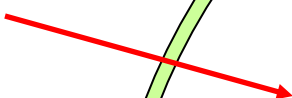


e^-



Latest developments in R-matrix Theory

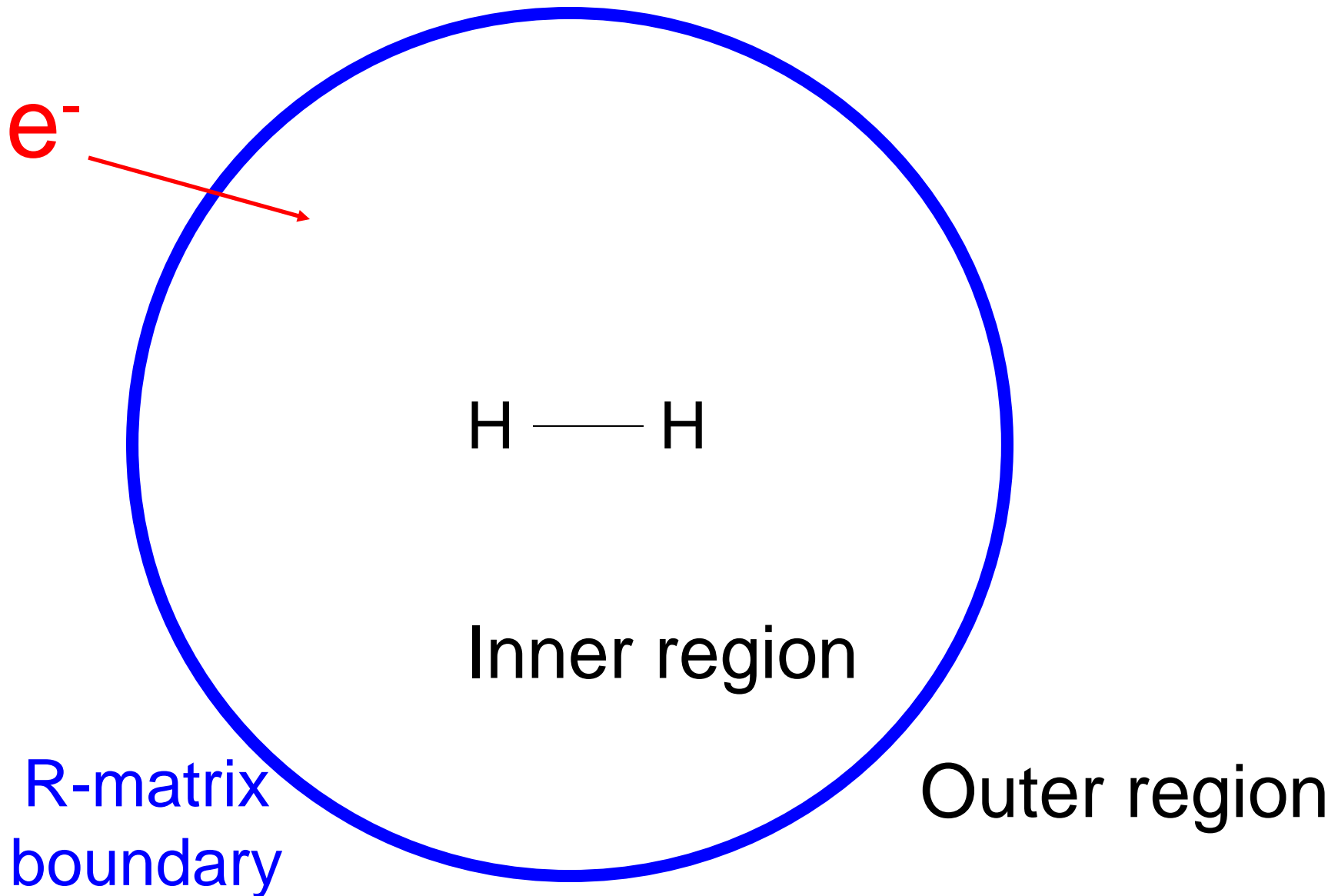
Jonathan Tennyson
University College London

