# Asymptotic basis set semiclassical coupled channel calculations for ion-atom collisions: background and test cases at intermediate impact energy

Alain Dubois and Nicolas Sisourat

Laboratory of Physical Chemistry – Matter and Radiation
UMR 7614 Sorbonne Université - CNRS

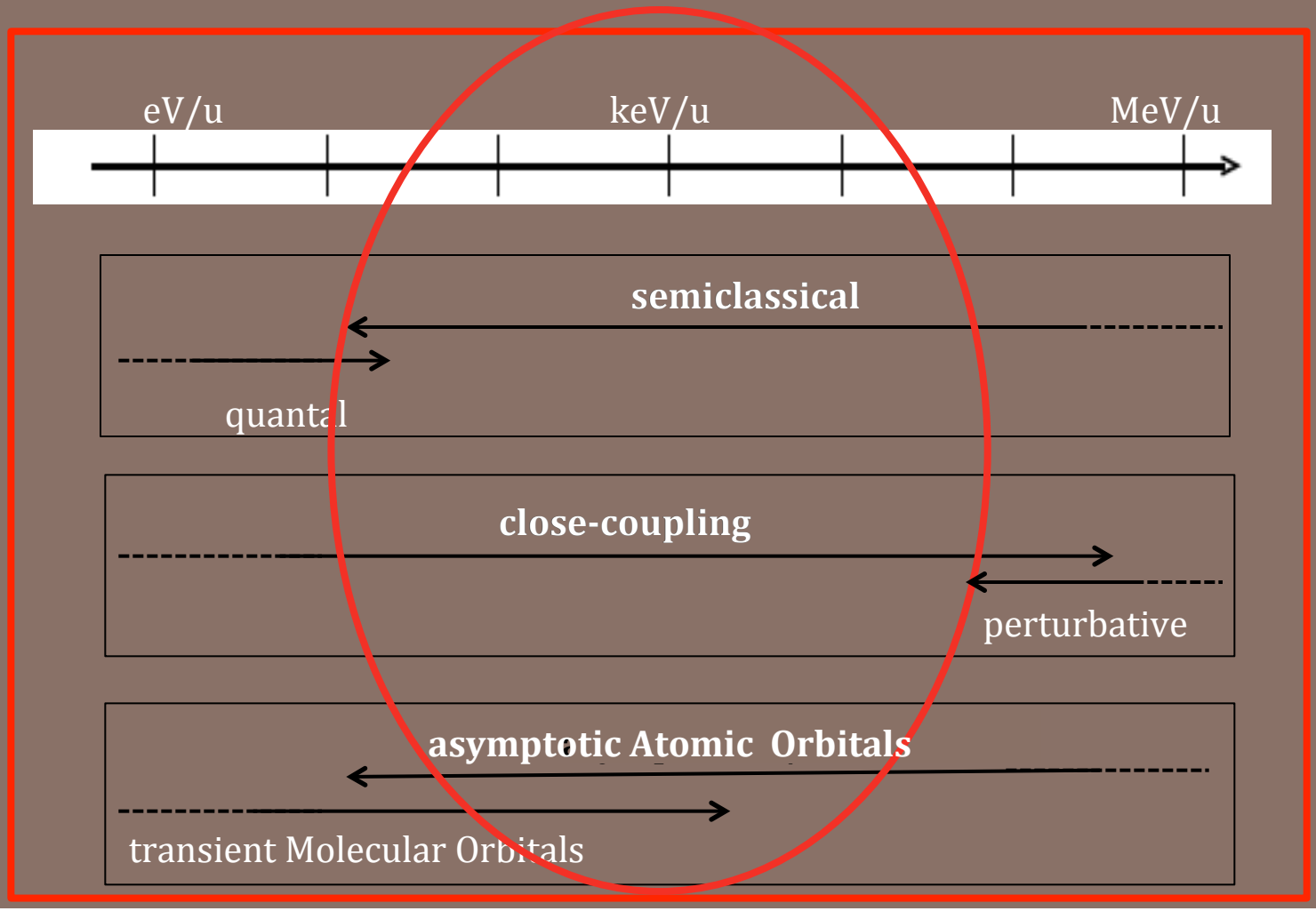
- ✓ the understanding and modeling of
  - the ultra-fast electronic dynamics in atomic and molecular systems
  - the interplay of the many open channels
  - …including the atomic/molecular electronic spectrum (+ somehow the continuum) …
  - … and the static and dynamical electronic correlations
- ✓ Fundamental aspects of dynamical few-body quantum systems and computations of cross sections for applications

$$P + T \rightarrow \begin{cases} P^* + T^* \\ P^- + T^+ \\ P + T^+ + e^- \end{cases}$$

**excitation**

**electron capture / electron transfer**

**ionisation**





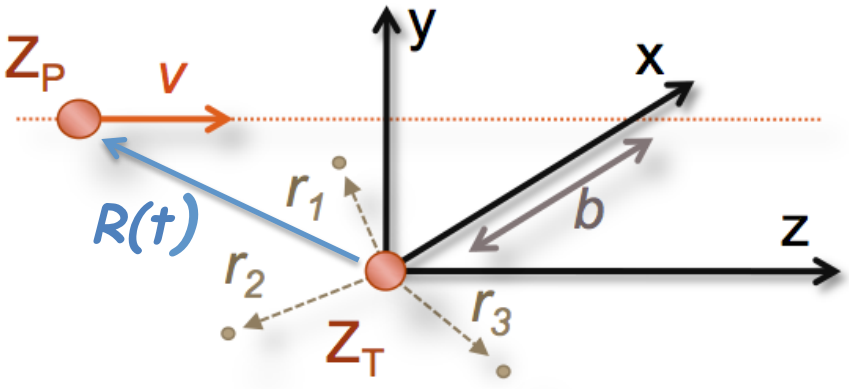

## APPROXIMATE REGIONS OF VALIDITY OF VARIOUS THEORETICAL APPROACHES

## THEORETICAL TREATMENT:

- **Semi-classical approach**

$$\vec{R}(t) = \vec{b} + \vec{v}\, t$$

*impact parameter approximation*




- **Sudden approximation** (for molecular targets)

$\Rightarrow$ Eikonal equation

$$\left[H_{el}(t) - i\frac{\partial}{\partial t}\right]\Psi(\{\vec{r}_i\}, t) = 0$$

with

$$H_{el}(t) = \sum_i \left[-\frac{1}{2}\Delta_i - \frac{Z_t}{r_i} - \frac{Z_p}{|\vec{r}_i - \vec{R}(t)|}\right] + \sum_{i<j}\frac{1}{r_{ij}}$$

## THEORETICAL TREATMENT:

and $$\Psi(\{\vec{r}_i\},t) = \sum_k a_k(t) \;\; \Phi_k^T(\{\vec{r}_{i'}\},t) \;\; \Phi_k^P(\{\vec{r}_{j'\neq i'}\},t)$$

expansion on a set of asymptotic target and ETF-augmented projectile states

$$\Phi_k^T(\{\vec{r}_{i'}\},t) = \phi_k^T(\{\vec{r}_{i'}\})\; e^{-i\epsilon_k^T t}$$

$$\Phi_k^P(\{\vec{r}_{j'}\},t) = \phi_k^P(\{\vec{r}_{j'}\})\; e^{-i\epsilon_k^P t} \qquad \prod_{j'} e^{i\vec{v}.\vec{r}_{j'}} e^{-i\frac{1}{2}v^2 t}$$

$ETF(\{\vec{r}_i\})$

$\phi^{T/P} \quad (\epsilon^{T/P})$

eigenfunctions (eigenvalues)

of the T/P Hamiltonians

## THEORETICAL TREATMENT:

- solve

$$\left[H_{el}(t) - i\frac{\partial}{\partial t}\right]\Psi(\{\vec{r}_i\},t) = 0 \quad \Longrightarrow \quad i\ \dot{\bar{a}} = \bar{\bar{S}}^{-1}\ \bar{\bar{M}}\ \bar{a}$$

with evaluation of all matrix elements, e.g.

$$< i^P\ \ j^P \mid \frac{1}{r_{12}}\ e^{-i\vec{v}.(\vec{r}_1+\vec{r}_2)} \mid k^T\ \ l^T >$$

- to compute probability and cross sections

$$P_{ij}(v,b) = \lim_{t\to+\infty} |a_j(b,v,t)|^2$$

$$\sigma_{ij}(v) = 2\pi \int_0^\infty P_{ij}(v,b)\ b\ db$$

and also differential cross sections ...

