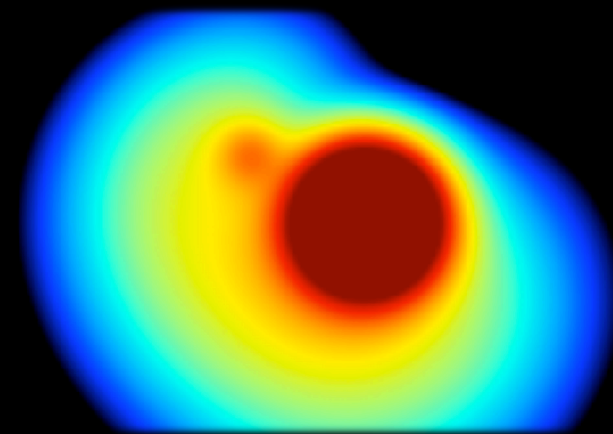
Close coupling CI-approach of atomic and molecular collisions: new perspectives on inner-shell processes in H+ - Li



GDR CORRÉLATION 29-11- 2013

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I. Context

The system:

Atomes, molecules, neutral or charged:

- v ~ [0.02-10] u.a. (1u.a ~2 10^6 m/s)
- E ~ 50eV - 1 MeV

$\longrightarrow$ not thermal, nor reactive, nor subatomic …

Study of electronic processes:

- Excitation : $H^+ + H \rightarrow H^+ + H^*$
- Ionisation : $H^+ + H \rightarrow 2H^+ + e^-$
- Capture : $H^+ + H \rightarrow H^* + H^+$

Observables:

total cross sections $\sigma(v)$

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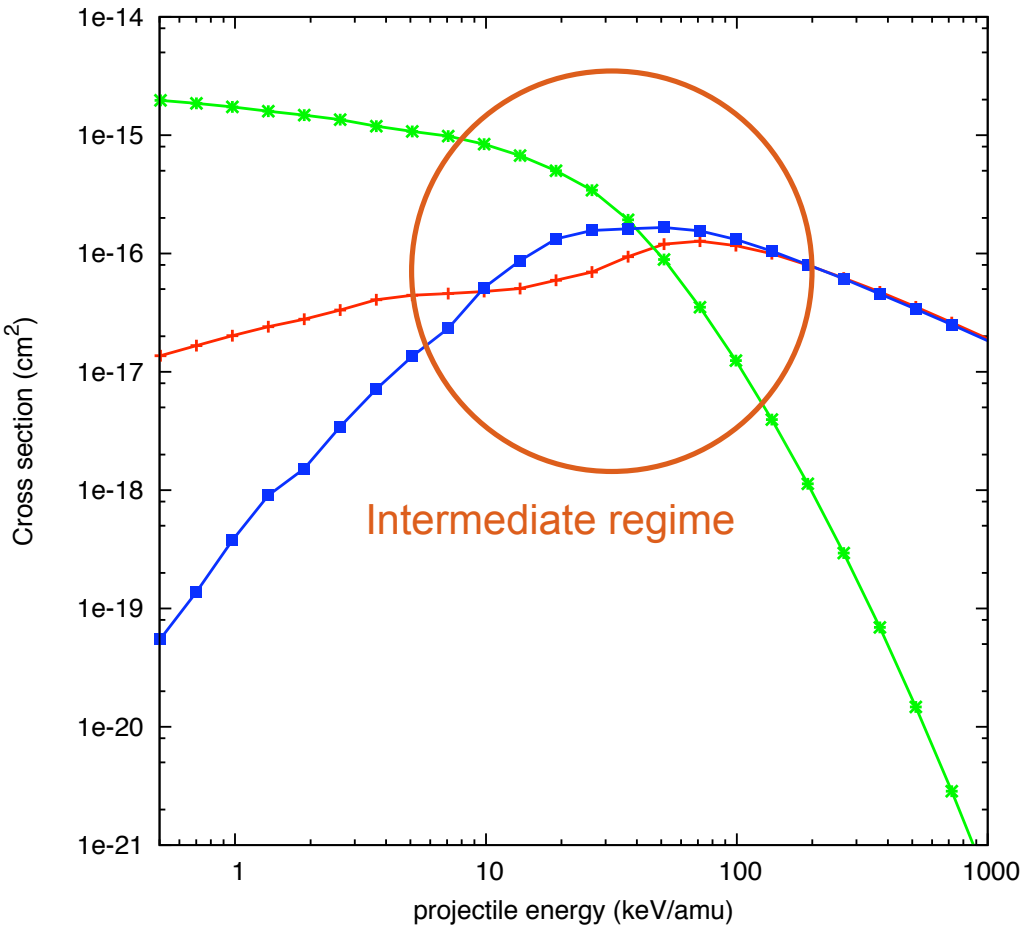

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Applications:

Plasma diagnostics: interstellar clouds / tokamaks …

Development to biological molecules: hadrontherapy

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Context, Quantum mechanics:

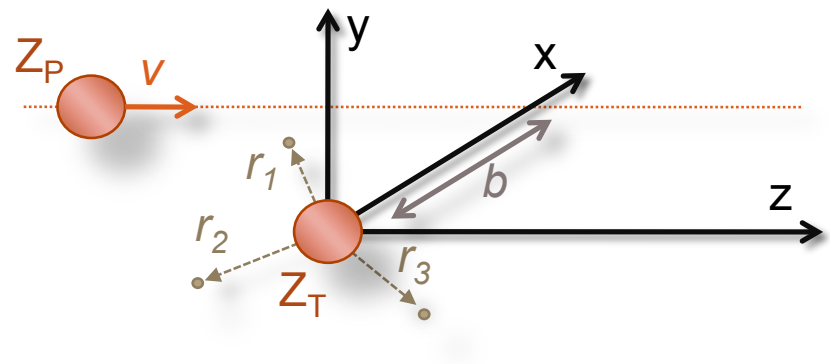
Schrödinger equation independent of time:

$$\hat{\mathrm{H}}^{tot}\Psi^{tot} = \mathrm{E}^{tot}\Psi^{tot}$$

Semi-classical approximation :

- Separation of nuclear and electronic coordinates

- Classical nuclear dynamics: so called impact parameter approximation



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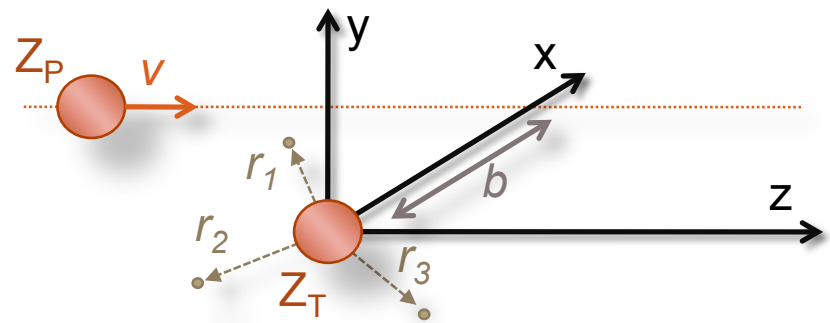