Outer region

Inner region

Quantemol workshop
June 2011

The R-matrix method



Dominant interactions

Inner region

Exchange
Correlation

Adapt quantum chemistry codes

High ℓ functions required

Integrals over finite volume

Include continuum functions

Special measures for orthogonality

configuration generation must be appropriate

Boundary

Target wavefunction has zero amplitude

Outer region

Adapt electron-atom codes

Long-range multipole polarization potential

Many degenerate channels

Long-range (dipole) coupling

More information:

J. Tennyson, Electron - molecule collision calculations using the R-matrix method, Phys. Rep., 491, 29 (2010).

Recent developments:

- Positron-molecule collisions and positron annihilation
- Partitioned R-matrix method
- OpenMP and 64-bit implementations
- R-matrix with pseudo-states (RMPS)

Pseudostates approximate second continuum.

Useful for

- Impact ionisation
- Extending energy range of calculations
- Representing target polarization
- e^- -- e^+ correlation and annihilation

R-matrix method: inner region wavefunction

$$\Psi_k = \mathcal{A} \sum_{i,j} a_{i,j,k} \phi_i^N \eta_{i,j} + \sum_i b_{j,k} \phi_j^{N+1}$$

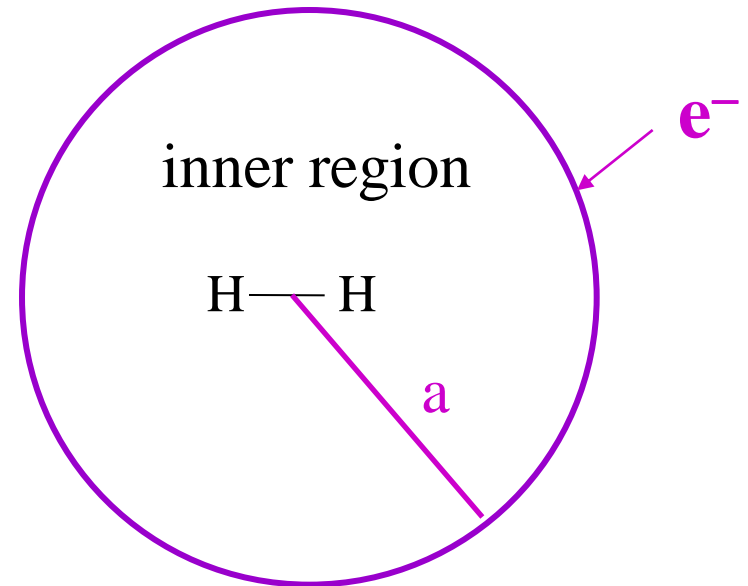
$\phi_i^N =$ target states = CI target built from nuclear centred GTOs

$\phi_j^{N+1} = L^2$ functions

$\eta_{i,j} =$ continuum orbitals =
GTOs centred on centre of mass

$\mathcal{A} =$ Anti-symmetriser

$a_{i,j,k}$ and $b_{j,k}$ variationally determined coefficients



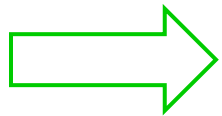
Intermediate impact energies



Ionization and large number of states energetically accessible

In principle, an infinite number of states needed in the close-coupling expansion

Semi-rigorous methods used for ionization (eg BEB in Quantemol-N): provide analytical expression for the cross section



Molecular R-matrix with Pseudo-States method
(RMPS)

R-matrix with pseudostates method (RMPS)