## THEORETICAL TREATMENT:

and $$\Psi(\{\vec{r}_i\},t) = \sum_k a_k(t)\ \ \Phi_k^T(\{\vec{r}_{i'}\},t)\ \ \Phi_k^P(\{\vec{r}_{j'\neq i'}\},t)$$

expansion on a set of asymptotic target and ETF-augmented projectile states

$$\Phi_k^T(\{\vec{r}_{i'}\},t) = \phi_k^T(\{\vec{r}_{i'}\})\ e^{-i\epsilon_k^T t}$$

$$\Phi_k^P(\{\vec{r}_{j'}\},t) = \phi_k^P(\{\vec{r}_{j'}\})\ e^{-i\epsilon_k^P t} \quad \prod_{j'} e^{i\vec{v}.\vec{r}_{j'}} e^{-i\frac{1}{2}v^2 t}$$

$ETF(\{\vec{r}_i\})$

$\phi^{T/P}\ \ (\epsilon^{T/P})$

eigenfunctions (eigenvalues)

of the T/P Hamiltonians

- **Description of the multi-electronic states**
  - developed on products of Gaussian Type Orbitals

$$|\phi> = \sum_{ijk} C_{ijk}|ijk> \quad \text{with} \quad |ijk> = G_i(\vec{r}_1)\ G_j(\vec{r}_2)\ \ldots$$

  - which should be spin-adapted (in our spin-free approach)

*implemented straightforwardly for 2 electrons but also for not separable $N_e$ > 2 electrons systems*

- example for $H^+$ - Li collision system which should describe

(when taking into account the 3 $e^-$ ) :

- ✓ elastic/excitation $H^+ + Li \rightarrow H^+ + Li^*$

$$\phi^{Li}(1s^2 2s^1\ ^2S), \phi^{Li}(1s^2 2p^1\ ^2P), ..., \phi^{Li}(1s^1 2s^2\ ^2S), ... \qquad \phi^{TTT}$$

- ✓ single transfer $H^+ + Li \rightarrow H^* + Li^+$

$$\phi^{Li^+}(1s^2\ ^1S)\phi^H(2s\ ^2S), ..., \phi^{Li^+}(1s2s\ ^1S)\phi^H(2s\ ^2S), \phi^{Li^+}(1s2p\ ^3P)\phi^H(2p\ ^2P), ... \quad \phi^{TTP}$$

- ✓ double transfer $H^+ + Li \rightarrow H^- + Li^{2+}$

$$\phi^{Li^{2+}}(1s\ ^2S)\phi^{H^-}(1s^2\ ^1S), ... \qquad \phi^{TPP}$$

- the total system is doublet (and stays doublet) but both partners change spin multiplicity during the collision $\Longrightarrow$ complexity and CPU
- $\Longrightarrow$ Group theory and Young diagrams ... to minimize $|\phi>=\sum_{ijk} C_{ijk}|ijk>$

- all together

$$\Psi(\{\vec{r}_i\},t) = \sum_k c_k^{TTT}(t)\ \phi_k^{TTT}(\{\vec{r}_i\})\ e^{-i\epsilon_k^{TTT}t}\quad ETF^{TTT}(\{\vec{r}_i\})\quad Li^* + H^+$$
$$+\sum_k c_k^{TTP}(t)\ \phi_k^{TTP}(\{\vec{r}_i\})\ e^{-i\epsilon_k^{TTP}t}\quad ETF^{TTP}(\{\vec{r}_i\})\quad Li^{+*} + H^*$$
$$+\sum_k c_k^{TPP}(t)\ \phi_k^{TPP}(\{\vec{r}_i\})\ e^{-i\epsilon_k^{TPP}t}\quad ETF^{TPP}(\{\vec{r}_i\})\quad Li^{2+*} + H^{-*}$$

with states of positive energies …

for $N_T = N_P = 14$ *(5 "s"+3*3 "p" GTO)* … and ≈ 400 states (cut-off in energy)

our philosophy : keep the same basis set (GTO, states) for all considered energies

*matrix sizes in non adapted basis for :* $(N_T+N_P)^6 \sim 5\ 10^8$

*matrix sizes in adapted basis :* $(N_T\,(N_T^2-1)/3 + N_T^2 N_P + N_T N_P (N_P+1)/2)^2 \sim 3\ 10^7$

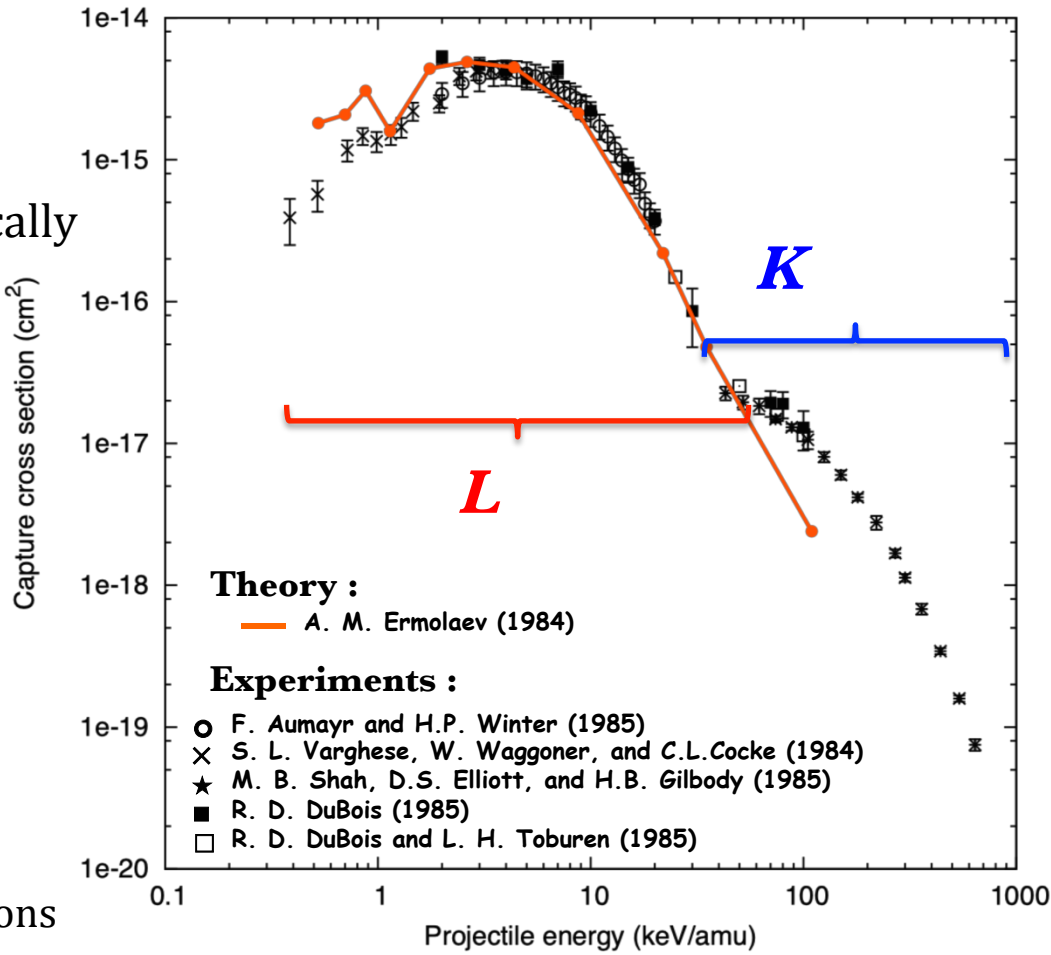
$H^+ + Li(1s^2 2s^1)$ → $H + Li^+(1s^2)$