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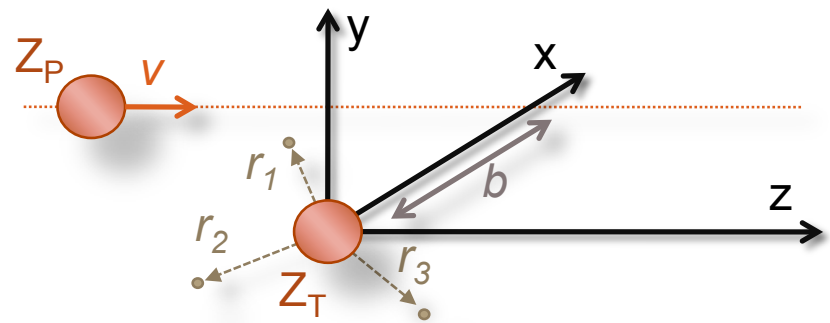

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with

$$\hat{\mathrm{H}}_{el}(t) = \sum_i \left[-\frac{1}{2}\nabla^2 - \frac{\mathrm{Z_T}}{|\vec{r_i}|} - \frac{\mathrm{Z_P}}{|\vec{r_i} - \vec{R}(t)|} \right] + \sum_{i>j} \frac{1}{|\vec{r_i} - \vec{r_j}|}$$

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

III. Benchmark: the proton – lithium collision

The system:

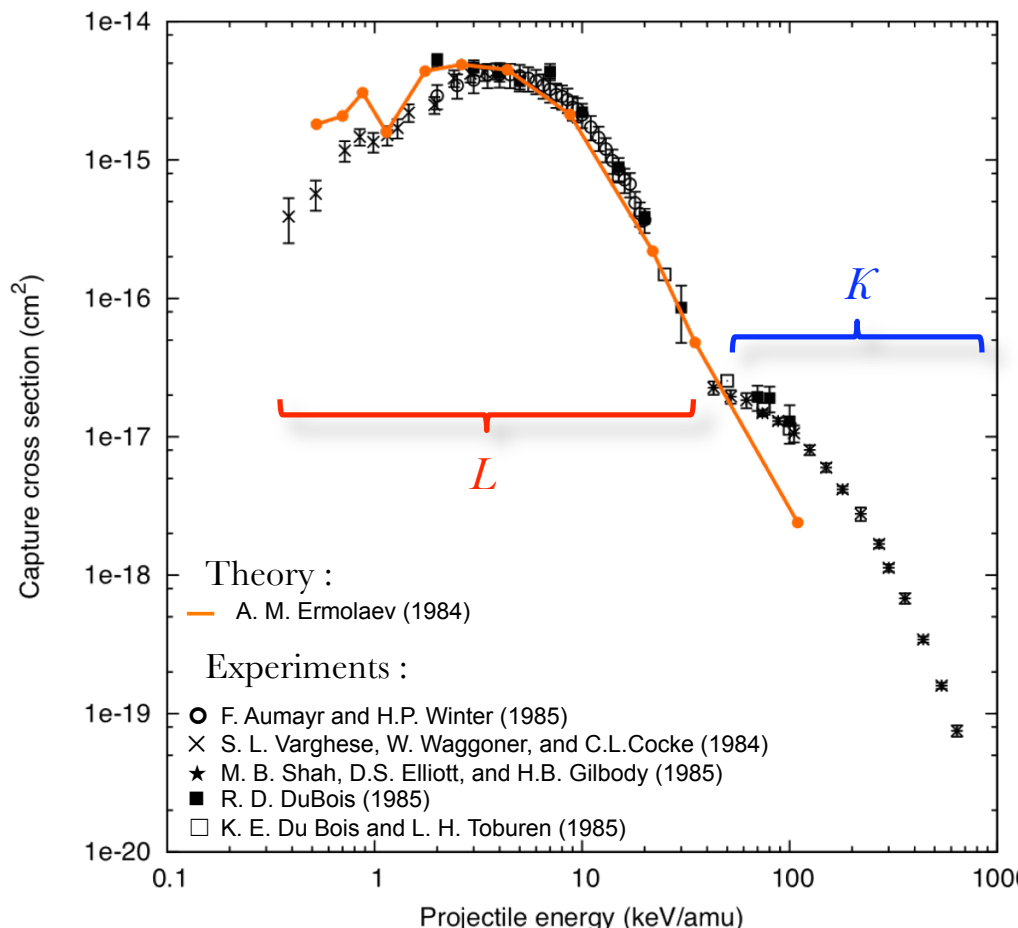
The charge exchange process in:

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

The reasons:

- Extensively studied:
  - but never completely
  - nor in a wide energy/velocity range
- Good candidate to check:
  - electronic correlation effects
  - frozen core/model potential approx.

- Two regimes: K and L



IV. 3 electrons non pertubative resolution

$$[\hat{\mathrm{H}}_{el}(t) - i\partial_t]\Psi(\{\vec{r_i}\}, t) = 0$$

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with $\tilde{\Phi}_j(\{\vec{r_i}\}, t) = \Phi_j(\{\vec{r_i}\})e^{-\mathrm{i}E_j t} \times \mathrm{ETF}$ $\quad \mathrm{ETF} = \prod_i e^{-\mathrm{i}\vec{v}\cdot\vec{r_i}}$

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For: $\mathrm{H}^+ + \mathrm{Li}(1s^2 2s^1) \rightarrow \mathrm{H}^+ + \mathrm{Li}^*$

$\Phi(\{\vec{r_i}\}) := \phi^{\mathrm{Li}}(1s^2 2s^1),\ \phi^{\mathrm{Li}}(1s^2 3s^1),\ \phi^{\mathrm{Li}}(1s^1 2s^1 2p^1)\ \ldots$ $\quad \Phi^{\mathrm{TTT}}$

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V. Description of multi-electronic states

- States are developed on an optimised set of gaussian orbitals:

$$\Phi(\{\vec{r_i}\}) = \sum_{i,j,k} C_{i,j,k}\mathcal{G}_i(\vec{r_1})\mathcal{G}_j(\vec{r_2})\mathcal{G}_k(\vec{r_3}) \qquad \mathcal{G}_i(\vec{r}) = \mathrm{Y}_{l_i,m_i}(\vec{r})e^{-\alpha_i r^2}$$

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- The big question is : How one can obtain spin adapated states ?

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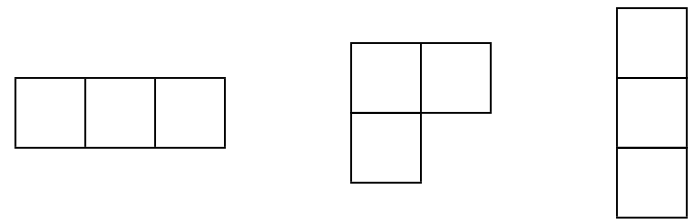
- The solution : Young diagrams and tableaux.