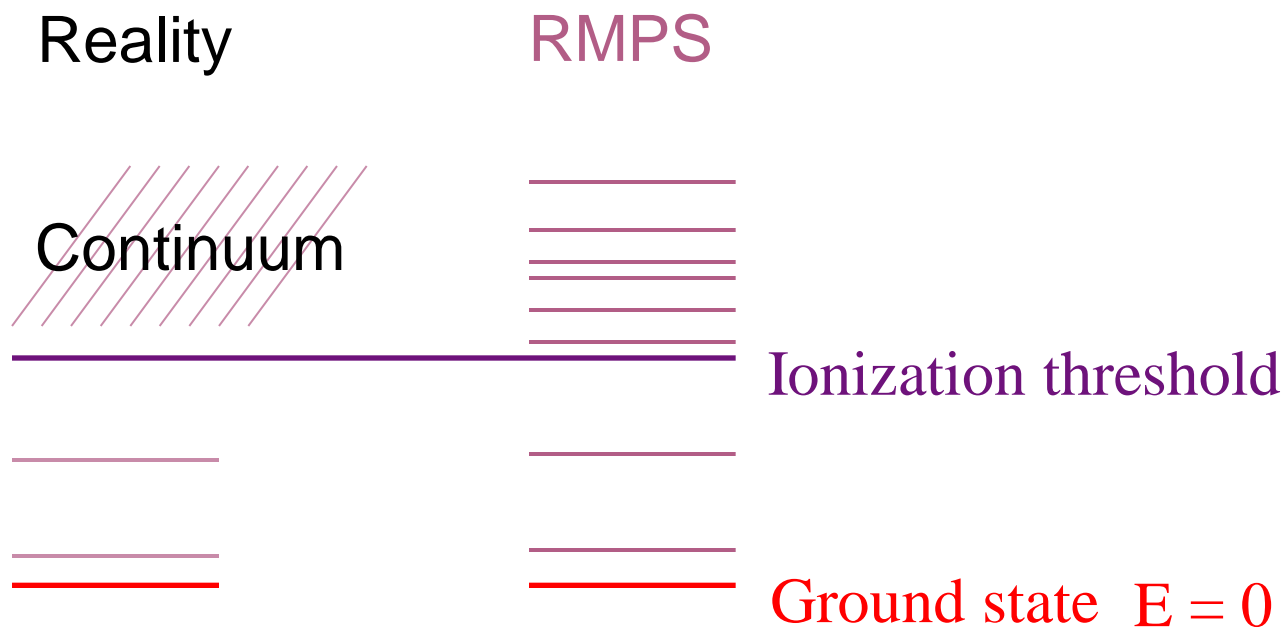
$$\Psi_k = \mathcal{A} \sum_{i,j} a_{i,j,k} \phi_i^N \eta_{i,j} + \sum_i b_{j,k} \phi_j^{N+1}$$

Add ϕ_i^N not true eigenstates of system:

- represent discretised continuum
- obtained by diagonalising target H
- do not represent physical states of the system
- transitions to these states give ionization (projection?)

