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

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2nd Research Coordination Meeting of the CRP on Data for Atomic Processes of Neutral Beams in Fusion Plasma
✓ 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**

- **Quantal**
- **Semiclassical**
- **Close-coupling**
- **Perturbative**
- **Asymptotic Atomic Orbitals**
- **Transient Molecular Orbitals**
THEORETICAL TREATMENT:

- **Semi-classical approach**

  \[ \vec{R}(t) = \vec{b} + \vec{v} \cdot t \]

  *impact parameter approximation*

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

  \[ \Rightarrow \quad \text{Eikonal equation} \]

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

  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

\[ \Psi(\{\vec{r}_i\}, t) = \sum_k a_k(t) \Phi^T_k(\{\vec{r}_i\}, t) \Phi^P_k(\{\vec{r}_{i'} \neq \vec{r}_i\}, t) \]

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

\[ \Phi^T_k(\{\vec{r}_i\}, t) = \phi^T_k(\{\vec{r}_i\}) e^{-i\epsilon^T_k t} \]

\[ \Phi^P_k(\{\vec{r}_{i'}\}, t) = \phi^P_k(\{\vec{r}_{i'}\}) e^{-i\epsilon^P_k t} \prod_{j'} e^{i\vec{v} \cdot \vec{r}_{i'}} e^{-i\frac{1}{2} v^2 t} \]

ETF(\{\vec{r}_i\}) eigenfunctions (eigenvalues) of the T/P Hamiltonians

\[ \phi^{T/P}(\epsilon^{T/P}) \]
THEORETICAL TREATMENT:

- solve

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

with evaluation of all matrix elements, e.g.

\[
\langle i^P j^P | \frac{1}{r_{12}} e^{-i\vec{v} \cdot (\vec{r}_1 + \vec{r}_2)} | k^T l^T \rangle
\]

- 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 \[ \Psi(\{\vec{r}_i\}, t) = \sum_k a_k(t) \Phi^T_k(\{\vec{r}_i\}, t) \Phi^P_k(\{\vec{r}_{i'} \neq i'\}, t) \]

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

\[ \Phi^T_k(\{\vec{r}_i\}, t) = \phi^T_k(\{\vec{r}_i\}) e^{-i\epsilon^T_k t} \]
\[ \Phi^P_k(\{\vec{r}_{i'}\}, t) = \phi^P_k(\{\vec{r}_{i'}\}) e^{-i\epsilon^P_k t} \prod_{j'} e^{i\vec{v} \cdot \vec{r}_{j'}} e^{-i\frac{1}{2} v^2 t} \]

\[ \Phi^T_k(\{\vec{r}_i\}) \text{ETF}(\{\vec{r}_i\}) \]

\[ \phi^T/P (\epsilon^T/P) \]

eigenfunctions (eigenvalues)
of the T/P Hamiltonians

• Description of the multi-electronic states

- developed on products of Gaussian Type Orbitals

\[ |\phi >= \sum_{ijk} C_{ijk} |i j k> \quad \text{with} \quad |i j k> = G_i(\vec{r}_1) \ G_j(\vec{r}_2) \ldots \]

- 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 \( H^+ + Li \rightarrow H^+ + Li^* \)

\[
\phi^{Li} (1s^2 2s^1 \ 2S), \phi^{Li} (1s^2 2p^1 \ 2P), ..., \phi^{Li} (1s^1 2s^2 \ 2S), ...
\]

  ✓ single transfer \( H^+ + Li \rightarrow H^* + Li^+ \)

\[
\phi^{Li^+} (1s^2 \ 1S)\phi^H (2s \ 2S), ..., \phi^{Li^+} (1s 2s \ 1S)\phi^H (2s \ 2S), \phi^{Li^+} (1s 2p \ 3P)\phi^H (2p \ 2P), ...
\]

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

\[
\phi^{Li^{2+}} (1s \ 2S)\phi^{H^-} (1s^2 \ 1S), ...
\]

• the total system is doublet (and stays doublet) but both partners change spin multiplicity during the collision \( \Rightarrow \) complexity and CPU

• \( \Rightarrow \) Group theory and Young diagrams ... to minimize \( |\phi > = \sum_{ijk} C_{ijk} |i.jk > \)
• all together