VI. Group theory and Young diagrams

- Young diagrams, for $N_e=3$:



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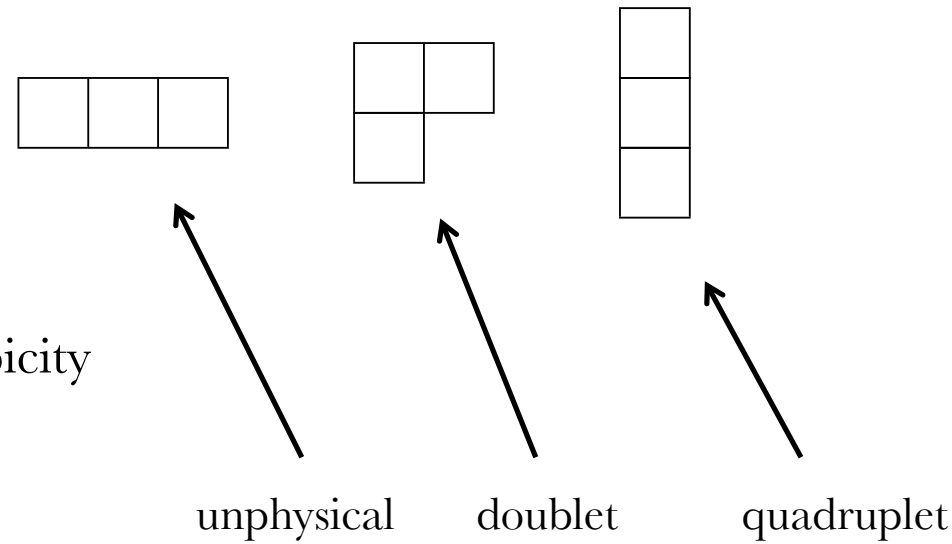

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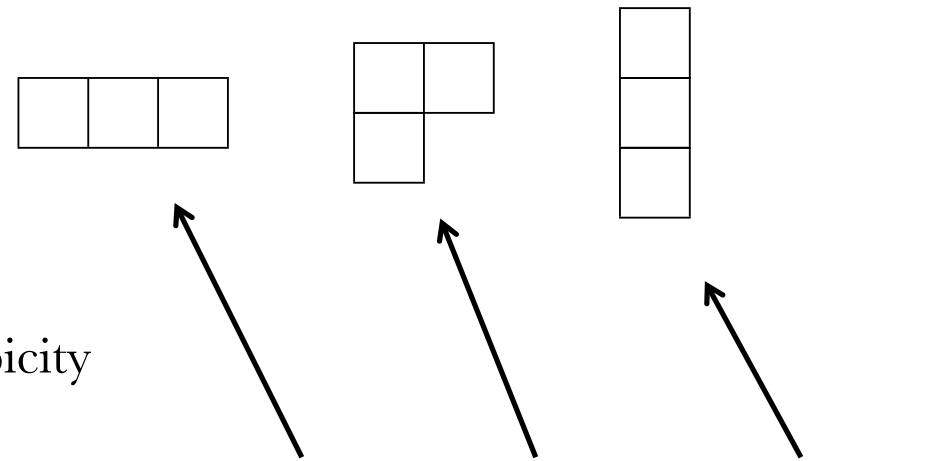

- For doublet states:

$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 \\ \cline{1-1}\end{array} \equiv \begin{cases} \hat{A}_{13}\hat{S}_{12} \\ \hat{S}_{12}\hat{A}_{13} \end{cases}$$

$$\begin{array}{|c|c|}\hline i & j \\ \hline k \\ \cline{1-1}\end{array} \leftrightarrow \text{LIC} : i \leq j,\, i < k$$

$$\phi(\{\vec{r_i}\}) = \sum_{i\leq j, i<k}^{N_G} C_{ijk}\, \hat{A}_{13}\hat{S}_{12}\, |ijk\rangle$$

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- Do not consider inherent properties of asymptotical states: $\langle i'j'k'|\mathrm{H_e}^*|ijk\rangle = 0$

  ⟶ existence of sub-symmetries: singlet+doublet, triplet+doublet for Φ^{TTP} states

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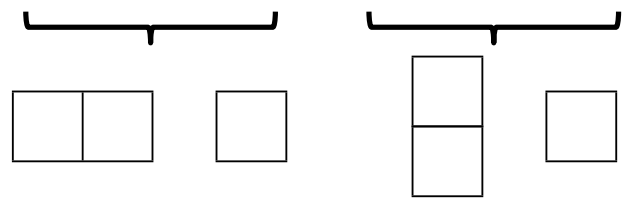
- A diagrammatic solution exists,
let's cut of the primary diagram:



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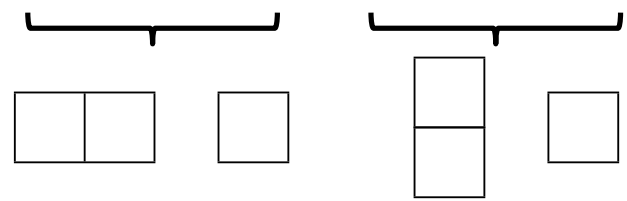

and tableaux:

$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline i & j \\ \hline \end{array}\quad \begin{array}{|c|}\hline 3 \\ \hline k \\ \hline \end{array} \quad \equiv \quad \hat{S}_{12}$$

$$\begin{array}{|c|}\hline 1 \\ \hline 3 \\ \hline \end{array}\quad \begin{array}{|c|}\hline 2 \\ \hline \end{array} \quad \equiv \quad \hat{A}_{13}$$

$$\begin{array}{|c|}\hline i \\ \hline k \\ \hline \end{array}\quad \begin{array}{|c|}\hline j \\ \hline \end{array} \quad \leftrightarrow \quad i<k \in [1,N_T]^2, j \in [1,N_P]$$

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VII. Conclusion of the theoretical part

$$
\begin{aligned}
\Psi &= \sum_j {c_j}^{\mathrm{TTT}}(t){\phi_j}^{\mathrm{TTT}}(\{\vec{r_i}\})e^{-\mathrm{i}\mathrm{E}_j t} \times {\varepsilon_j}^{\mathrm{TTT}}(t) \qquad \varepsilon_j(t) \equiv \mathrm{ETF} \\
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- matrix sizes in non adapted basis for $N_T = N_P = 14$, $(N_T+N_P)^6 \sim 5\ 10^8$
- matrix sizes in adapted basis $(N_T(N_T^2\text{-}1)/3 + N_T^2N_P + N_TN_P(N_P+1)/2)^2 \sim 3\ 10^7$

