Electron scattering from the molecular hydrogen ion and heavy particle collisions with atoms and molecules

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Outline

- CCC method for electron-molecule collisions: e-H_2^+
  - Formulation of the CCC method for molecules
  - e-H_2^+ : convergence and accuracy for fixed-nuclei calculations
  - e-H_2^+ : adiabatic-nuclei calculations: challenges and accuracy
- CCC method for heavy particle collisions
  - Single-centre approach: antiproton collisions with noble gas atoms and H_2 molecule
  - Two-centre approach: proton collisions with hydrogen atom
- Conclusions

CCC method for electron-molecule scattering

- Born-Oppenheimer approximation, Fixed-nuclei approximation
- One-center approach
- one-electron functions: Sturmian basis $f_{n,l}(2\lambda r) \propto (2\lambda r)^{l+1} e^{-\lambda r} L_n^{2l+2}(2\lambda r)$
- Target Hamiltonian H_T is diagonalized

$$\langle \phi_f^N | H_T | \phi_i^N \rangle = \epsilon_f^N \delta_{fi}$$

- N-state multi-channel expansion

$$\Psi_i^{(+)}(\mathbf{x}_1,...,\mathbf{x}_M,\mathbf{x}_p) = \mathcal{A} \sum_{n=1}^{N} F_n(\mathbf{x}_p)\ \phi_n(\mathbf{x}_1,...,\mathbf{x}_M)$$

- integral Lippmann-Schwinger equation for the T-matrix

$$T_{fi}(\vec{k}_f,\vec{k}_i) = V_{fi}(\vec{k}_f,\vec{k}_i) + \sum_{n=1}^{N} \int d^3k \frac{V_{fn}(\vec{k}_f,\vec{k}) T_{ni}(\vec{k},\vec{k}_i)}{E + i0 - \varepsilon_n - k^2/2}$$

- solved by partial-wave expansion
- reduced to a system of linear equations

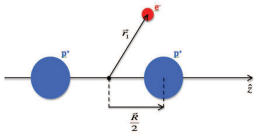
CCC method for electron-molecule scattering: e-H_2^+

Born-Oppenheimer approximation

$$\Phi = \phi_{Nuclear}(\vec{R}) \phi_{Electronic}(\vec{r}, R)$$

Fixed-nuclei approximation, $R = 2.0$ (fixed)

$$H_T \equiv H_{Elec} = -\frac{1}{2}\nabla^2 - \frac{1}{|\vec{r} - \vec{R}/2|} - \frac{1}{|\vec{r} + \vec{R}/2|}$$



- One-centre approach: origin at the midpoint
- Target Hamiltonian H_T is diagonalized in a Sturmian (Laguerre) basis
- Basis: $N_l = 17 - l$, $l_{max} = 4$
  The *1s & 2p* one-electron orbitals are replaced by accurate H_2^+ $1s\sigma_g$ and $2p\sigma_u$ orbitals (diagonalized in the basis with $l_{max} = 9$, $N_l = 60$)
- Leads to 351 states

CCC method: e-H_2^+ scattering

Checked that we produce correct

- energy levels

	$1s\sigma_g$		$2p\sigma_u$		$2p\pi_u$	
R	CCC	[1]	CCC	[1]	CCC	[1]
2.0	-0.601	-0.603	-0.166	-0.168	0.071	0.071

- oscillator strength

	$1s\sigma_g \rightarrow 2p\sigma_u$		$1s\sigma_g \rightarrow 2p\pi_u$	
R	CCC-L(V)	[1]	CCC-L(V)	[2]
2.0	0.320(0.311)	0.319	0.461(0.456)	0.460

- static dipole polarisability

	α_{par}		α_{perp}	
R	CCC-L	[2]	CCC-L	[2]
2.0	5.084	5.078	1.767	1.758

[1] D. R. Bates, J. Chem. Phys. 19, 1122 (1951)
[2] D. M. Bishop and L. M. Cheung, J. Phys. B 11, 3133 (1978)