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

with states of positive energies ...

for \( N_T = N_P = 14 \) (5 "s"+3*3 "p" GTO) ... and \( \approx 400 \) 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**: \((N_T + N_P)^6 \sim 5 \times 10^8\)

**matrix sizes in adapted basis**: \((N_T (N_T^2 - 1)/3 + N_T^2 N_P + N_T N_P (N_P + 1)/2)^2 \sim 3 \times 10^7\)
\[ H^+ + Li(1s^22s^1) \rightarrow H + Li^+(1s^2) \]

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

Theory:

Experiments:
- F. Aumayr and H.P. Winter (1985)
- R. D. DuBois (1985)
RESULTS 1: GLOBAL PROCESSES

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 independent 1e calc. +
    Independent Electron Approx
  • 1e calc. fail to reproduce peak at
    \( \approx 4 \text{ keV} \) for capture and excitation

Cross sections (cm\(^{-2}\))
\[
\begin{align*}
H^+ + H^-(1s^2) & \rightarrow H(n) + H \quad \text{SEC (neutralization)} \\
& \rightarrow H(n) + H^* \quad \text{Transfer-Excitation} \\
& \rightarrow H^-(1s^2) + H^+ \quad \text{DEC} \\
& \rightarrow H^+ + H^+ + e \quad \text{ionisation}
\end{align*}
\]

Why?

- relative (physical) stiffness of the equations
- importance of correlation ...
- convergence of the basis in two directions ...
TEST CASE 2 : $\text{H}^+ + \text{H}^-$ COLLISIONS

Junwen Gao et al,
PRL accepted (2019)
Convergence:

- GTO basis 1: $11 \, \text{s} + 8 \ast 3 \, \text{p} + 2 \ast 5 \, \text{d}$
- but also $9 \, \text{s} + 6 \ast 3 \, \text{p} + 1 \ast 5 \, \text{d}$
- and $11 \, \text{s}, 8 \ast 3 \, \text{p} + 4 \ast 5 \, \text{d}$
- 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:

\[ \text{Cross section (10^{-16} \text{ cm}^2)} \]

\[ E_{\text{keV}} \]

\[ \text{Ions} \]

\[ \text{Atoms} \]

\[ \text{Cations} \]

\[ \text{Anions} \]
Convergence and oscillations

in-and-out Rosenthal’s model

\[
T = \frac{\pi}{\int_{R_i}^{R_e} \Delta E dR}
\]

when plotted as \(1/v_p\)

Molecular energy curves of importance for DEC process
\[ \text{H} + \text{H} \rightarrow \text{H}^* + \text{H}^* \quad \text{excitation and di-excitation} \]

same method but 20 years ago we used

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

\[ H + H \rightarrow H^* + H^* \quad \text{excitation and di-excitation} \]
\[ \rightarrow H^+ + H^- \quad \text{transfer} \]
\[ \rightarrow H^+ + H^+ + e \quad \text{ionisation} \]

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 " " " " "

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

\[ \text{H}^+ + \text{H}(n \ell m) \rightarrow \text{H}(n'\ell'm') + \text{H}^+ \text{ SEC} \]

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

we performed also microcanonical CTMC calculations
TEST CASE 1: $H^+ + H(n)$ COLLISIONS

A. Taoutioui, JPB 51, 235202 (2018)

$H^+ + H(n = 3) \rightarrow H + H^+$

TCS of capture (cm$^2$)

- SC-AOCC results
- Janev Fit [32]
- CTMC results
- ADAS DATA [4]
Scaling laws

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

A. Taoutioui, JPB 51, 235202 (2018)
Scaling laws

• impact velocity: \( v_{sc} = \frac{v}{v_e^{(n)}} \approx v \cdot n \)

• \( n^4 \) scaling of SEC TCS at high energies (geometrical)

• \( n^3 \) scaling of SEC TCS at low energies
Scaling laws

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

- combined scaling

\[
\sigma_c^n(v) = n^3 (1 - g^n(v)) A^n(v) + n^4 g^n(v) B^n(v)
\]

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 overcompleteness)
  - 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)