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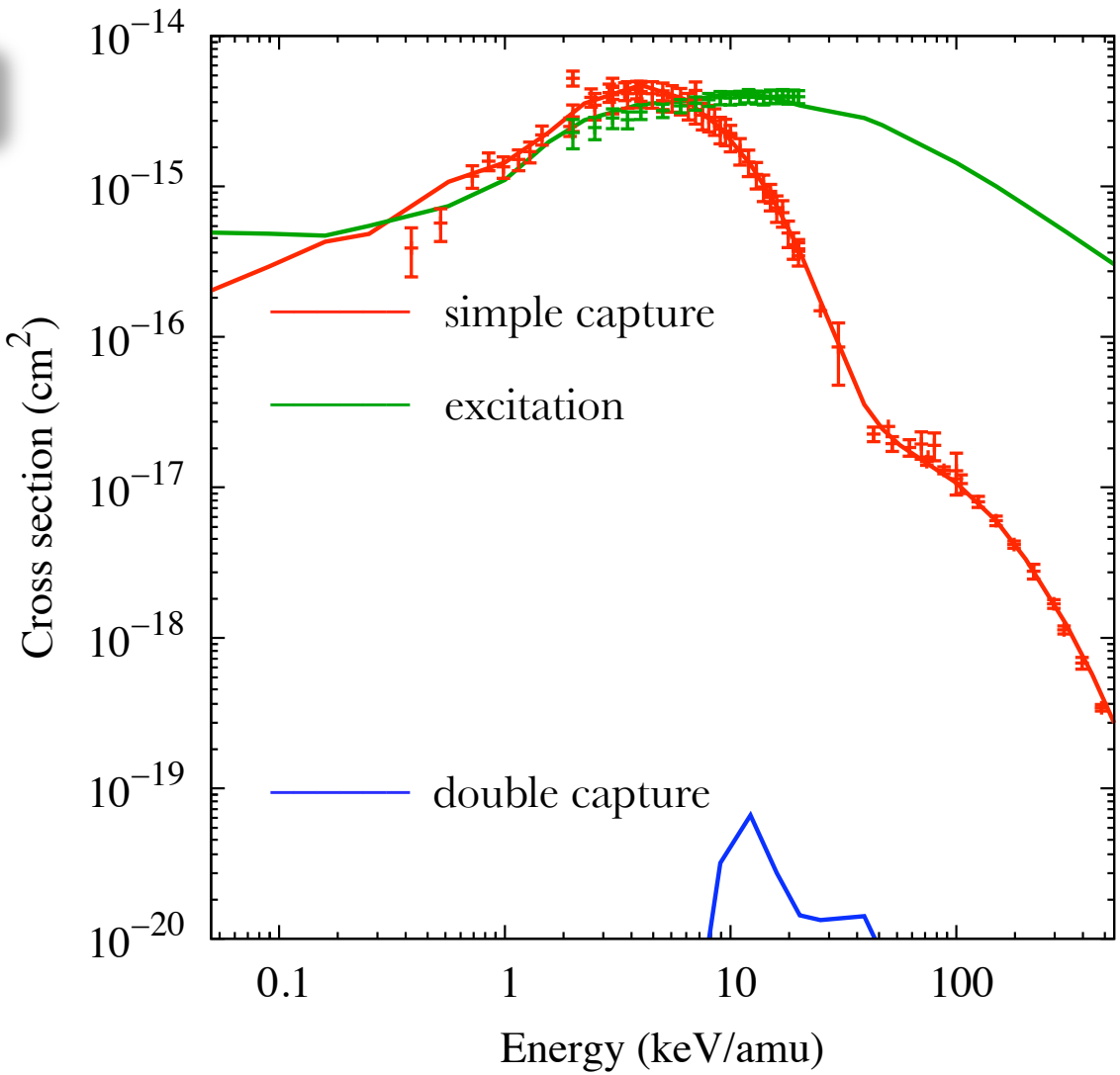
$$\sigma_{ij}(v) = \lim_{t\to\infty} 2\pi \int_{-\infty}^{\infty} |c_j(v,b,t)|^2 b db$$

IIX. Results, global processes

Comparison to experiment:

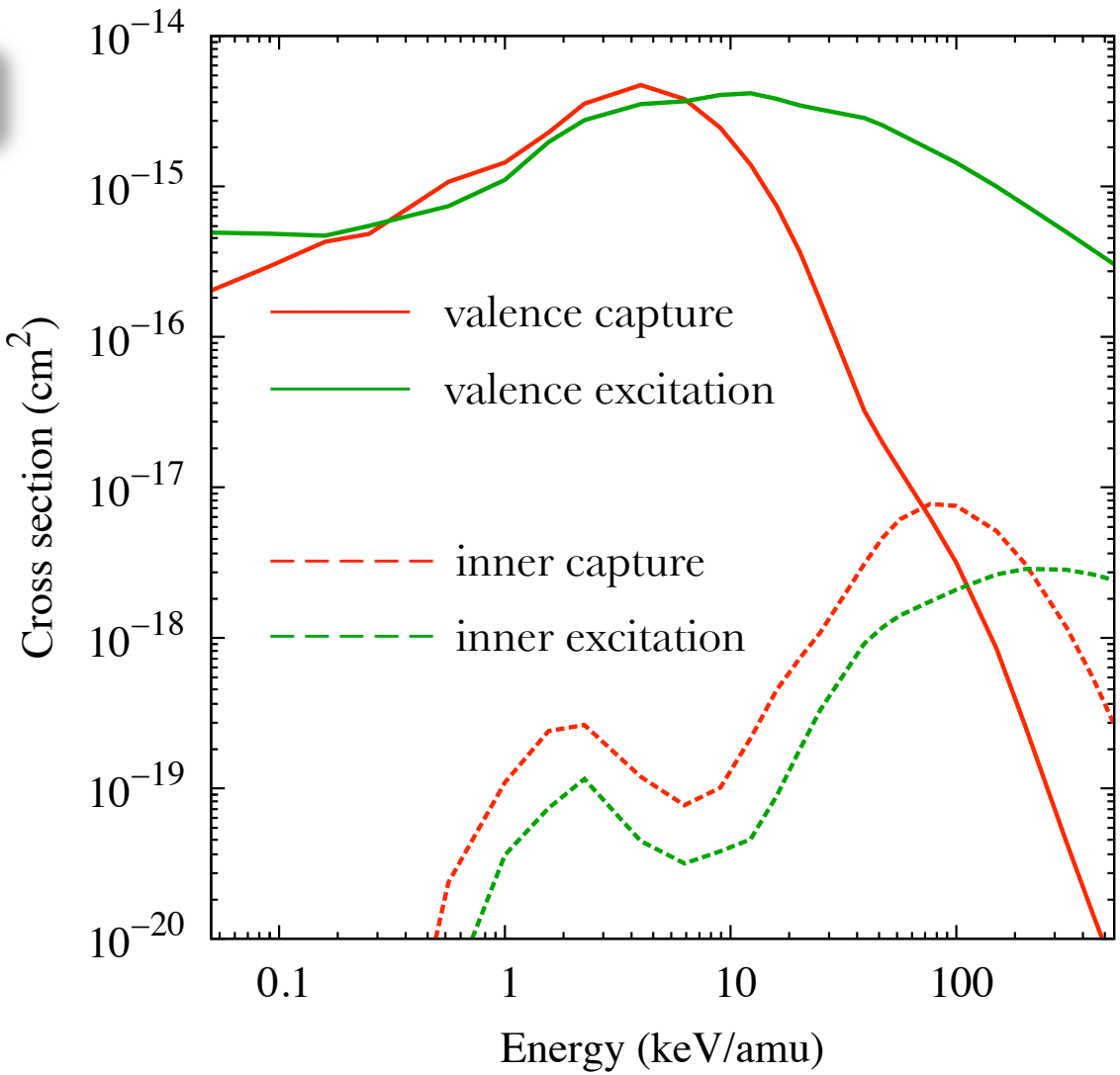
Very good agreement with experiment !



IIX. Results, valence and inner-shell components

Decomposition into sub-procs:

Inner-shell capture becomes dominant over valence above 80keV/amu

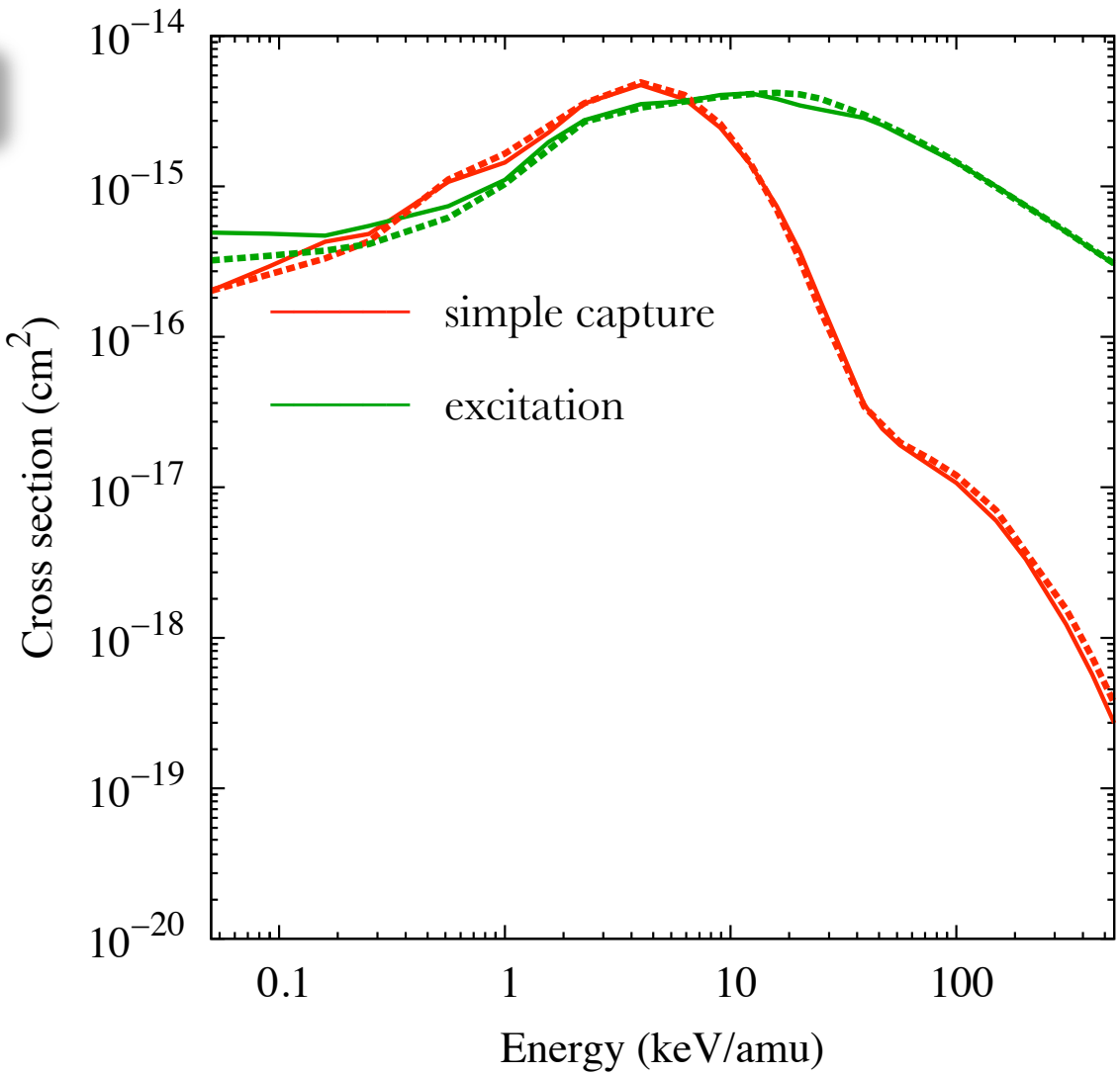


IIX. Results, global processes (2)

Comparison to 1e simulations

Electronic correlation effects are weak!

⟶ Quasi one-electron system.