CCC method: e-H_2^+ scattering

Solution of the Lippmann-Schwinger equation:

- partial-wave expansion: from 3D to 1D equation
- reduction to a system of linear equations using a quadrature rule
- use of conserved quantum numbers (M, S, Π) to reduce the size
- Projectile partial wave expansion: maximum angular momentum $L_{max} = 9$

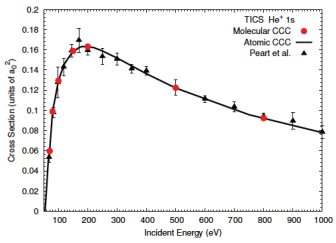
  Analytical Born subtraction technique is used to account for larger partial waves
- Calculations are performed in the body frame.

  Appropriate orientation averaging is done to compare with experimental data.

e$^-$-H_2^+ dissociative ionization (DI)

Convergence in the combined-nuclei limit (R=0)

Total ionisation cross sections (TICS) for electron scattering from the ground state of He$^+$



Basis size
351-state calculation generated with basis $N_l = 17 - l$, $l_{max} = 4$

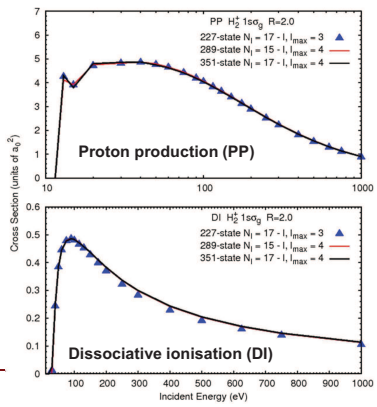
Basis size convergence for H_2^+: target expansion

Proton production (PP)
$\sigma_{PP} = \sigma_{DE} + 2\sigma_{DI}$
Dissociative excitation (DE):
$e^- + H_2^+(1s\sigma_g) \rightarrow e^- + H^+ + H(nl)$
Dissociative ionisation (DI):
$e^- + H_2^+(1s\sigma_g) \rightarrow 2e^- + H^+ + H^+$

Basis sizes
227-state calculation generated with basis $N_l = 17 - l$, $l_{max} = 3$

289-state calculation generated with basis $N_l = 15 - l$, $l_{max} = 4$

351-state calculation generated with basis $N_l = 17 - l$, $l_{max} = 4$

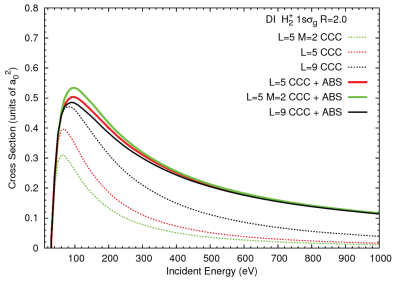


e^--H_2^+ dissociative ionization (DI)

Convergence of the partial-wave expansion

use of plane-wave analytical Born subtraction (ABS) technique

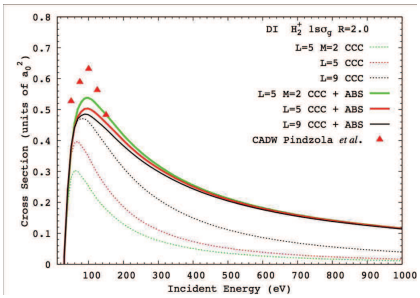
$$\sigma = \sum_{l=0}^{L_{max}} (\sigma_l - \sigma_l^B) + \sigma^B$$



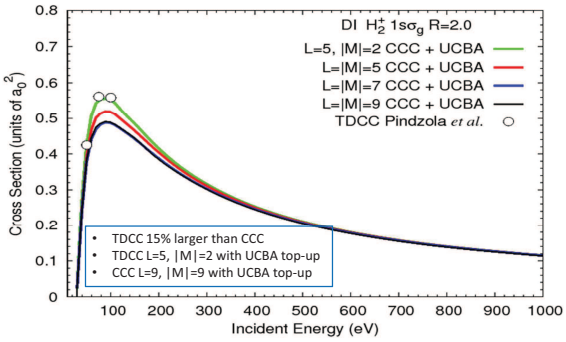
Partial-wave expansion is taken to convergence

e^--H_2^+ dissociative ionization (DI)

Channel coupling: DW is larger than CCC by about 30% at the cross section maximum



e^--H_2^+ dissociative ionization (DI)



H_2^+ molecule: adiabatic-nuclei approximation

H_2^+ ions are produced by ionization of H_2. Vibrational levels have long lifetimes (10^6s).