$H + Li^+(1s^1 2s^1)$

## Why ?

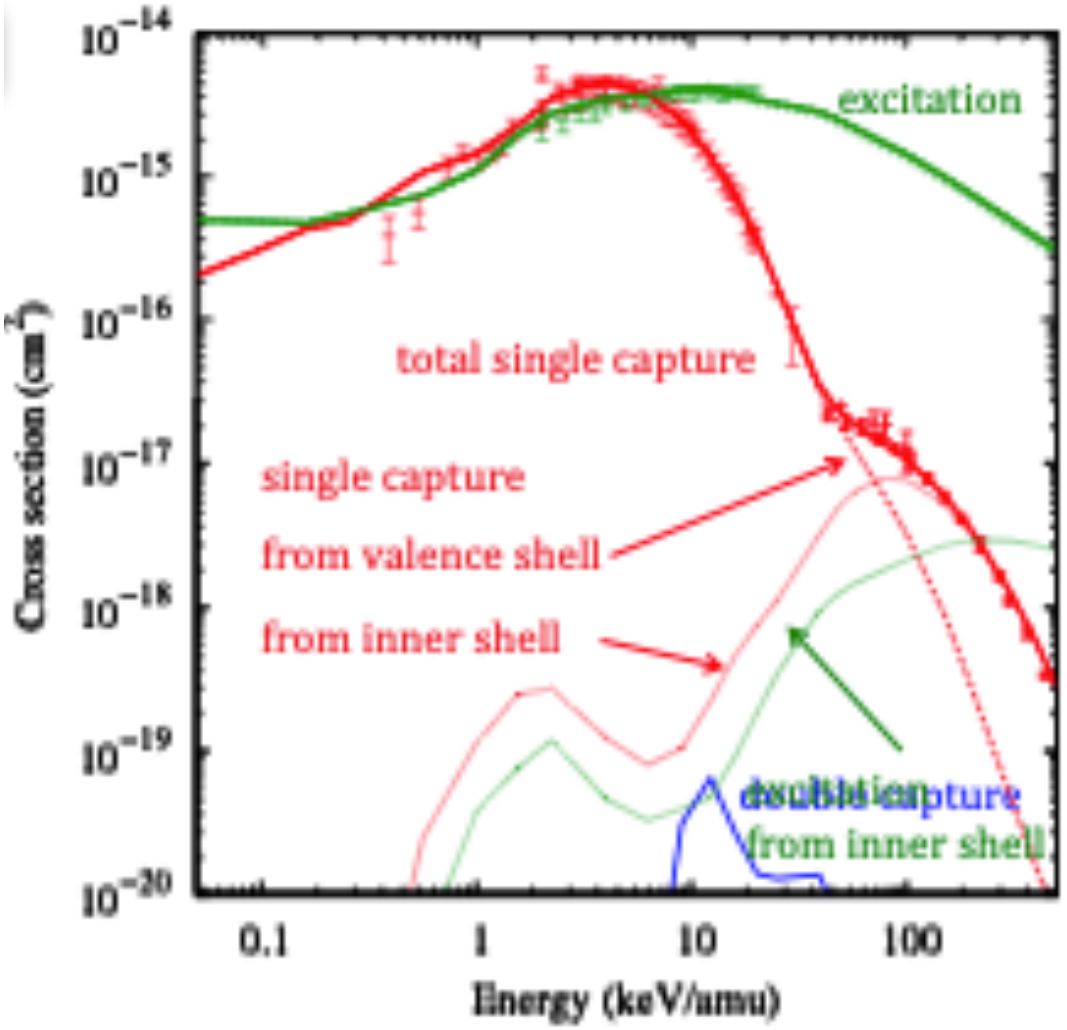
- studied, experimentally and theoretically but never completely nor over a wide energy domain
- a genuine 3-electron system with low T and P charges
- good candidate to check :

  - processes from valence or inner-shells
  - electronic correlation effects
  - frozen core/model potential approximations



## Comparison with experiments

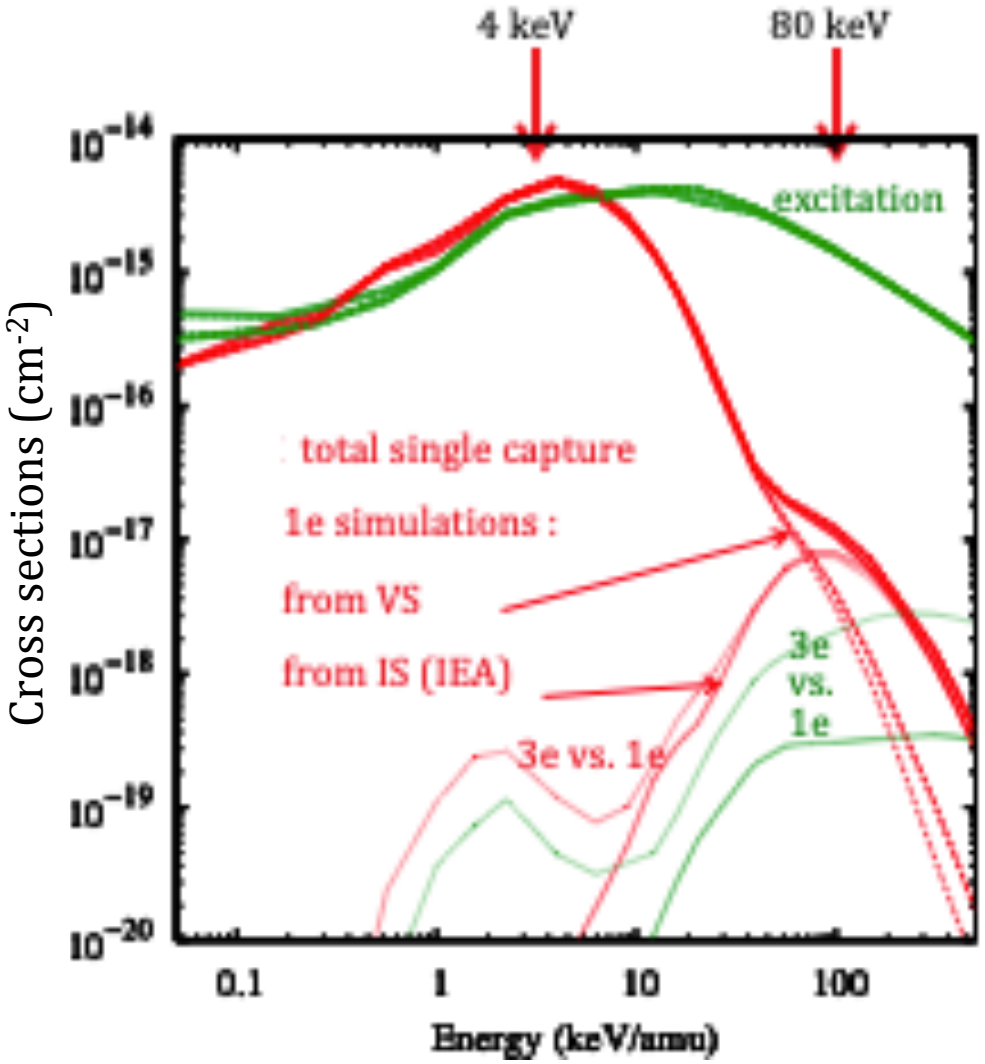
- ✓ Very good agreement !
- ✓ 1st time processes from inner-shell (IS) and valence-shell (VS)



