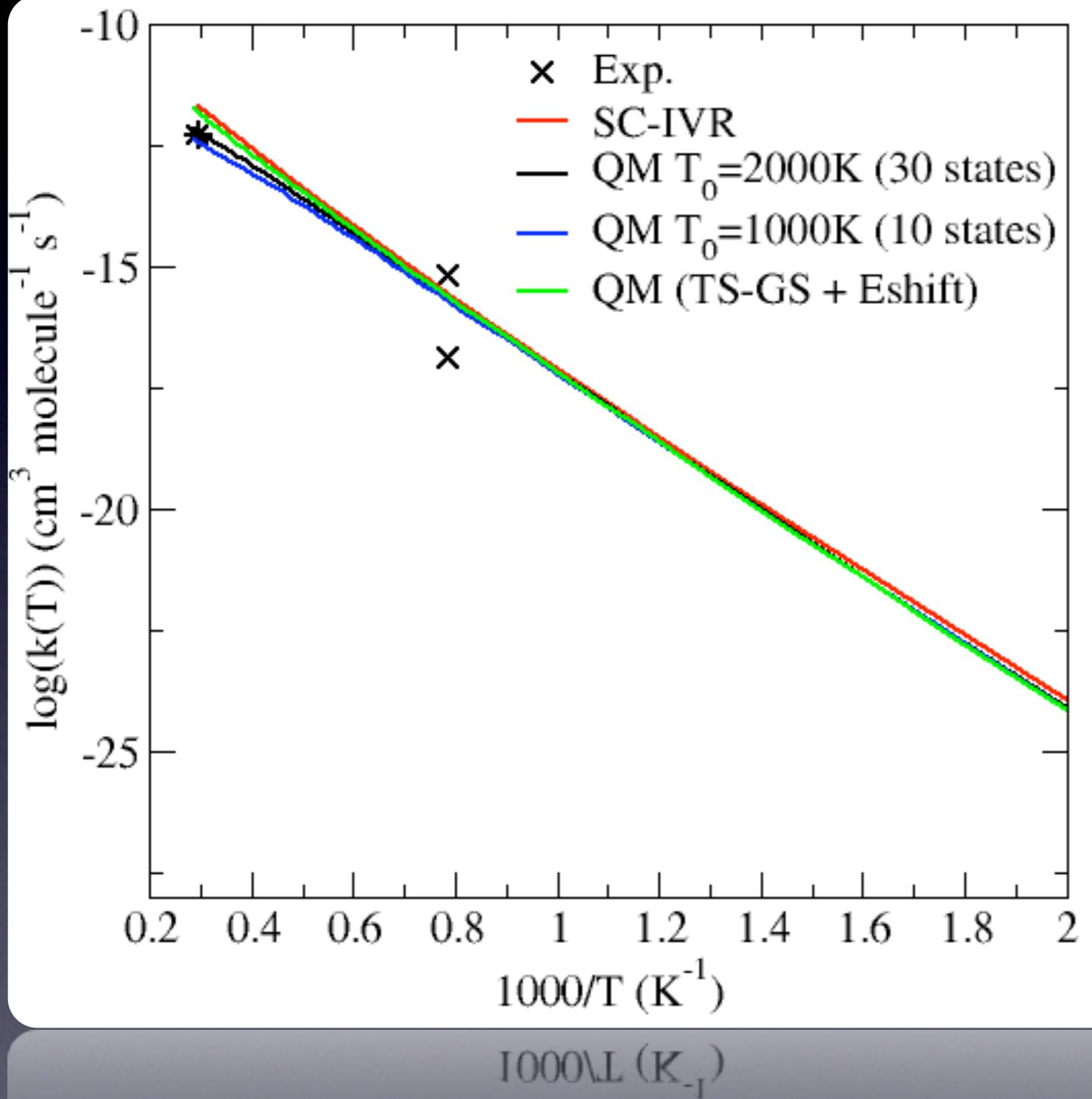
# $k(T)$ Quantum vs. Semiclassical Dynamics



- Good agreement with Exp.
- SC-IVR(\*) is reliable
- 10 q-states for  $T < 2000\text{K}$
- more states @  $T \sim 3000\text{K}$ ?