R=2.0 *R=1.4*

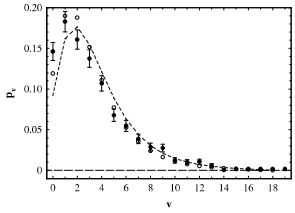


Figure 5. Vibrational population of H_2^+. Full circles: present measurements; open circles: measurements of von Busch and Dunn (1972); dashed line: Franck–Condon factors of Dunn and Van Zyl (1967).

El Ghazaly etal, J. Phys. B: 37 (2004) 2467

Busch and Dunn, Phys. Rev. A 5(1972)1726

T-matrix for transition between vibrational states:

$$T_{fi}^{\nu\mu} = \int dR \phi_{f\mu}(R)\, T_{fi}(R)\, \phi_{i\nu}(R)$$

Ionization from vibrational level v of electronic state i

$$Q_{i\nu}^{ionization} = \int dR\, Q_i^{ionization}(R) |\phi_{i\nu}(R)|^2$$

$$Q_i^{ionization} = \sum_\nu p_\nu\, Q_{i\nu}^{ionization}$$

$$Q_{fi}(R) \propto |T_{fi}(R)|^2$$

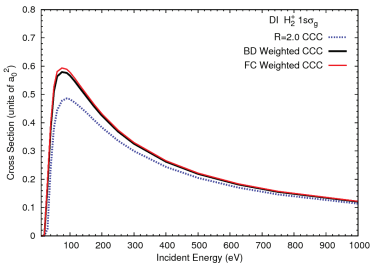
the same for H_2^+ and its isotopologues

D_2^+, T_2^+, HD$^+$, HT$^+$, DT$^+$

$\phi_{i\nu}(R)$ vibrational wave functions are calculated separately for H_2^+, D_2^+, T_2^+, HD$^+$, HT$^+$, DT$^+$

Details: Zammit etal, PRA 90, 022711 (2014)

e^--H_2^+ dissociative ionization (DI)



Errors:

Fixed-nuclei to Adiabatic-nuclei 15%-20%

FC to BD distributions: 2-3%

Major uncertainty in the calculation comes from the integration over R

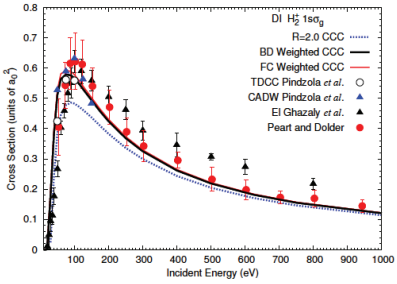
$$Q_{i\nu}^{ionization} = \int dR\, Q_i^{ionization}(R) |\phi_{i\nu}(R)|^2$$

present model: calculate Q(R) to R=5.5 extrapolate for R > 5.5

error less than 5%

This aspect can be checked against accurate FBA results. [Peek and Green, Phys. Rev. 183, 202 (1969)]

e^--H_2^+ dissociative ionization (DI)



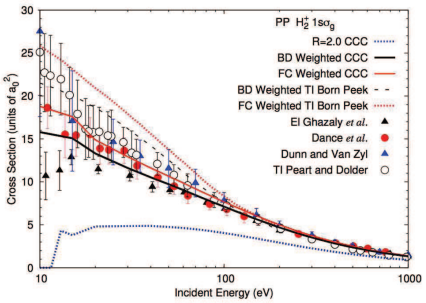
To differentiate between DE and DI :