# RESULTS 2 : GLOBAL PROCESSES (VS VS. IS)

Comparison with 1-electron simulations
(model potential)

- ✓ weak correlation effects
- ✓ model potential validated but
  - 2 independant 1e calc. + Independent Electron Approx
  - 1e calc. fail to reproduce peak at ≈4 keV for capture and excitation



$H^+ + H^-(1s^2)$ → $H(n) + H$ SEC (neutralization)

→ $H(n) + H^*$ Transfer-Excitation

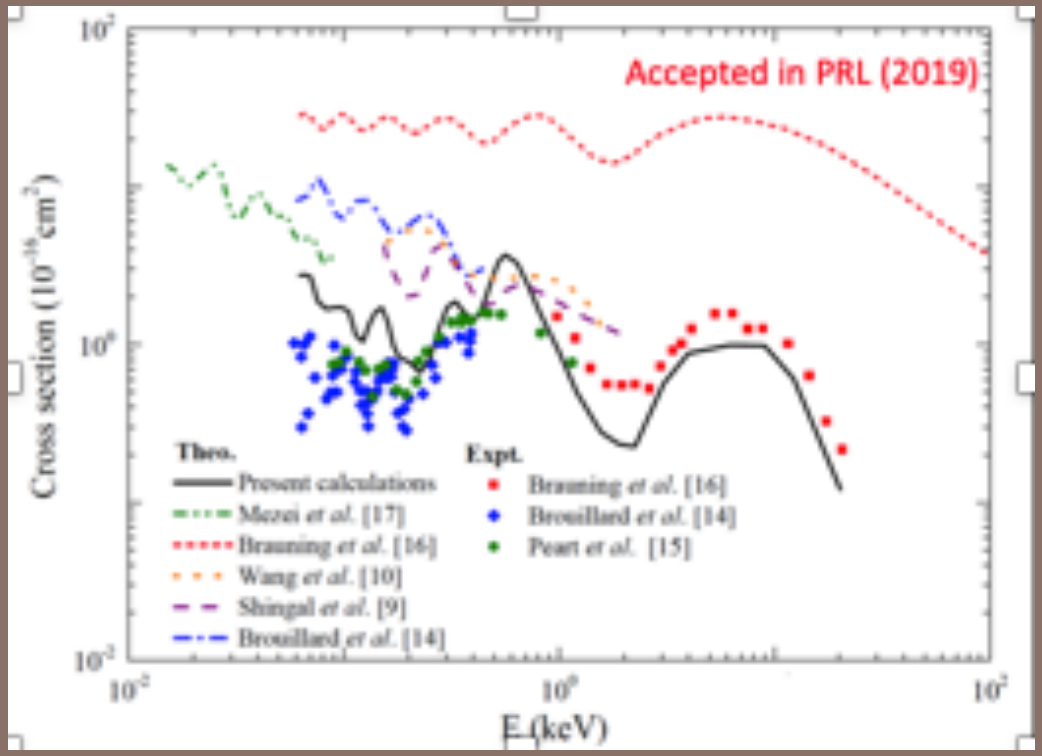
→ $H^-(1s^2) + H^+$ DEC

→ $H^+ + H^+ + e$ ionisation

Why ?

- relative (physical) stiffness of the equations
- importance of correlation …
- convergence of the basis in two directions …

DEC cross sections




Junwen Gao et al,
PRL accepted (2019)

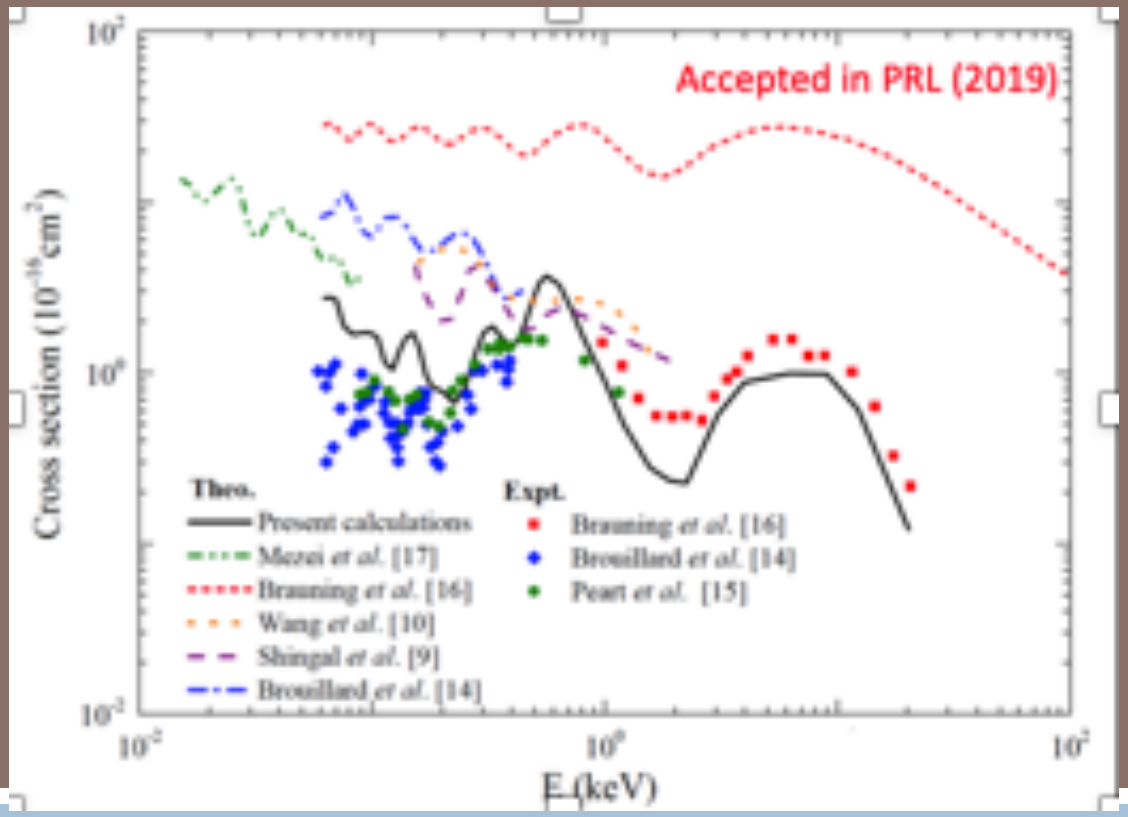
Convergence :

- GTO basis 1 : 11 « s » + 8*3 « p » + 2*5 « d »
- but also 9 « s » + 6*3 « p » + 1*5 « d »
- and 11 « s », 8*3 « p » + 4*5 « d »
- for GTO basis 1 : 1977 states, with 1446 above ionisation threshold (1425, 3725)