(\*) By N. Faginas Lago (PG)

# $k(T)$ Quantum vs. Semiclassical Dynamics



- Good agreement with Exp.
- SC-IVR(\*) is reliable
- 10 q-states for  $T < 2000\text{K}$
- more states @  $T \sim 3000\text{K}$ ?
- TS-GS + Harmonic shift: good compromise

(\*) By N. Faginas Lago (PG)

# Grid-fluss and Grid-MCTDH: Performance issues

		ns		
		10	20	30
Cluster	flux	0.17	0.31	0.48
	t-prop	13.07	26.20	35.52
EGEE	flux	0.16	0.35	0.5
	t-prop tasks	10	20	30
	$\langle t\text{-prop} \rangle$	6.27	5.89	6.15

Table 3

Cluster: single-node execution (AMD64 Opteron 2,2GHz)

EGEE-COMPCHEM: no CE special requirement!!!

Heterogeneity of available CEs slows down performance!

# Grid-fluss and Grid-MCTDH: Performance issues

- Some CEs did not have a \$FC
- Some CEs did not see se.grid.unipg.it
- Some jobs Aborted
- Occasionally executable crashed

# MCTDH Simulations using the Grid

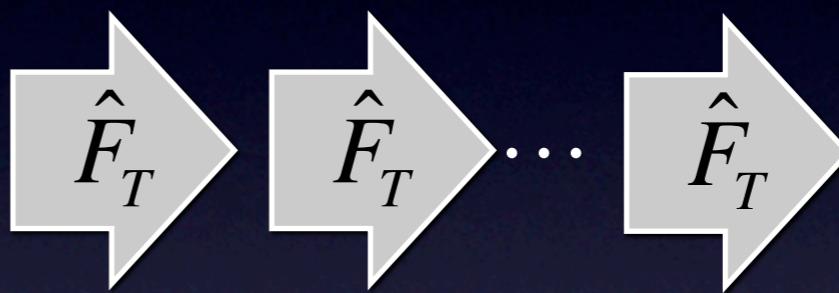
## Outline

- GEMS and the FLUSS/MCTDH module
- Computational scheme
- Test case:  $N + N_2$
- New tools
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- Conclusions & Outlook

# State Averaged Method

Alternative to Lanczos diagonalization

$$\begin{aligned}\Psi_0^{(0)}(\underline{x},t) &= \sum_i A_i(t) \prod_k \phi_{i,k}(x_k, t) \\ \Psi_1^{(0)}(\underline{x},t) &= \sum_j B_j(t) \prod_k \phi_{j,k}(x_k, t) \\ &\vdots \\ \Psi_N^{(0)}(\underline{x},t) &= \sum_l C_l(t) \prod_k \phi_{l,k}(x_k, t)\end{aligned}$$



$$\begin{aligned}\Psi_0^{(NI)}(\underline{x},t) \\ \Psi_1^{(NI)}(\underline{x},t) \\ \vdots \\ \Psi_N^{(0)}(\underline{x},t)\end{aligned}$$

Set of trial wfns: vibrational states  
of the activated complex.

