Calculation of Atomic and Molecular Collisions

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Outline

1. Introduction
   - Motivation
   - Challenges
2. Convergent close-coupling theory
   - Electron-atom/molecule scattering
   - Computational details

Motivation

The primary motivation is to provide accurate atomic and molecular collision data for science and industry

- Astrophysics
- Fusion research
- Fluorescent lighting
- Nanolithography
- Neutral antimatter formation
- Medical: cancer imaging and therapy

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Challenges

Collisions between particles on the atomic scale are difficult to calculate:

- Governed by the Laws of Quantum Mechanics
  1. Countably infinite discrete target spectrum
  2. Uncountably infinite target continuum
  3. Charged particles interact at infinite distances

Close-coupling bypasses these three problems!

- Finite number of square-integrable target states
- Effectively, only one charged particle at infinity
- Unitary excitation of −ve- and +ve-energy states

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Convergent close-coupling theory

Use complete Laguerre basis $\xi_{n\ell}^{(\lambda)}(r) \propto \exp(-\lambda r)$:

- "one-electron" (H, Ps, Li,...,Cs, H_2^+)

$$\phi_{n\ell}(r) = \sum_{n'=1}^{N_\ell} C_{n\ell}^{n'} \xi_{n'\ell}^{(\lambda)}(r),$$

- "two-electron" (He, Be,..., Hg, Ne, ..., Xe, H_2, H_2O)

$$\phi_{n\ell s}(r_1, r_2) = \sum_{n',n''} C_{n\ell s}^{n'n''} \xi_{n'\ell'}^{(\lambda)}(r_1) \xi_{n''\ell''}^{(\lambda)}(r_2),$$

- Diagonalise the target (FCHF) Hamiltonian

$$\langle \phi_f | H_{\mathrm{T}} | \phi_i \rangle = \varepsilon_f \delta_{fi}, \quad i, f = 1, \dots, N$$

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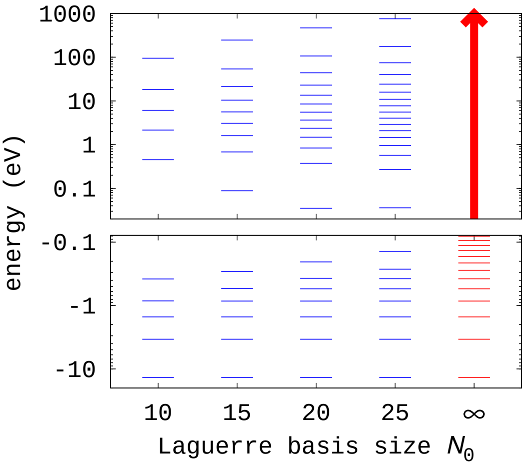
- H energies ε_f for Laguerre bases: $N_0 = 10, 15, 20, 25$



- $I_{N_\ell} = \sum_{n=1}^{N_\ell} |\phi_{n\ell}\rangle\langle\phi_{n\ell}|, \quad \lim_{N_\ell\to\infty} I_{N_\ell} = I_\ell.$

Electron-atom/molecule scattering

- Electron-atom/molecule wavefunction is:

$$|\Psi_i^{(+)}\rangle \approx \mathcal{A} I_N |\psi_i^{(+)}\rangle = \mathcal{A} \sum_{n=1}^{N} |\phi_n F_{ni}\rangle. \quad (1)$$

  - $\mathcal{A}$ leads to non-uniqueness of F_{ni}
- Solve for $T_{fi} \equiv \langle \boldsymbol{k}_f \phi_f | V | \Psi_i^{(+)} \rangle$ at $E = \varepsilon_i + k_i^2/2$,

$$\langle \boldsymbol{k}_f \phi_f | T | \phi_i \boldsymbol{k}_i \rangle = \langle \boldsymbol{k}_f \phi_f | V | \phi_i \boldsymbol{k}_i \rangle + \sum_{n=1}^{N} \int d^3k \frac{\langle \boldsymbol{k}_f \phi_f | V | \phi_n \boldsymbol{k} \rangle \langle \boldsymbol{k} \phi_n | T | \phi_i \boldsymbol{k}_i \rangle}{E + i0 - \varepsilon_n - k^2/2}. \quad (2)$$

  - $\lim_{N\to\infty} \langle \boldsymbol{k}_f \phi_f | T | \phi_i \boldsymbol{k}_i \rangle = 0$ for $k_f^2/2 < \varepsilon_f$ i.e. $\epsilon_f > E/2$.
- Cross sections: $\sigma_{fi} = \frac{k_f}{k_i} |\langle \boldsymbol{k}_f \phi_f | T | \phi_i \boldsymbol{k}_i \rangle|^2$.