for DEC
10% at 0.2 keV and
30% for lower ones

and for ionization

ionization cross sections

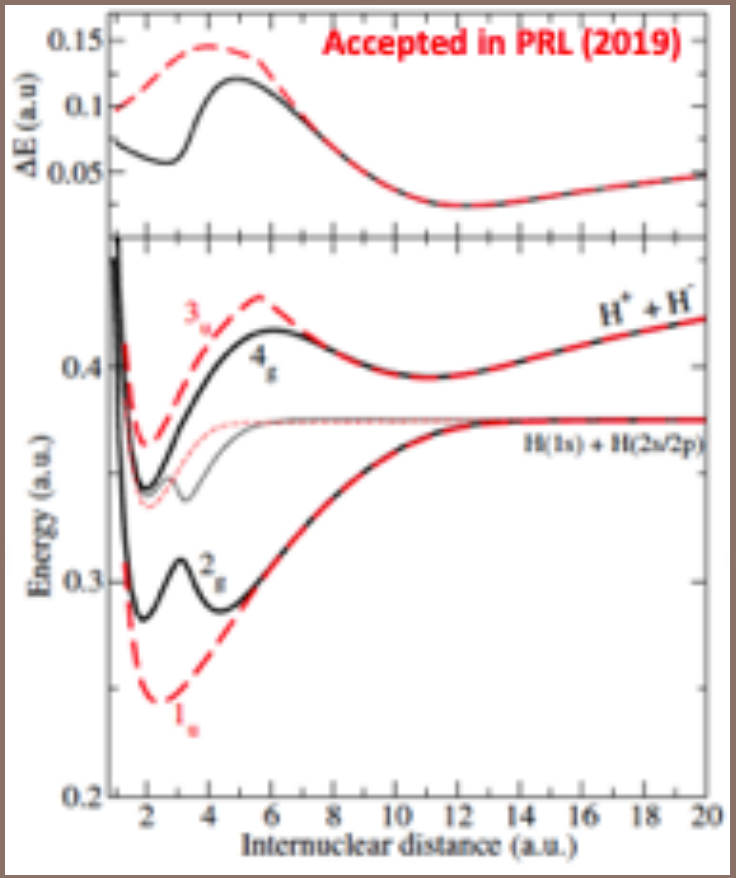


Convergence and oscillations

in-and-out Rosenthal's model

$$T = \frac{\pi}{\int_{Ri}^{Re} \Delta E dR}$$

when plotted as $1/v_P$




Molecular energy curves of importance for DEC process

$H + H \rightarrow H^* + H^*$ excitation and di-excitation

same method but 20 years ago we used

Paleolithic CC !

- exact bound H-states
- with full calculation of all coupling (including correlation)
- H(n=1,2,3) on both centers,
- i.e. including single excitation and di-excitation
  H(n=2)+H(n=2) and H(n=2)+H(n=3)

Hansen and Dubois, JPB 31 L861 (1998)

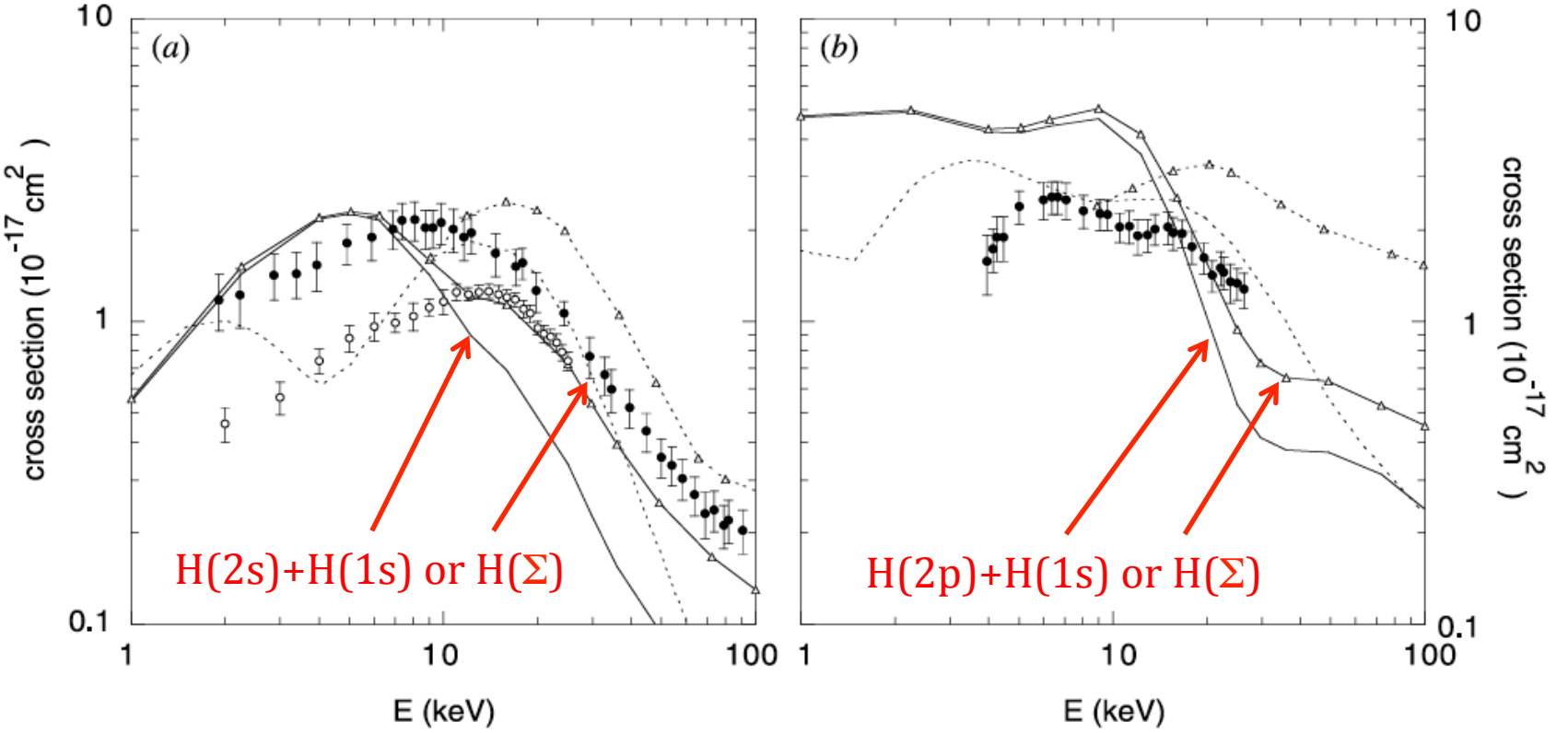



**Figure 1.** (*a*) Spin-averaged cross sections for H(2s) excitation. Theory: ——, present calculations for SE 2s, 1s and TE 2s, Σ (—Δ—); - - - -, results from Shingal *et al* [10] for SE 2s, 1s and TE 2s, Σ (- -Δ- -). Experiment for TE 2s, Σ: ●, Morgan *et al* [7]; ○, Hill *et al* [5]. (*b*) Spin-averaged cross section for H(2p) excitation. Theory, same as in (*a*) for H(2p). Experiment, for TE 2p, Σ: ●, Morgan *et al* (1974).

Hansen and Dubois, JPB 31 L861 (1998)