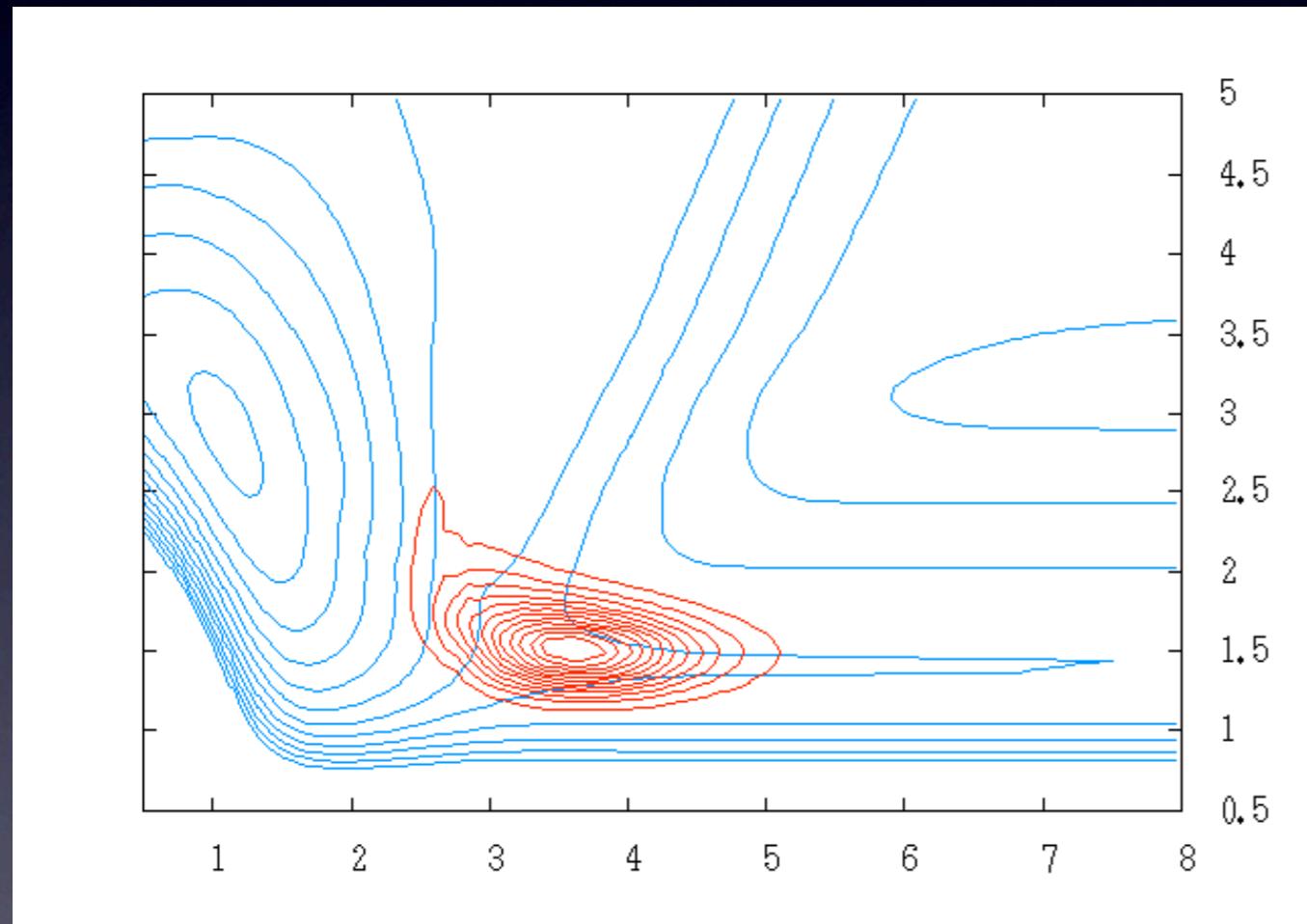
The MCTDH basis is common!!!

Less propagation effort, but  
makes less sense to  
distribute in the Grid.

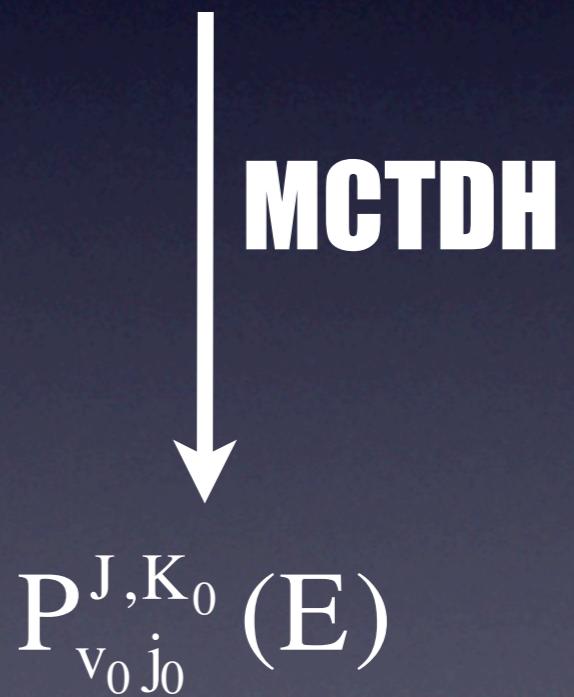
# State Selected MCTDH

Goal: Initial state selected all-J reaction probabilities

$$\Psi(R, r, \theta, \omega_E, t=0) = g_{k_0}(R) \phi_{v_0, j_0}(r) P_{j_0}^{K_0}(\cos \theta) D_{J, K_0}(\omega_E)$$