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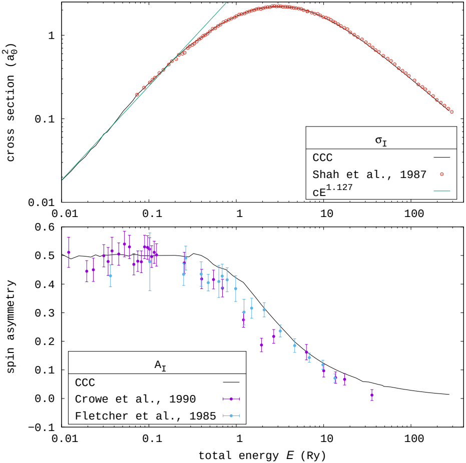
Electron-impact ionization of hydrogen

- total ionization cross section and spin asymmetry



[I. Bray *et al.* PRL **121**, 203401 (2018)]

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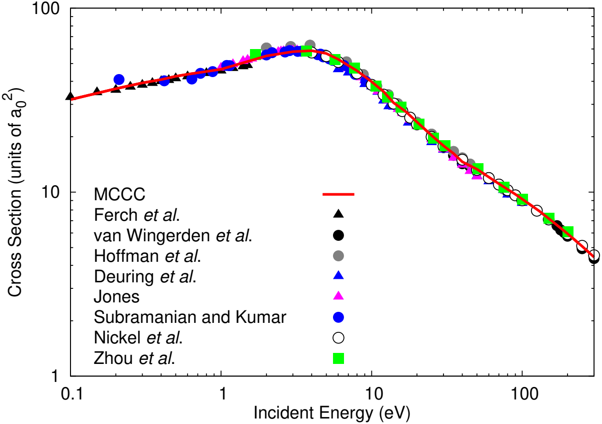
Electron scattering on molecular hydrogen

- e^--H_2 collisions: MCCC-calculated total cross section



[M. Zammit *et al.* PRL **116**, 233201 (2016)]

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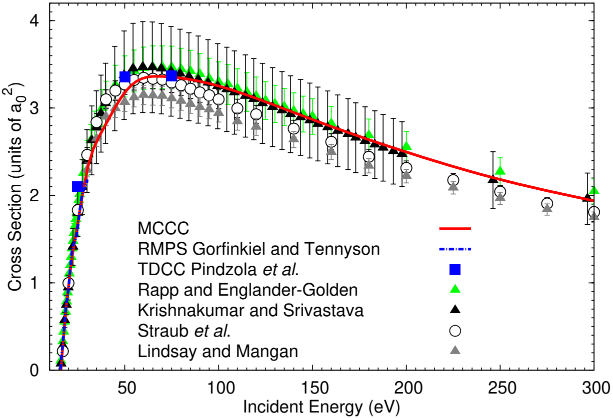

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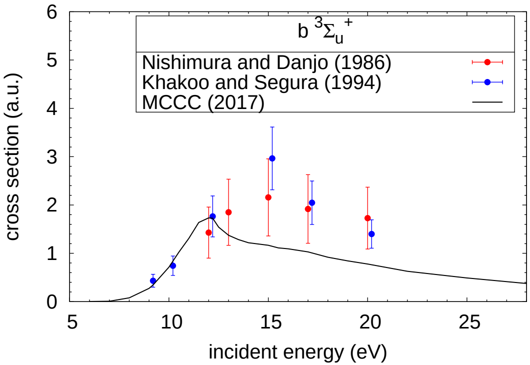
- e^--H_2 collisions: $b^3\Sigma_u^+$ excitation



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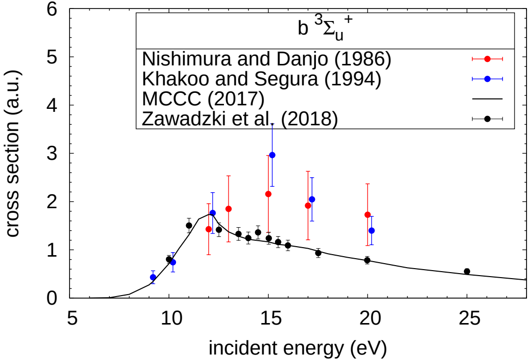

[M. Zawadski *et al.* PRA **98**, 050702R (2018)]

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Computational details

1. Calculate four-dimensional array $\langle k_f \phi_f | V | \phi_i k_i \rangle$
2. Write $T^{(N)} = V + VGT^{(N)}$ as $(I - VG)T^{(N)} = V$, and solve as $A(\theta)x = b(\theta)$ to yield unique x for $\theta \neq 0$
3. Increase N until $\langle k_f \phi_f | T^{(N)} | \phi_i k_i \rangle$ converges

- Early 1990s: single CPU; $60,000 for 512Mb of RAM
  - Used LAPACK
  - Matrix size: $10,000 \times 10,000$
- Mid 1990s: implemented OpenMP on "symmetric multiprocessing" architecture
  - No rewrite of code
  - More RAM
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Next generations of parallelisation:

- Early 2010s: implemented MPI to split the matrix calculation across "loosely connected fat nodes"
  - Use ScaLAPACK across all nodes to solve $Ax = b$
  - Matrix size: $500,000 \times 500,000$ and increasing
  - Made molecular targets accessible
- GPUs are more energy-efficient than CPUs; Implementing NVIDIA and AMD GPU acceleration
  - Order of magnitude speedup for $\langle k_f \phi_f | V | \phi_i k_i \rangle$
  - Utilising OpenMP and OpenACC directives or HIP/CUDA
  - Paying attention to data flow (CPU and GPU) is vital
  - For GPUs SLATE replaces ScaLAPACK
  - Scaling with nodes is perfect for V, poor for $Ax = b$
- Partnerships of HPC staff and scientists make for great new science!

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Concluding remarks

- CCC valid at all energies for (anti)electrons, photons, (anti)protons scattering on quasi one- and two-electron atoms and molecules, as well as inert gases.
- Atomic CCC available: https://amosgateway.org.
- Data available: LXCAT, mccc-db.org, CCC-WWW.

To-do list

- GPU acceleration for multi-electron atoms
- GPU acceleration for molecular targets
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