## Bronze age CC !

$H + H \rightarrow H^* + H^*$ excitation and di-excitation

$\rightarrow H^+ + H^-$ transfer

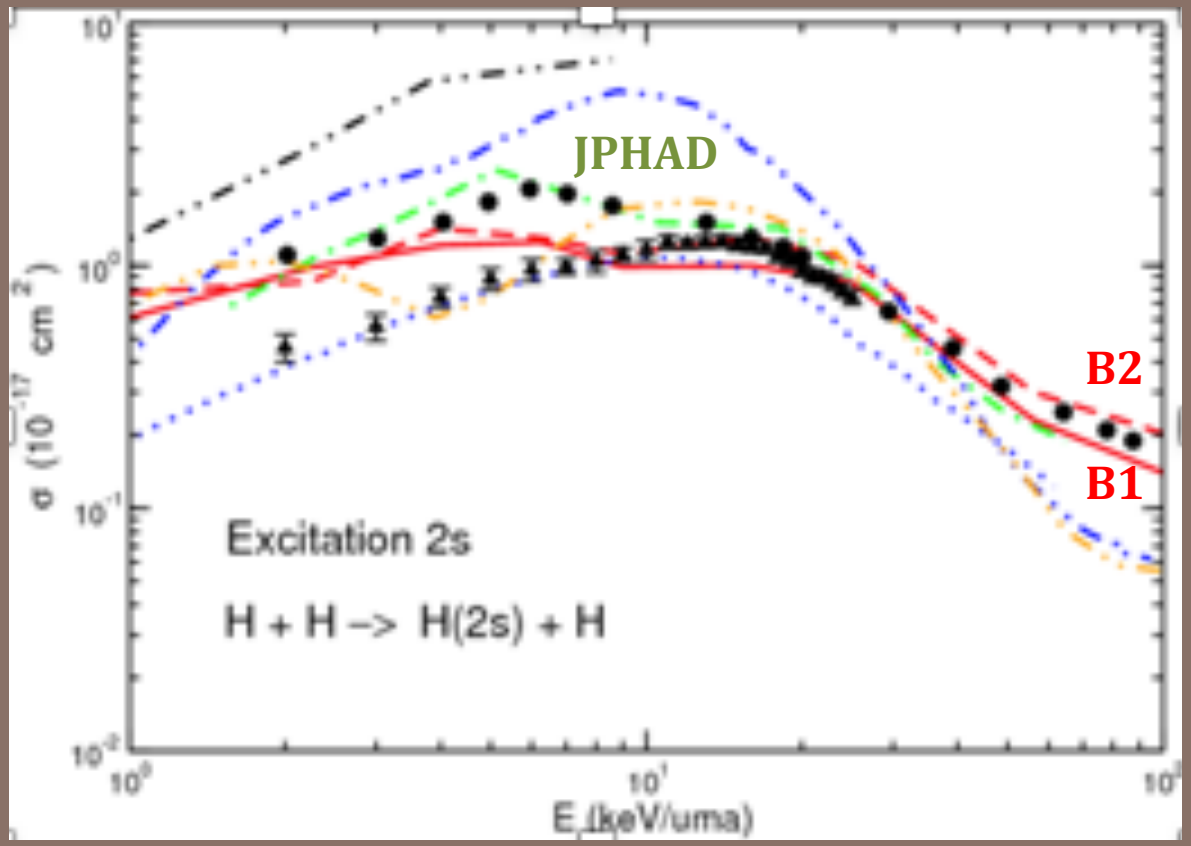
$\rightarrow H^+ + H^+ + e$ ionisation

B1 on each center : 9 GTO « s » and 6 * 3 GTO « p »
B2 " " 12 " " " 7 " "

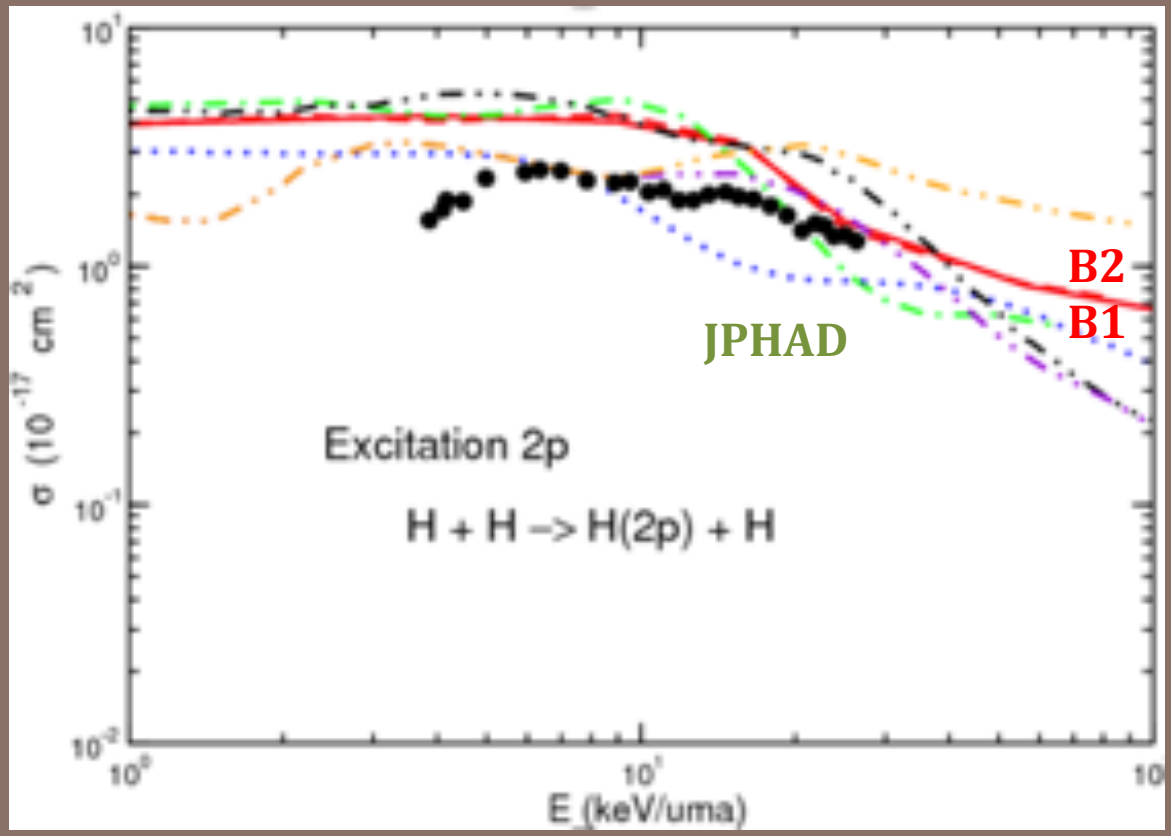
B1 includes 135 states H*H and $H^-$ (including pseudo-states)

B2 " 189 " " " "

Nicolas Sisourat PhD thesis (2008)