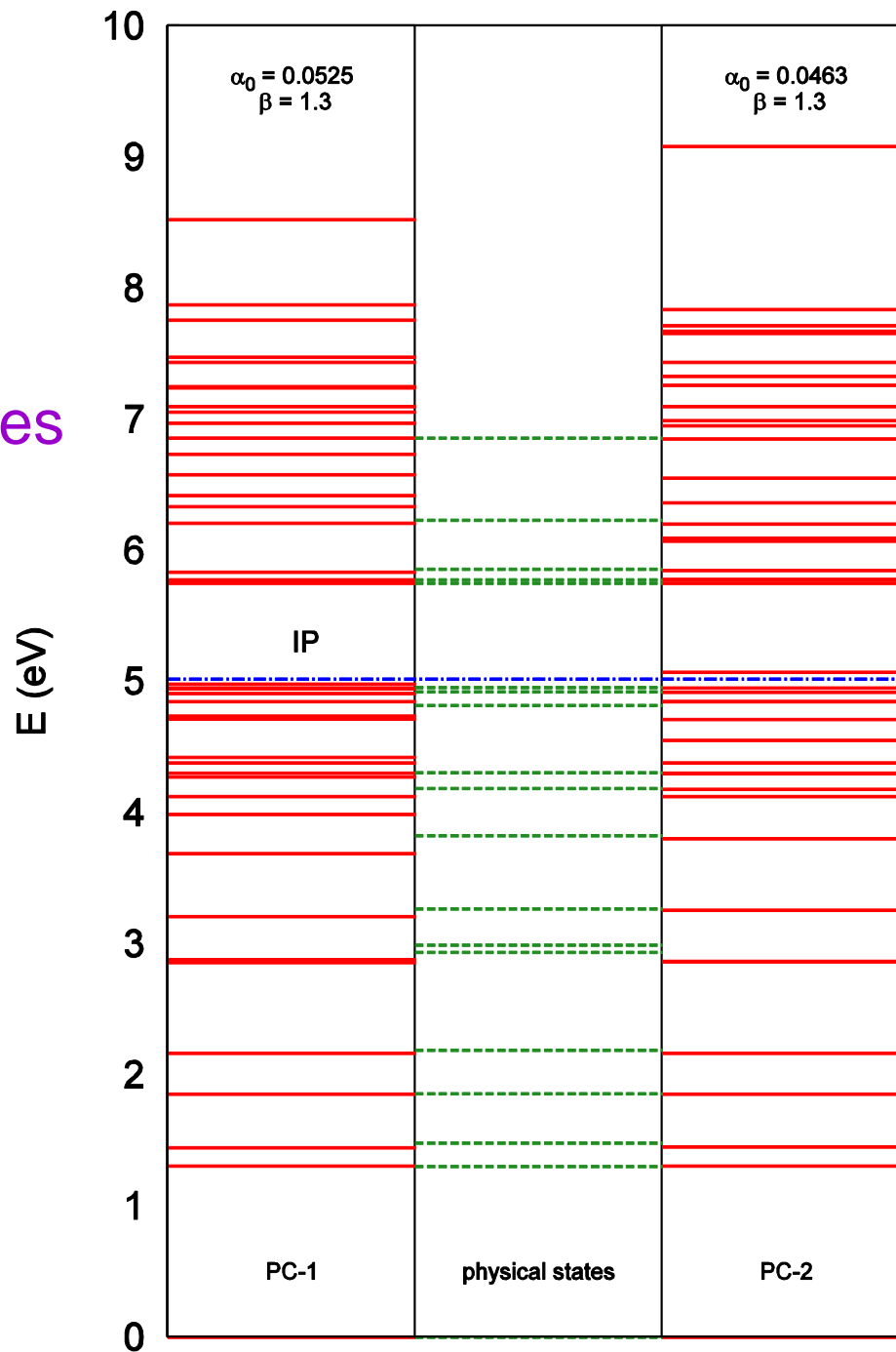
Pseudostates

R-matrix with pseudostates (RMPS) method



J D Gorfinkiel and J Tennyson, J. Phys. B, **37**, L343 (2004).

Li₂:
RMPS
Target states



Ground state E = 0

Example: H_3^+

Positive ion, electron density compact \Rightarrow can keep box small ($a = 10 a_0$)