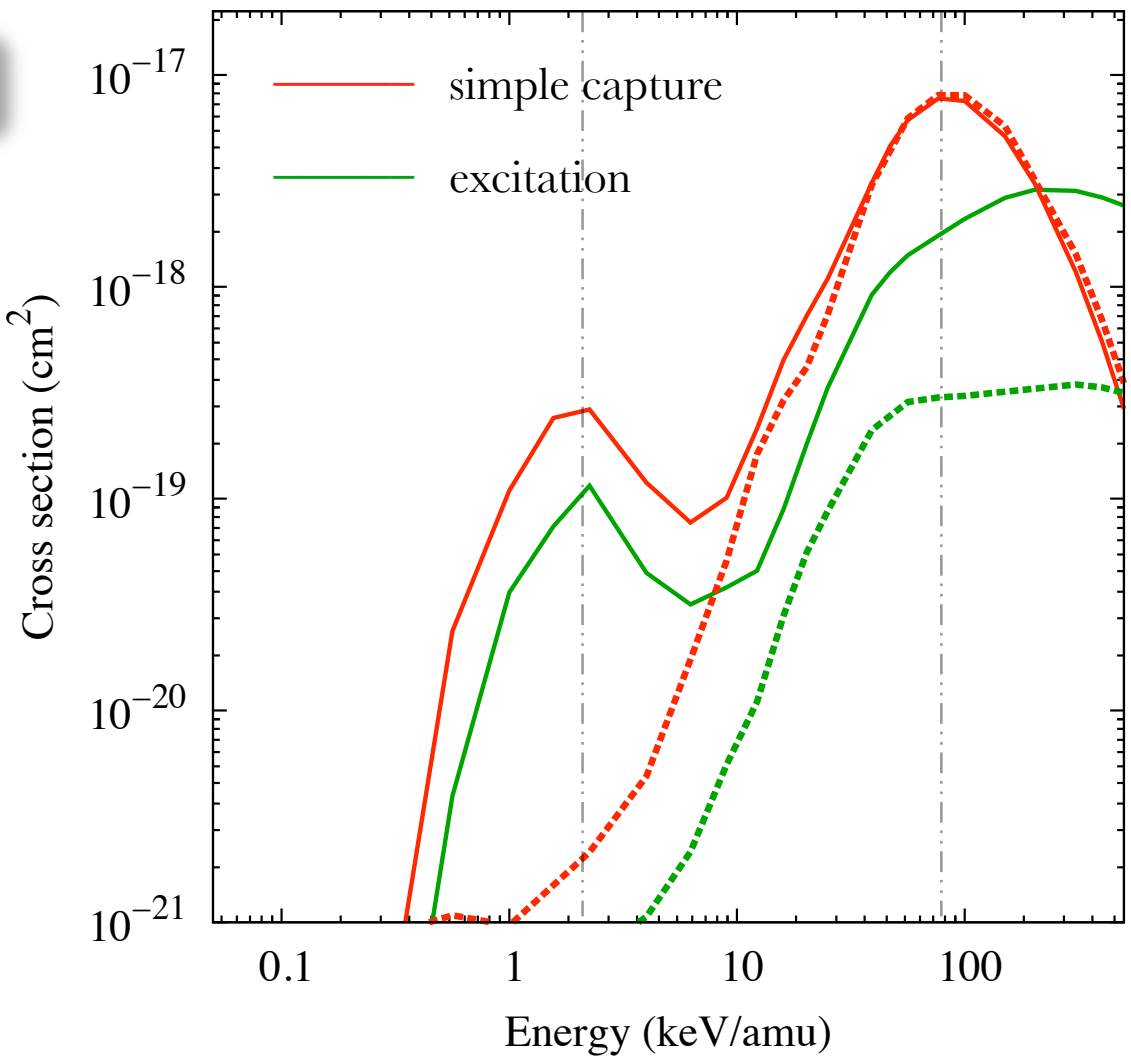


IX. Results, inner-shell processes

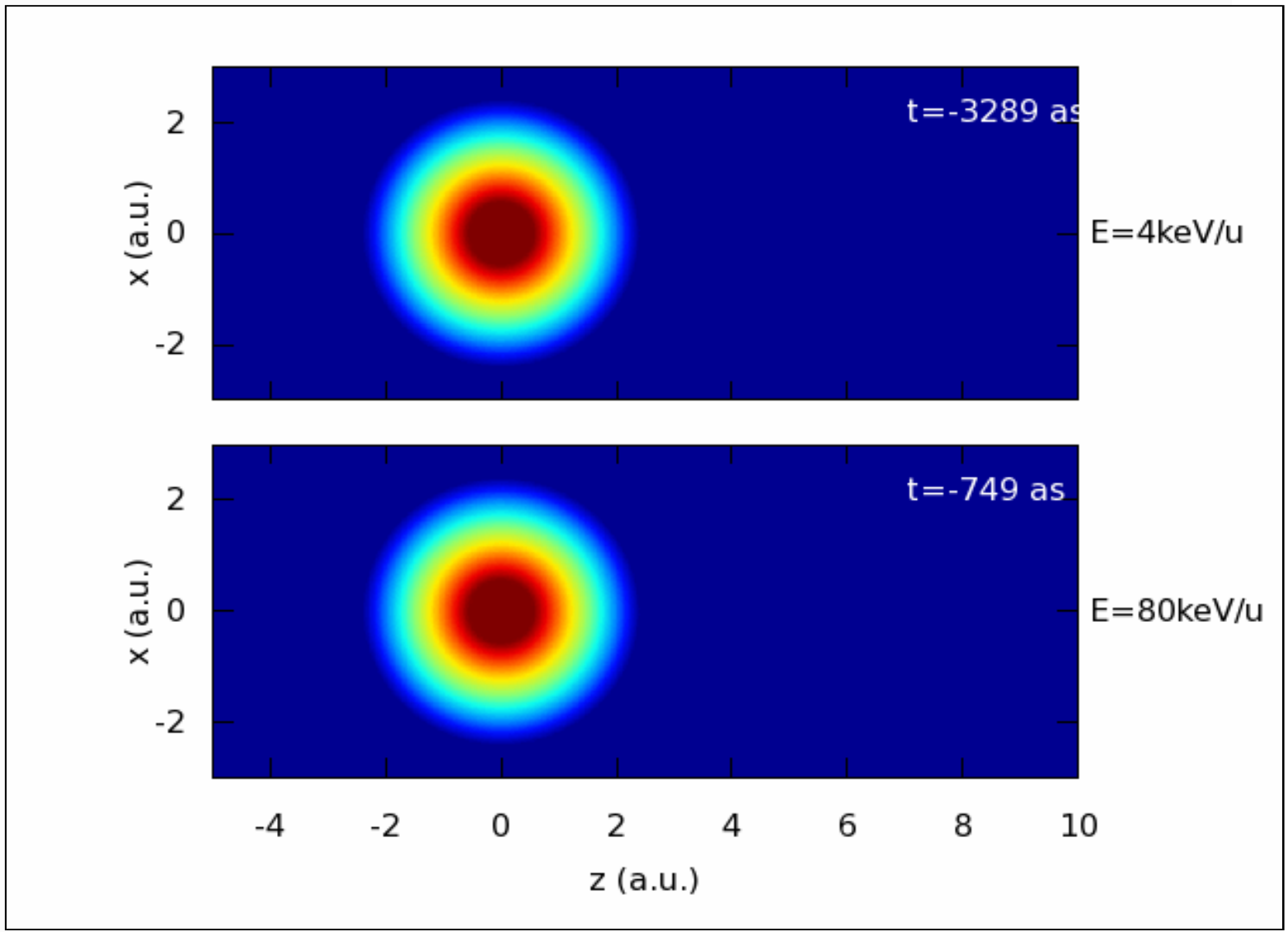
Comparison to 1e simulations

1e model fails to reproduce inner excitation.

1e model fails to reproduce second peak at 2keV.
⟶ Signature of multielectronic processes.

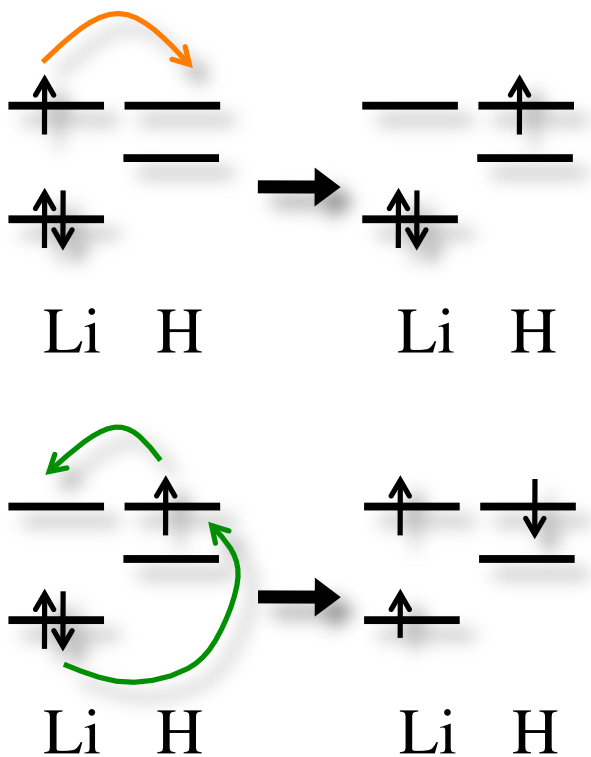


X. β electronic density temporal profile

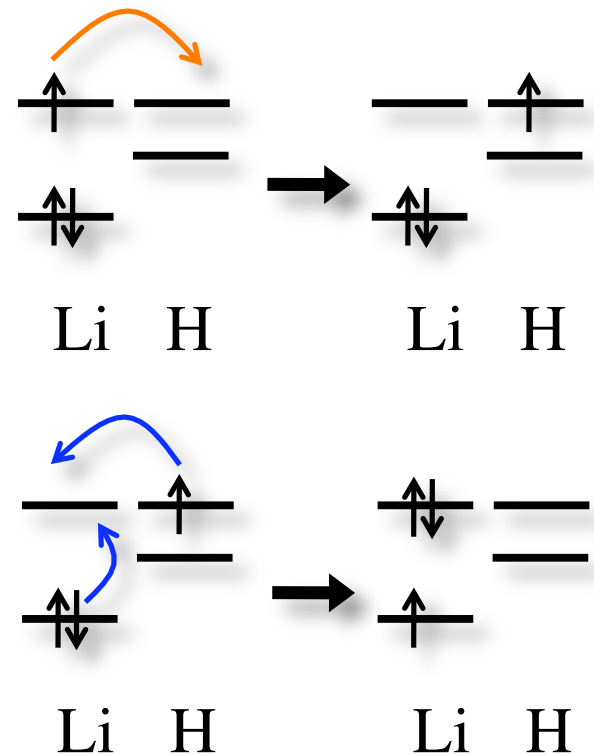


XI. Two steps model for inner shell processes

Inner-shell capture



Inner-shell excitation



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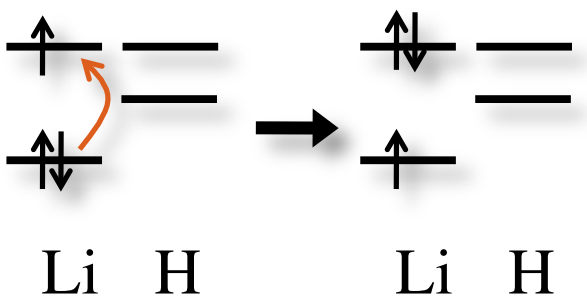