El Ghazaly *et al.* analysed the kinetic energy release spectrum

Peart & Dolder measured protons in coincidence

Peart & Dolder, J. Phys. B 6(1973)2409
Ghazaly etal, J. Phys. B: 37(2004)2467
Pindzola etal , Phys. Rev. A 72(2005)012716; J. Phys. B38(2005)L285

e^--H_2^+ proton production (PP)



$$Q_{PP} = Q_{DE} + 2\, Q_{DI}$$

$$Q_{TI} = Q_{DE} + Q_{DI}$$

Errors:

Fixed-nuclei to Adiabatic nuclei > 100%

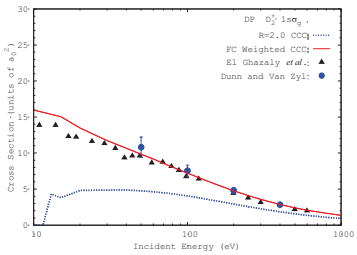
FC to BD distributions: 10-20%

Channel coupling : 50% by comparing with Born results

El Ghazaly *et al.*, J. Phys. B 37(2004)2467
Dance *et al.*, Proc. Phys. Soc. 92(1967)577
Dunn and Zyl, Phys. Rev. 154(1967)40
Peek, Phys. Rev. A 10(1974)539

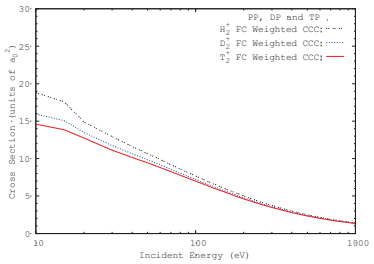
e^--D_2^+ deutron production (DP)

Vibrational cross sections are weighted according to the Franck-Condon (FC) factors.



Proton production (PP), deuteron production (DP), and triton production (TP) cross sections for electron scattering from vibrationally excited H_2^+, D_2^+, or T_2^+

Vibrational cross sections are weighted according to the Franck-Condon (FC) factors.



Heavy particle collisions with atoms and molecules

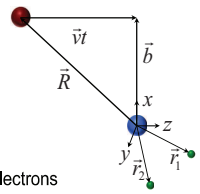
1-centre semi-classical CC approach

A lab frame: the origin at the target, z-axis $\parallel \vec{v}$ and x-axis $\parallel \vec{b}$

Projectile position $\vec{R}(t) = \vec{b} + \vec{Z} = \vec{b} + \vec{v}t$

The w.f. is a solution to SC TDSE

$$i\frac{\partial \Psi(\vec{r},t)}{\partial t} = (H_T + V_P)\Psi(\vec{r},t)$$



Expand Ψ in terms of pseudostates of H_T

$$\Psi(\vec{r},t) = \sum_\alpha a_\alpha(t)\exp(-i\varepsilon_\alpha t)\phi_\alpha(\vec{r})$$

$\vec{r} = \{\vec{r}_1, \vec{r}_2, ...\}$ is a collective coordinate of all electrons

Solve for a_α $\quad i\dot{\mathbf{a}} = \mathbf{D}\mathbf{a}$

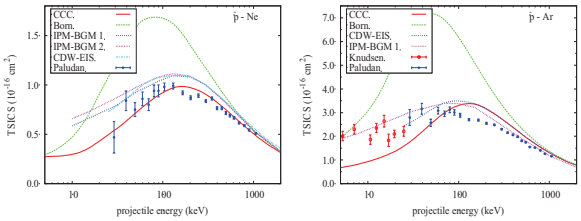
Heavy particle collisions with atoms and molecules