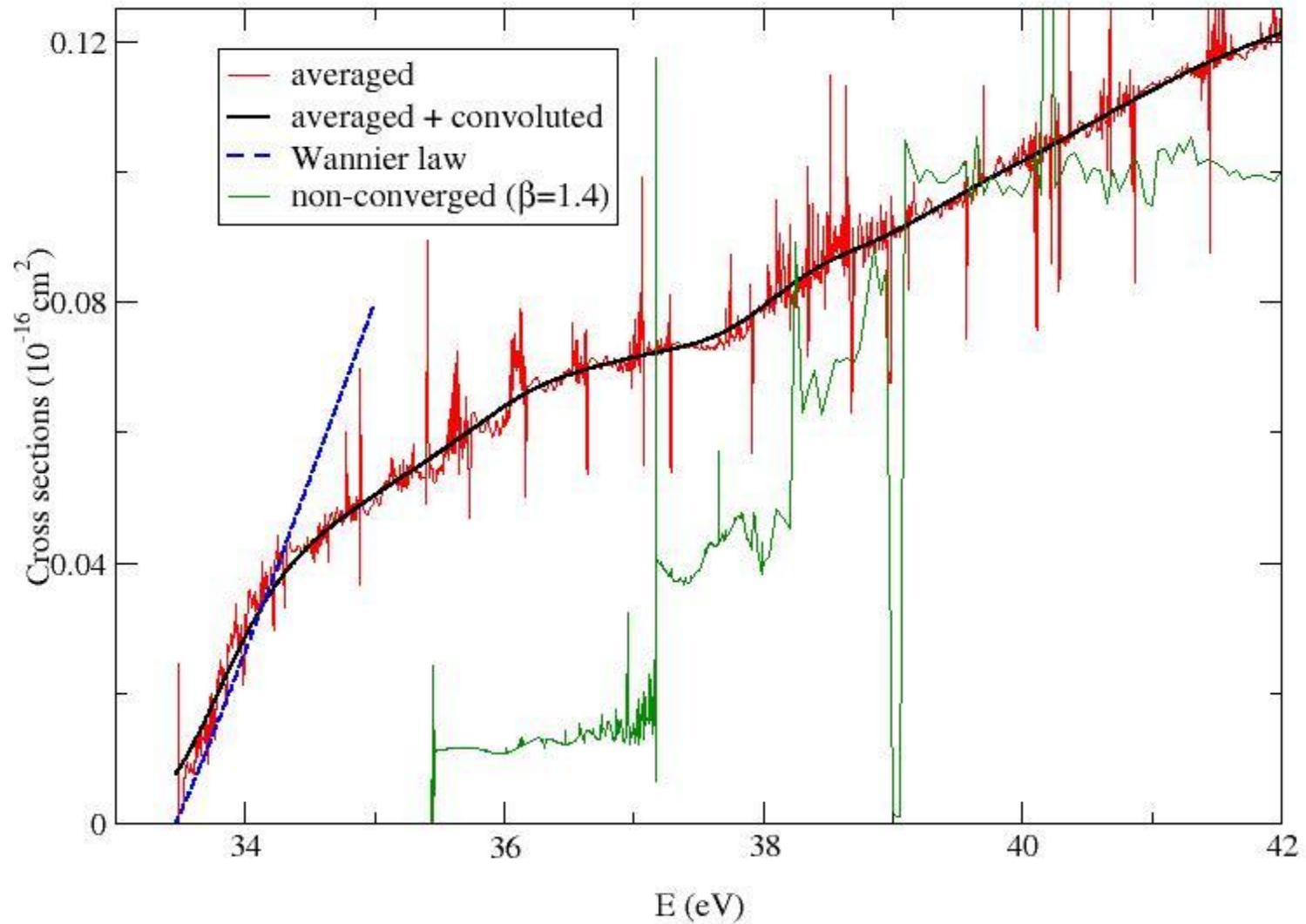
Previous ‘Standard’ calculations for electronic excitation, $E < 20$ eV

- Kohn calculation: Orel (1992)
- R-matrix calculation: Faure and Tennyson (2002) (6 target states)

In our calculation:

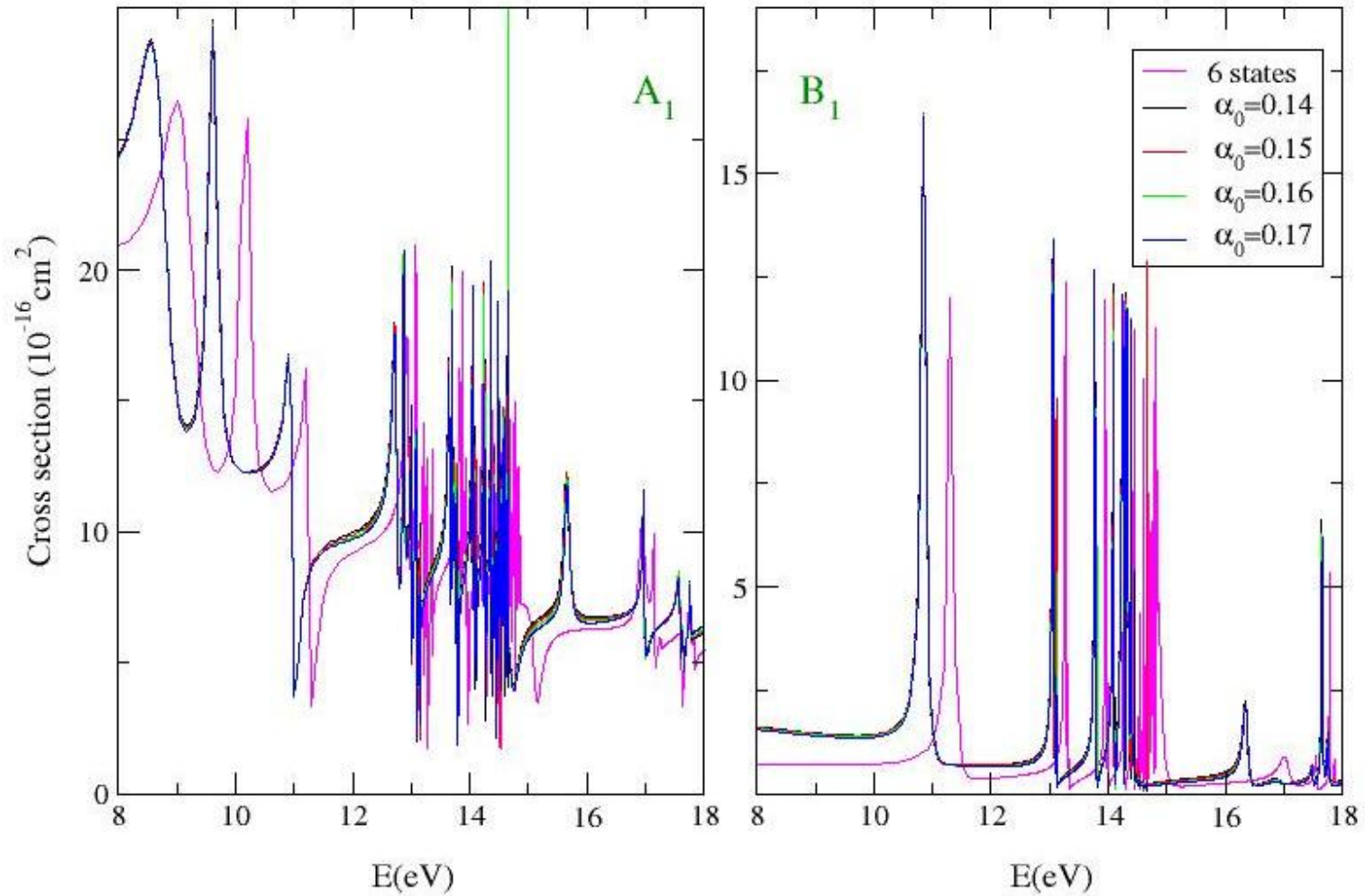
- Target basis set and continuum basis set ($l = 0, 1, 2, 3, 4$)
from standard calculation
- Different basis sets for PCOs with $\beta=1.3$, $\alpha_0=0.14, 0.15, 0.16, 0.17$ and $l = 0, 1, 2$, and others

Electron impact ionisation of H_3^+



J D Gorfinkiel & J Tennyson, *J Phys B*, **37**, L343 (2004); **38**, 1607 (2005).