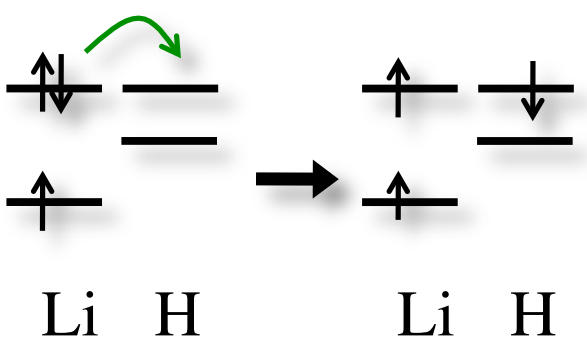

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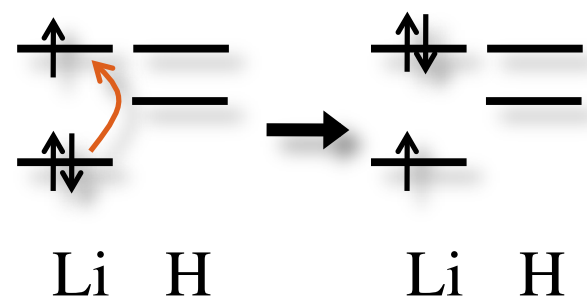
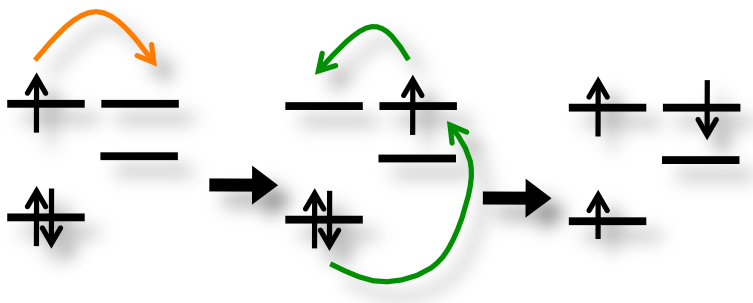
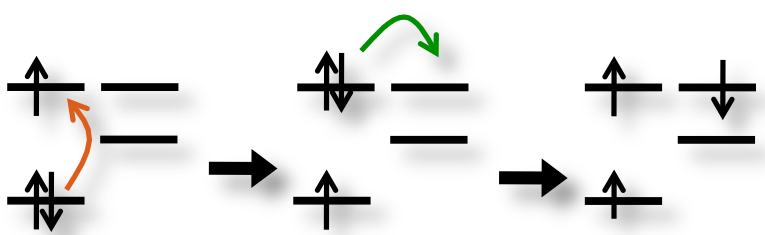


And then what?

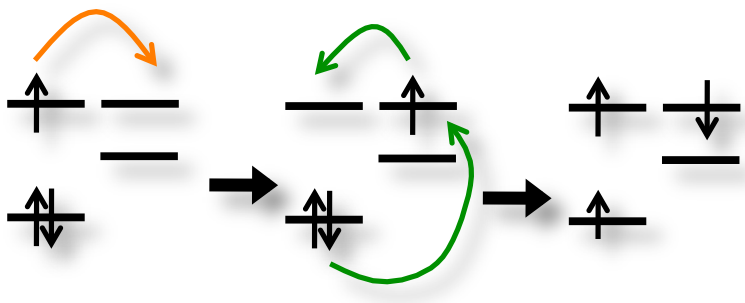
XII. Two-steps models final confrontation



How one can be proove which mechanism is the good one?



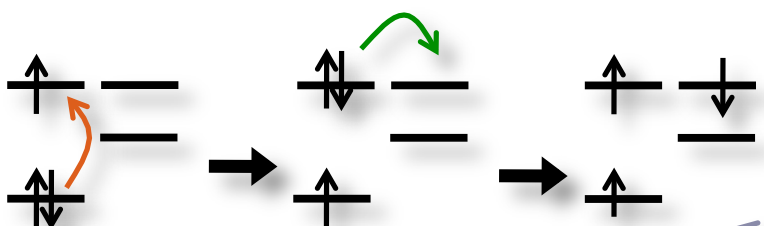
XII. Two-steps models final confrontation



How one can be proove which mechanism is the good one?

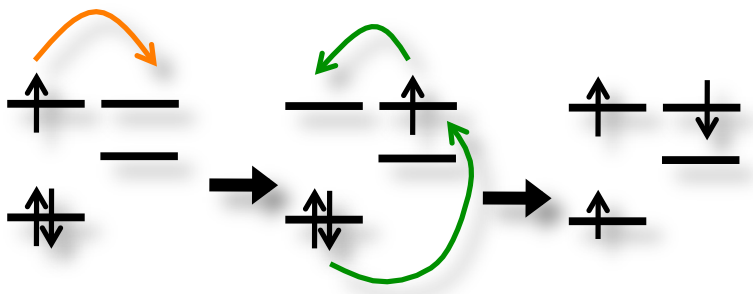
Answer : Fordid intermediate transitions

- This mechanism is forbidden without valence capture channels.

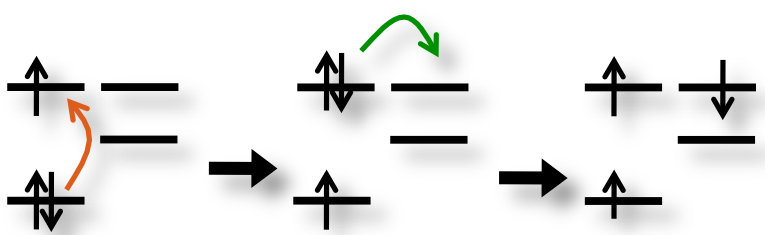


- This mechanism is forbidden without inner-shell excitation channels.

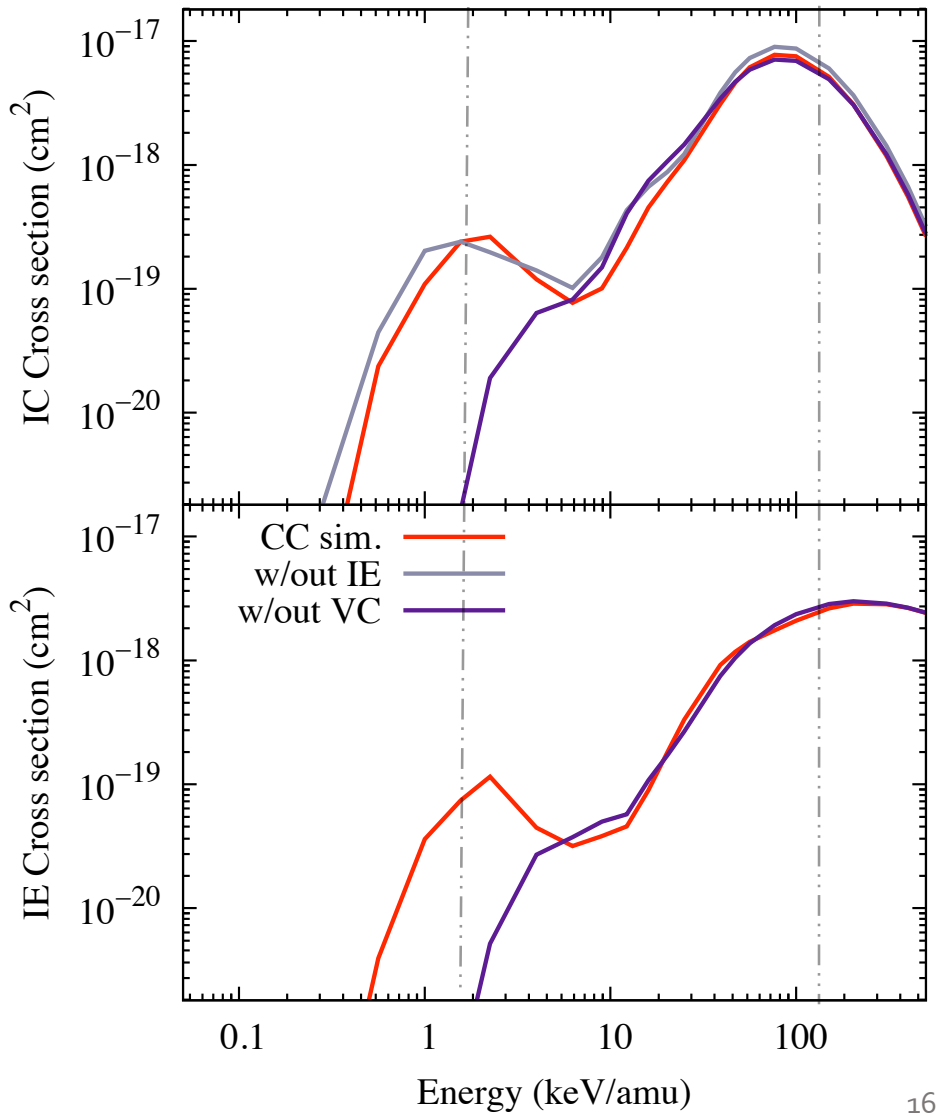
XII. Two-steps models final confrontation