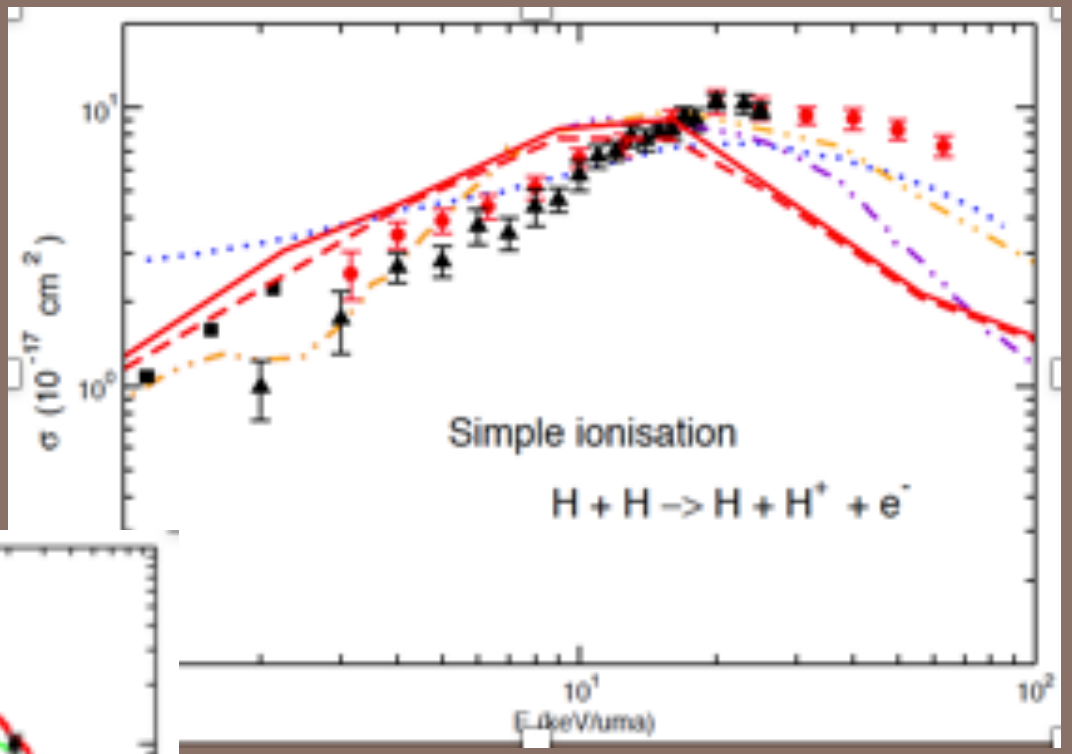


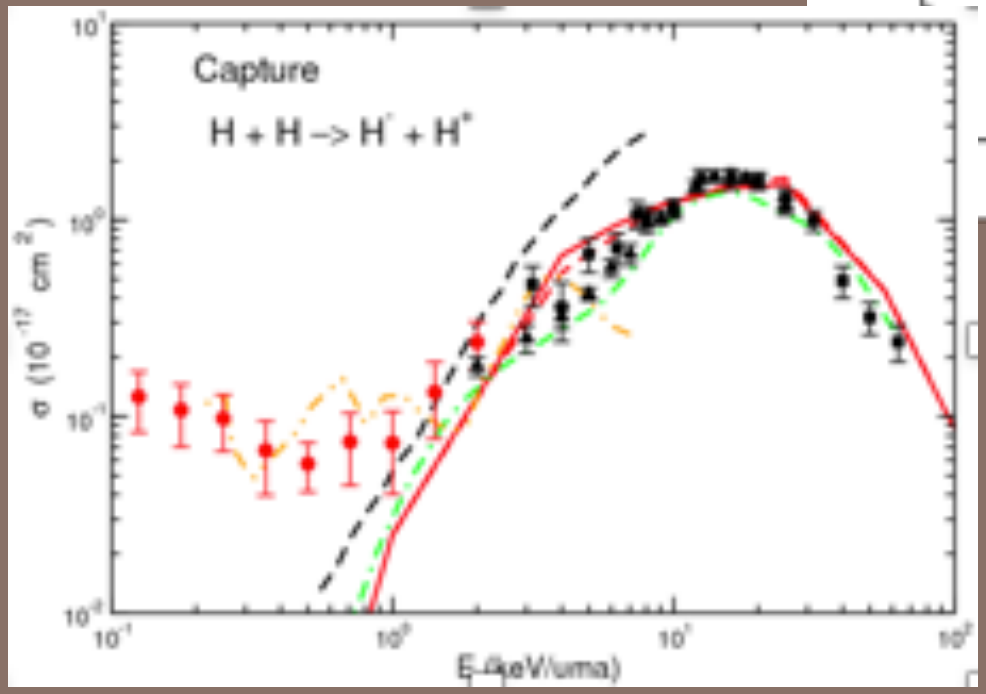

Nicolas Sisourat PhD thesis (2008)




3s, 3p, 4s and 4p excitation

Nicolas Sisourat PhD thesis (2008)




Nicolas Sisourat PhD thesis (2008)

$H^+ + H(nlm) \rightarrow H(n'l'm') + H^+$ SEC

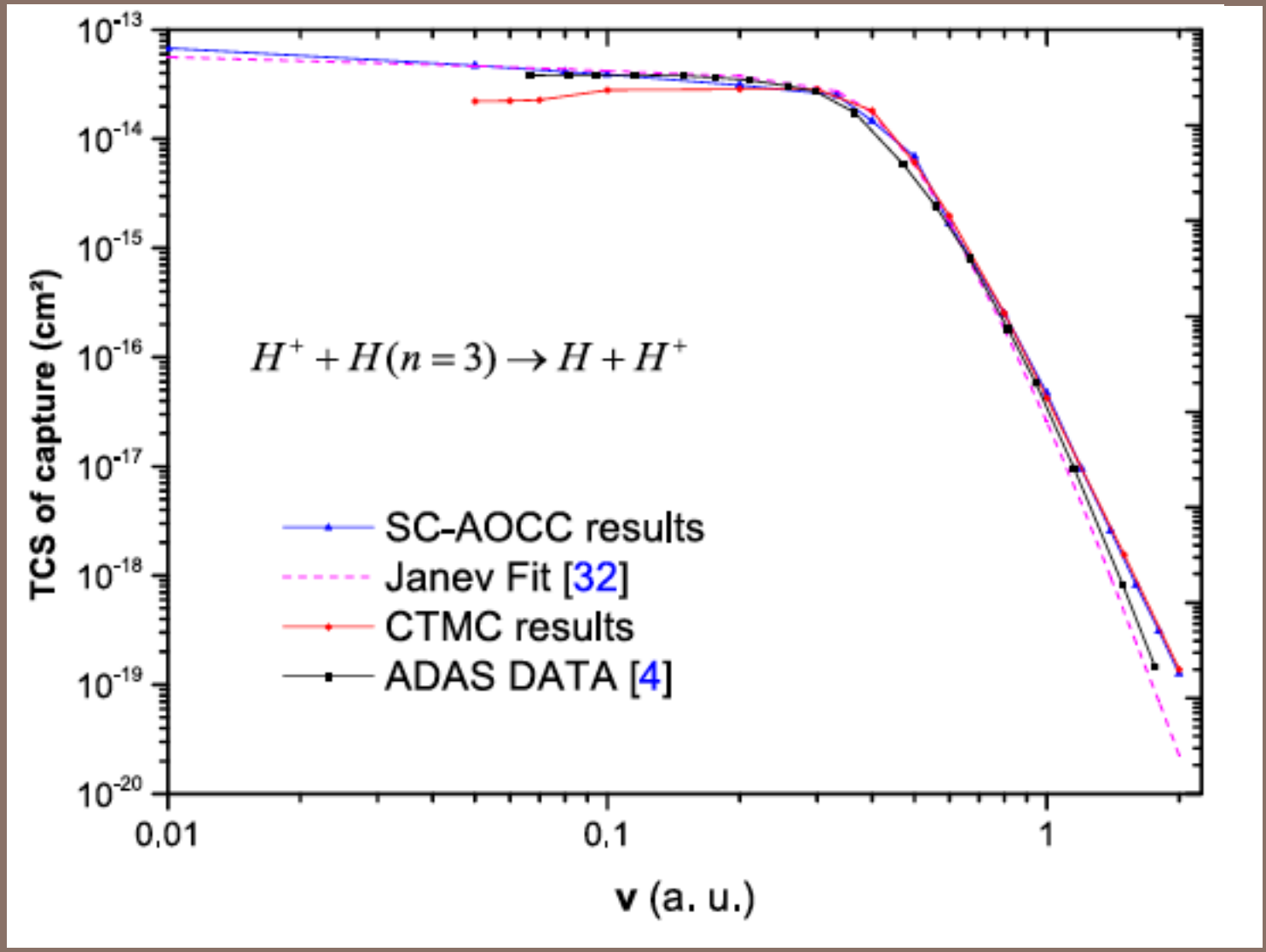
- very rare studies so far …
- quantities of computations (10 for only n=1 to n=3)
- many open channels
- so that convergence issues
  - ✓ the basis should include large n' and so large l'
  - ✓ therefore very large number of GTO
  - ✓ time propagations are very long

Convergence :

- s , p, d, f , g GTO on each center
- Actual basis set : 160 states on each center (OK up to n=7)
- Test basis set: 191 states on each center

- for H(n=1,2) initial states : < 3% for shell capture and for all energies 2.5ev/u-100keV/u
- for H(n=3) initial states : 4% for highest and lowest energies
  10% for intermediate energies