Electronic excitation of H_3^+



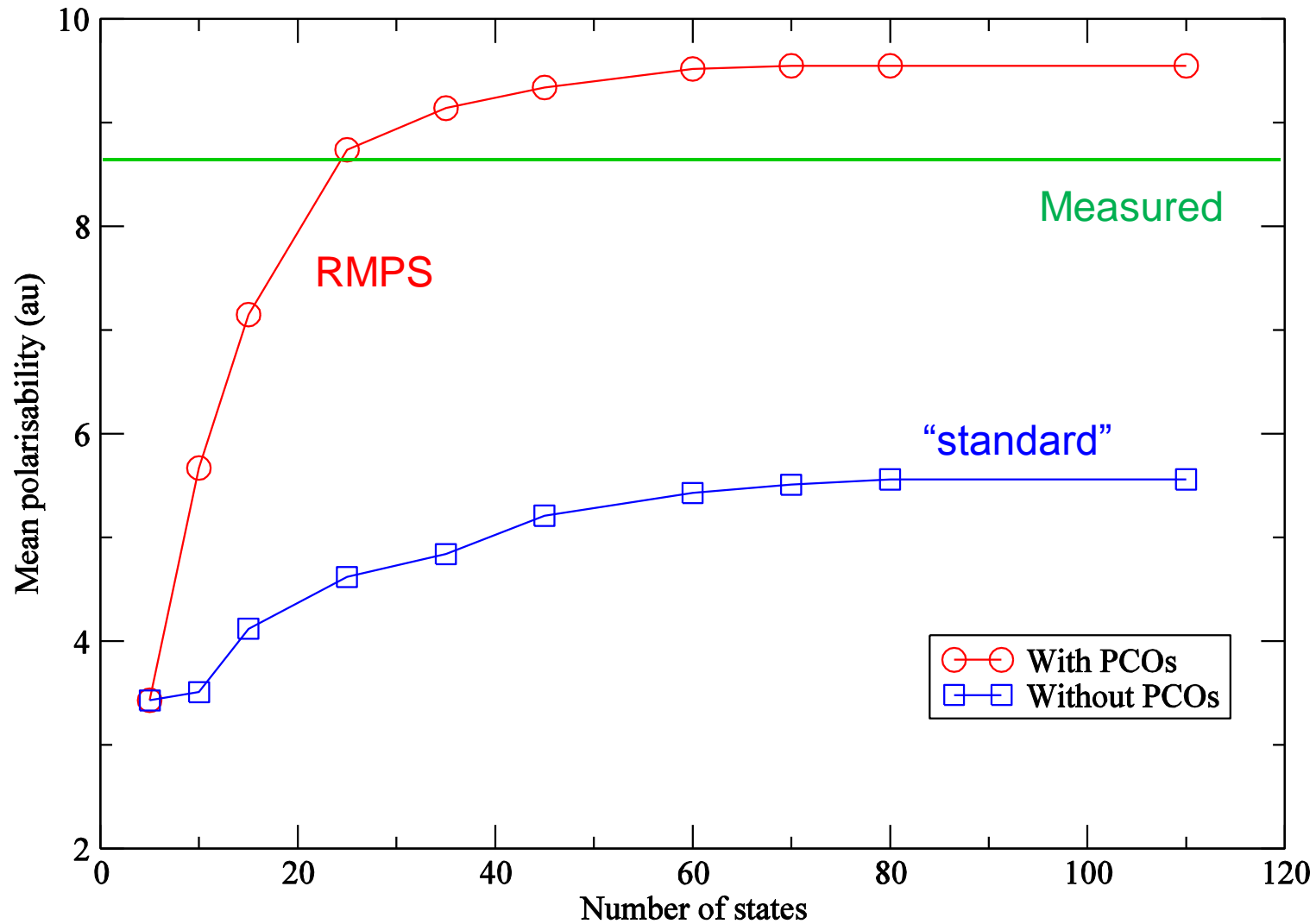
Quantum defect for resonances increased by about 0.05

Molecular R-matrix with Pseudostates Method (MRMPS)

Polarizability of H_3^+ (in a.u.)

States in close-coupling expansion	α_{parallel}	$\alpha_{\text{perpendicular}}$
6 (physical target states)	-3.2848	-0.0638
28 ($E_{\text{cut}}=33.47$ eV)	-3.4563	-2.0893
64 ($E_{\text{cut}}=45$ eV)	-3.5247	-2.2093
152 ($E_{\text{cut}}=132$ eV)	-3.5336	-2.2480
Accurate <i>ab initio</i> value	-3.5978	-2.2454

Mean polarizability of H₂O (in a.u.)