$$\Psi(v_0, j_0, J, K_0)$$



# State Selected MCTDH

Grid-implementation scheme: similar to std-WP

Loop over J

Loop over  $K_0$

Loop over  $v_0$

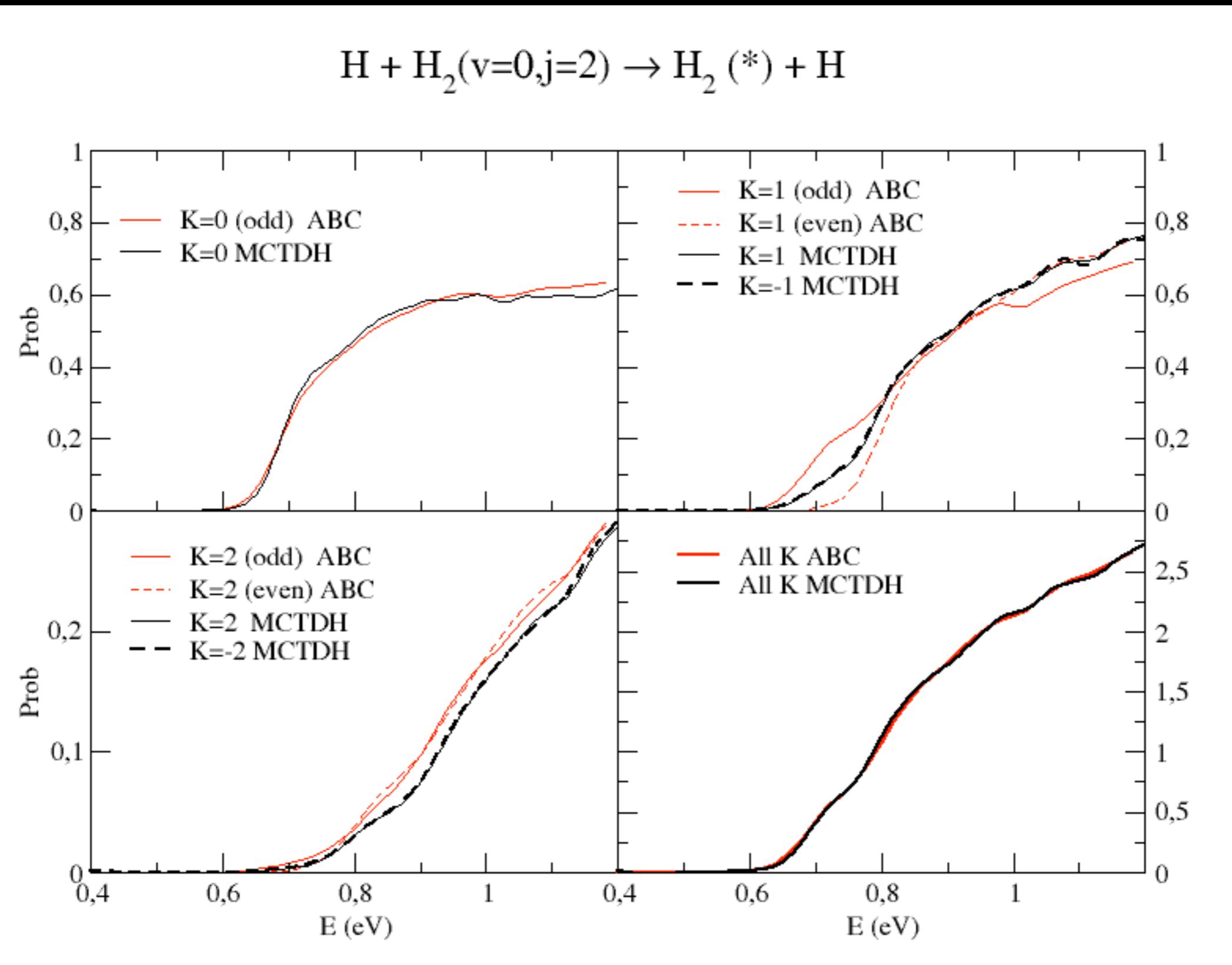
Loop over  $j_0$

**submit job to CE**

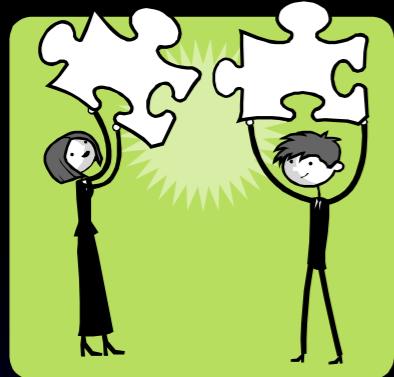
Should be easy to implement using existing php scripts

Work in progress: Statistical sampling to eliminate J and K loops

# State Selected MCTDH: First results



# Conclusions



**Grid-MCTDH & Grid-Fluss:**  
tools for polyatomic reaction simulation

- all-J Q-dyn on the grid routinely executed
- Sophistication of job control scripts (in progress...)
- Common data format for Q-dyn?
- Visualization tools?

# People and institutions acknowledged

Marc Moix Teixidor (PCB-Barcelona)  
Dr. Noelia Faginas Lago (Perugia)  
Prof. Uwe Manthe (Bielefeld)  
Prof. Antonio Laganà (Perugia)



Parc Científic de Barcelona  
Universitat de Barcelona  
Università di Perugia



CTQ2008-6000



COST-D37: GRIDCHEM



Allocated computer time