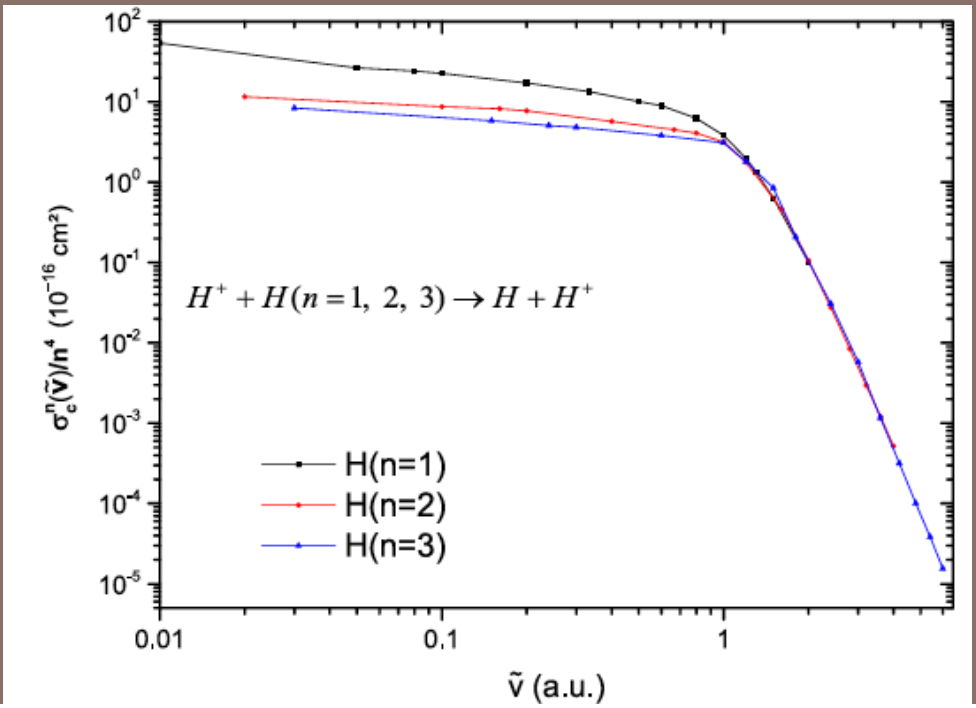
we performed also microcanonical CTMC calculations




A. Taoutioui, JPB 51, 235202 (2018)

## Scaling laws

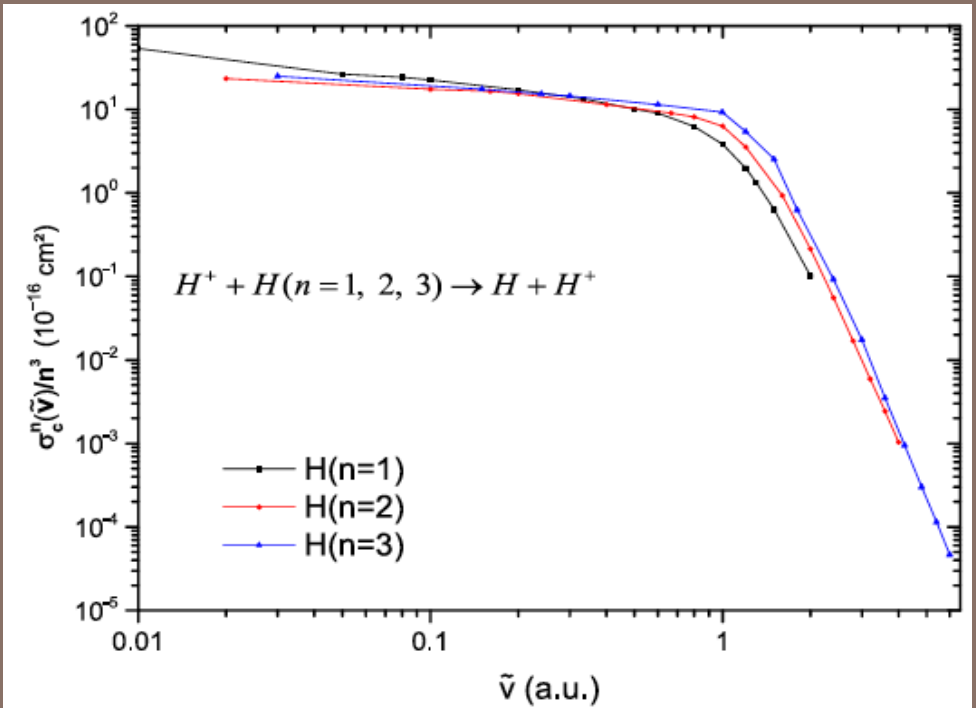
- impact velocity : $v_{sc} = v/v_e^{(n)} \approx v\,n$
- $n^4$ scaling of SEC TCS at high energies (geometrical, as CTMC)




A. Taoutioui, JPB 51, 235202 (2018)

# Scaling laws

- impact velocity : $v_{sc} = v/v_e^{(n)} \approx v\,n$
- $n^4$ scaling of SEC TCS at high energies (geometrical)
- $n^3$ scaling of SEC TCS at low energies

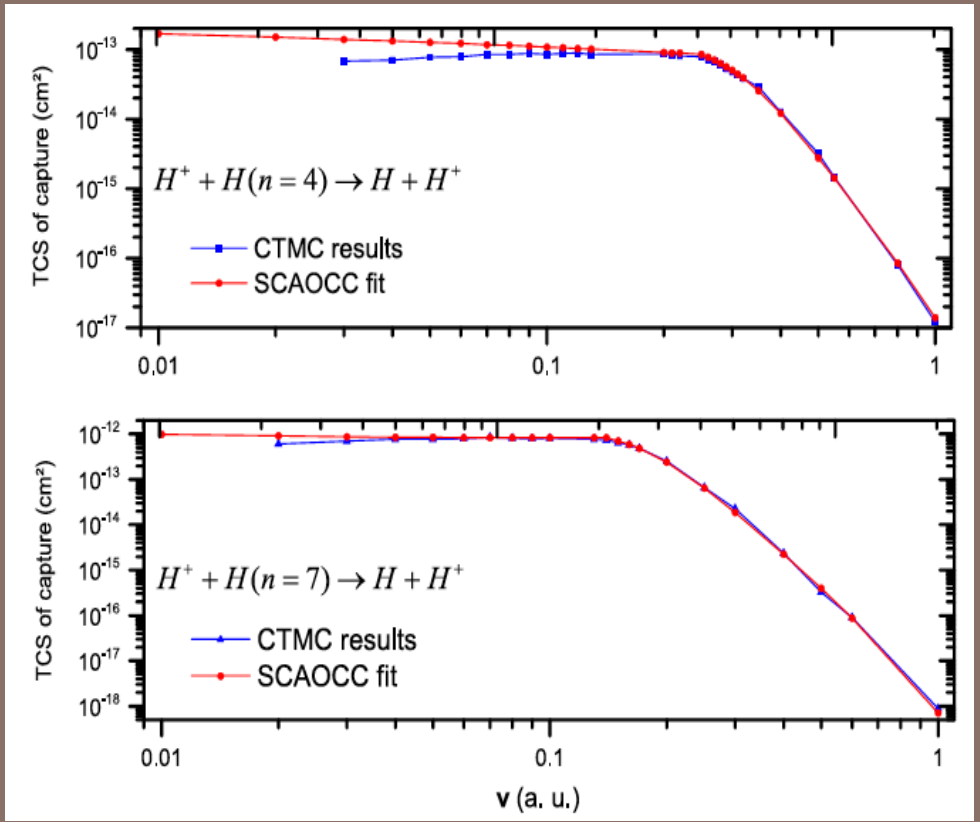



A. Taoutioui, JPB 51, 235202 (2018)

# Scaling laws

- impact velocity : $v_{sc} = v/v_e^{(n)} \approx v\,n$
- combined scaling

$$\sigma_c^n(v) = n^3(1 - g^n(v))\mathcal{A}^n(v) + n^4 g^n(v)\mathcal{B}^n(v)$$




A. Taoutioui, JPB 51, 235202 (2018)

The field is old but just starting for applications : **Renaissance**

there exist few fantastic codes/groups worldwide which try to do the same, with different independent close-coupling approaches (QM, SC MO, SC AO)

- but they face
  - ✓ different numerics
  - ✓ different convergence issues (also including overcompletness)
  - ✓ different range of validity
- For (quasi) one-electron systems we can go to the end of it

  but multi-active electron systems are still very challenging …

WP : … $C^{6+}$-H (JPB 2000), $Li^{3+}$ - H (JPB 2016, Nicolas), $C^{4+}$ - He (PRA 2017)

Jan Petter Hansen

Jérémie Caillat

Nicolas Sisourat

Gabriel Labaigt

Junwen Gao