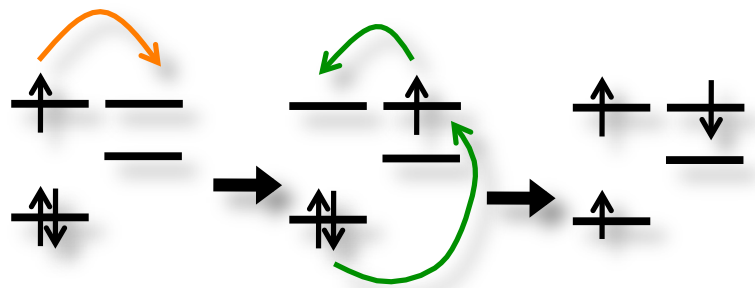
Forbidden without valence capture channels



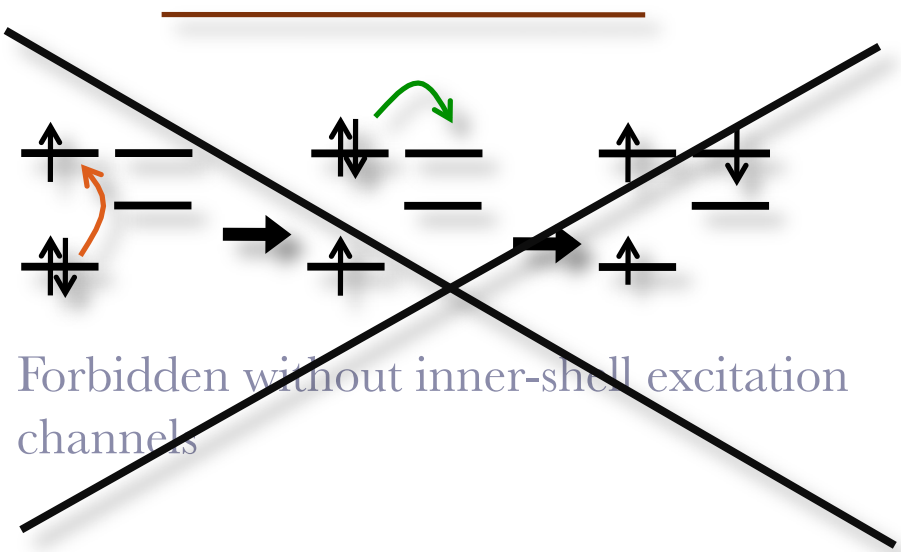
Forbidden without inner-shell excitation channels



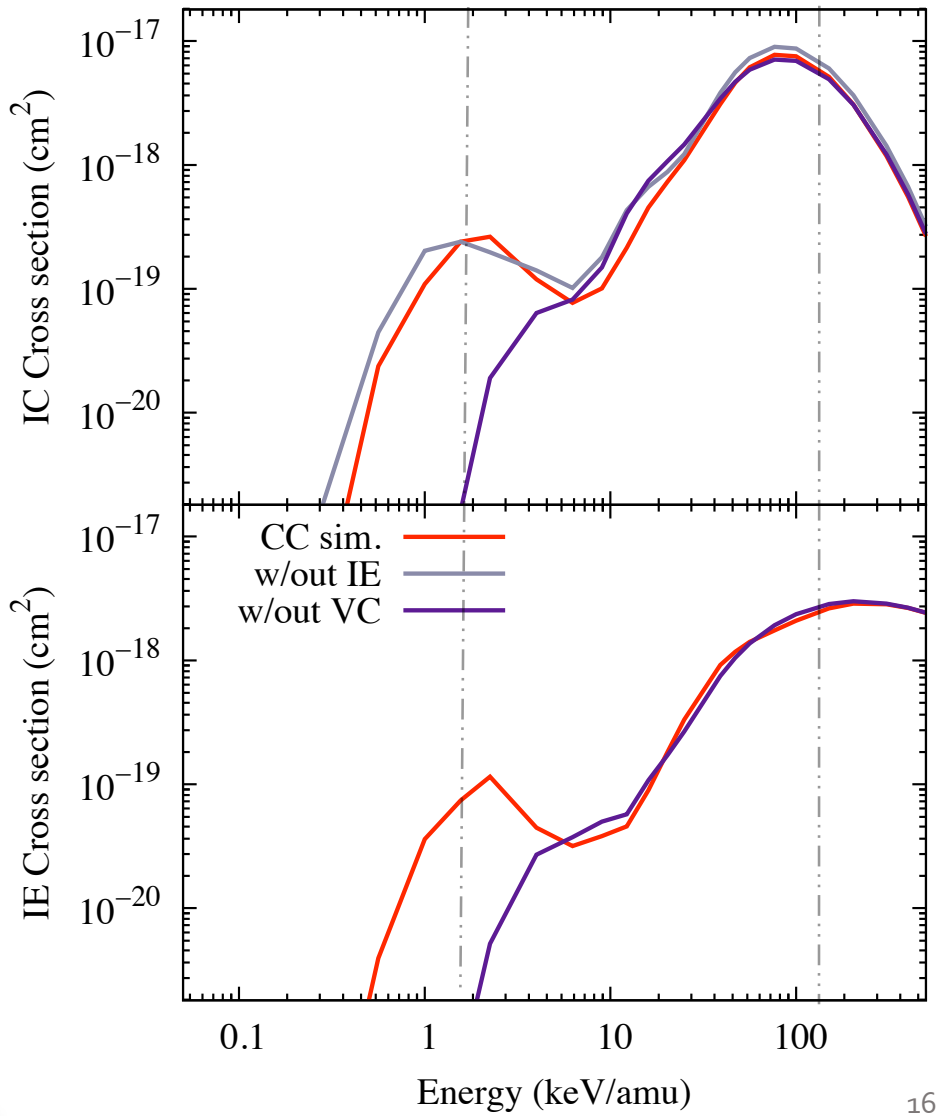
XII. Two-steps models final confrontation



Forbidden without valence capture channels



Forbidden without inner-shell excitation channels



XIII. Conclusion

Summary:

- ☑ Highly effective and easy to use Young diagrams.
- ☑ Code implementation check thanks to the proton-lithium benchmark
- ☑ Quasi one-electron model for p^+ - Li validated
- ☑ Two steps mechanism analogy in inner-shell processes highlighted

Perspectives:

- ☐ Development beyond 3 electrons (in progress)
- ☐ Hybride approach using model potential and several active electron

Merci pour votre attention !

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