1-centre semi-classical CC approach

Antiprotron scattering

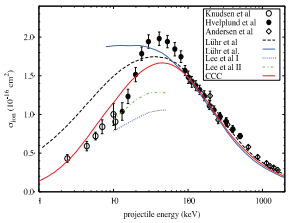
- We consider antiproton scattering from noble gases (Ne, Ar, Kr and Xe)
- We describe target wave functions by a model of 6 p-electrons above an inert Hartree–Fock core
- Excited states are obtained by allowing one-electron excitations from the p shell
- Structure code thoroughly tested: e^+ on noble gases
  details: Fursa & Bray NJP 14 (2012) 035002

Single-ionisation of Ne and Ar by antiprotons



Antiproton - H_2 collisions

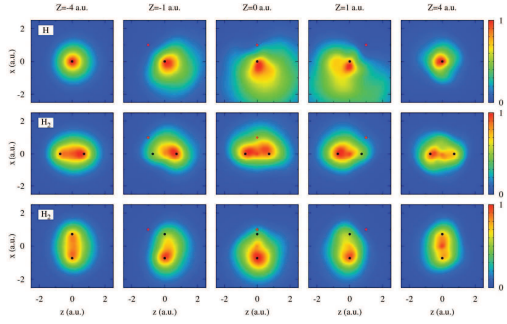
H_2 structure details: Zammit & Fursa PRA 87(2013) 020701



- Analytical orientation averaging procedure
- Correctly describe the suppression of ionization at low energies compared to atoms

Single-ionisation cross section
PRL 111 (2013) 173201

The electron distribution dynamics

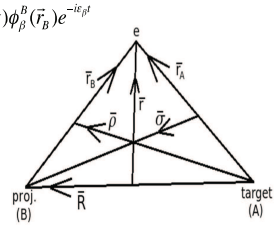


2-centre semi-classical approach

$$\Psi(\vec{r},t) = \sum_\alpha a_\alpha^A(t)\phi_\alpha^A(\vec{r}_A)e^{-i\varepsilon_\alpha t} + \sum_\beta a_\beta^B(t)\phi_\beta^B(\vec{r}_B)e^{-i\varepsilon_\beta t}$$

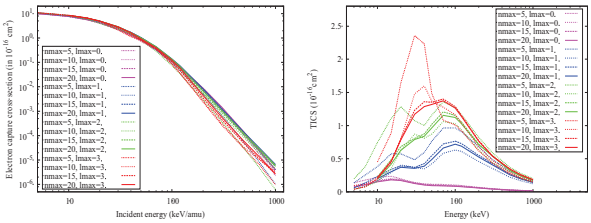
It is a solution to TDSE

$$i\frac{\partial \Psi(\vec{r},t)}{\partial t} = H\Psi(\vec{r},t)$$

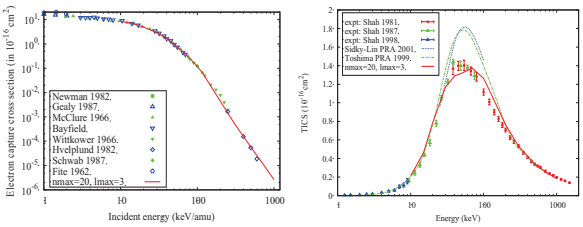


Now we consider p-H scattering including electron capture.

Electron capture and ionisation in p-H collisions



Electron capture and ionisation in p-H collisions



lmax=4 and 5 may be required for ionisation.
Calculations in progress

Conclusions

- Molecules pose a serious problem for a straightforward close-coupling approach
- For H_2^+ we could achieve the same accuracy as for atoms for fixed-nuclei calculations and hope that this can be replicated for other diatomic molecules
- One-center approach to molecular scattering proved to be feasible & sufficiently accurate, will work well for hydrates in particular
- Beyond the fixed-nuclei approximation: adiabatic-nuclei approach, extremely expensive computationally, but has to be done if a molecule is not in the ground vibrational state
- heavy particle collisions: demonstrated that CCC method works well for single-centre problems (antiproton scattering)
- heavy particle collisions: first results for two-centre approach are encouraging….
- Channel coupling is important, coupling to ionization continuum is important…
- Even more important is to have a sufficiently accurate target description

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