Electron collisions with C_2^-

- ➡ Search for the C_2^{2-} resonances observed in photodetachment measurements from ASTRID

C_2 target

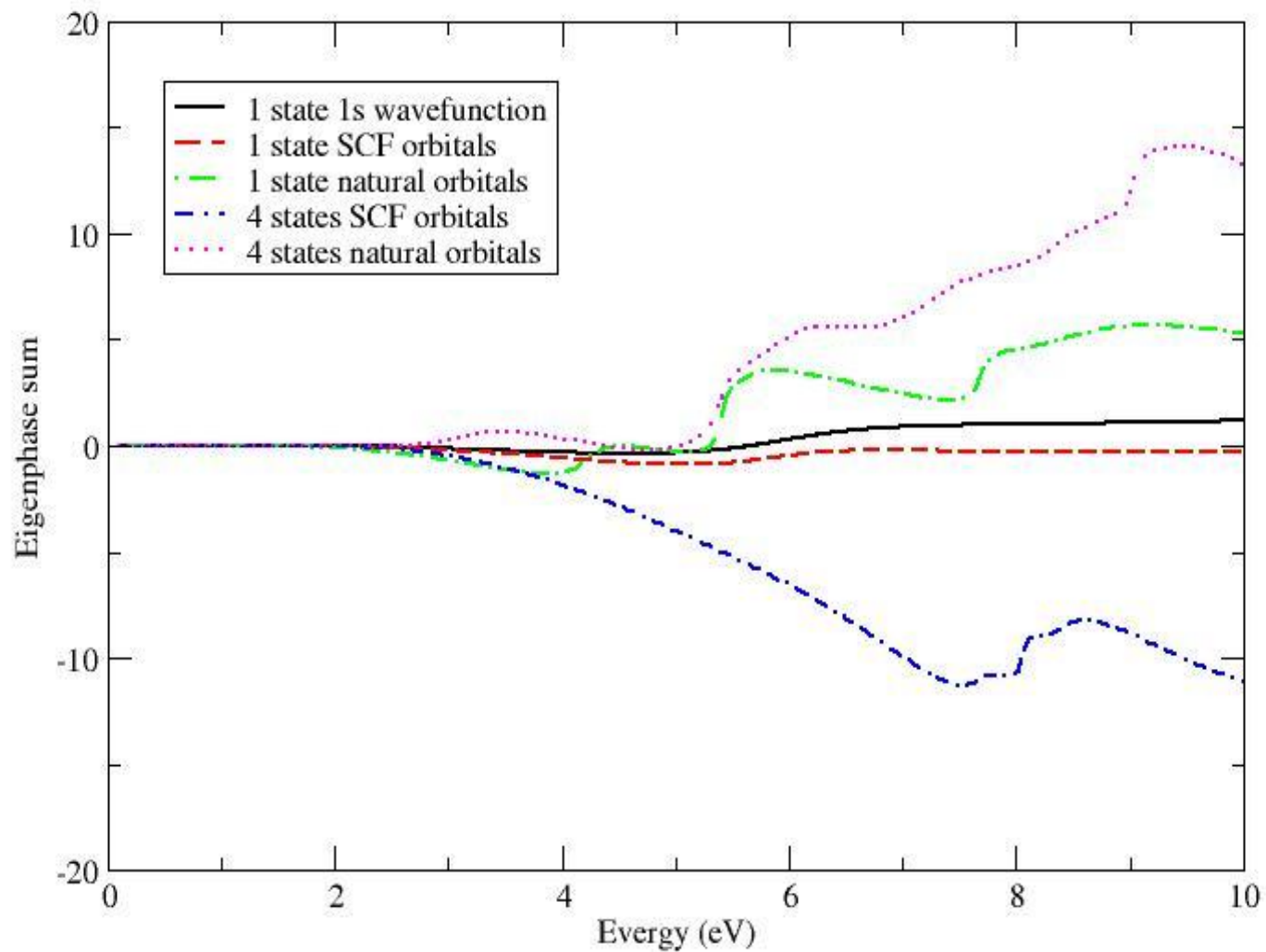
- ➡ 3 bound states of C_2^- of doublet spin symmetry
- ➡ Low-lying resonance of quartet spin symmetry

G Halmova, JD Gorfinkel & J Tennyson, J Phys B 39, 2849 (2006).

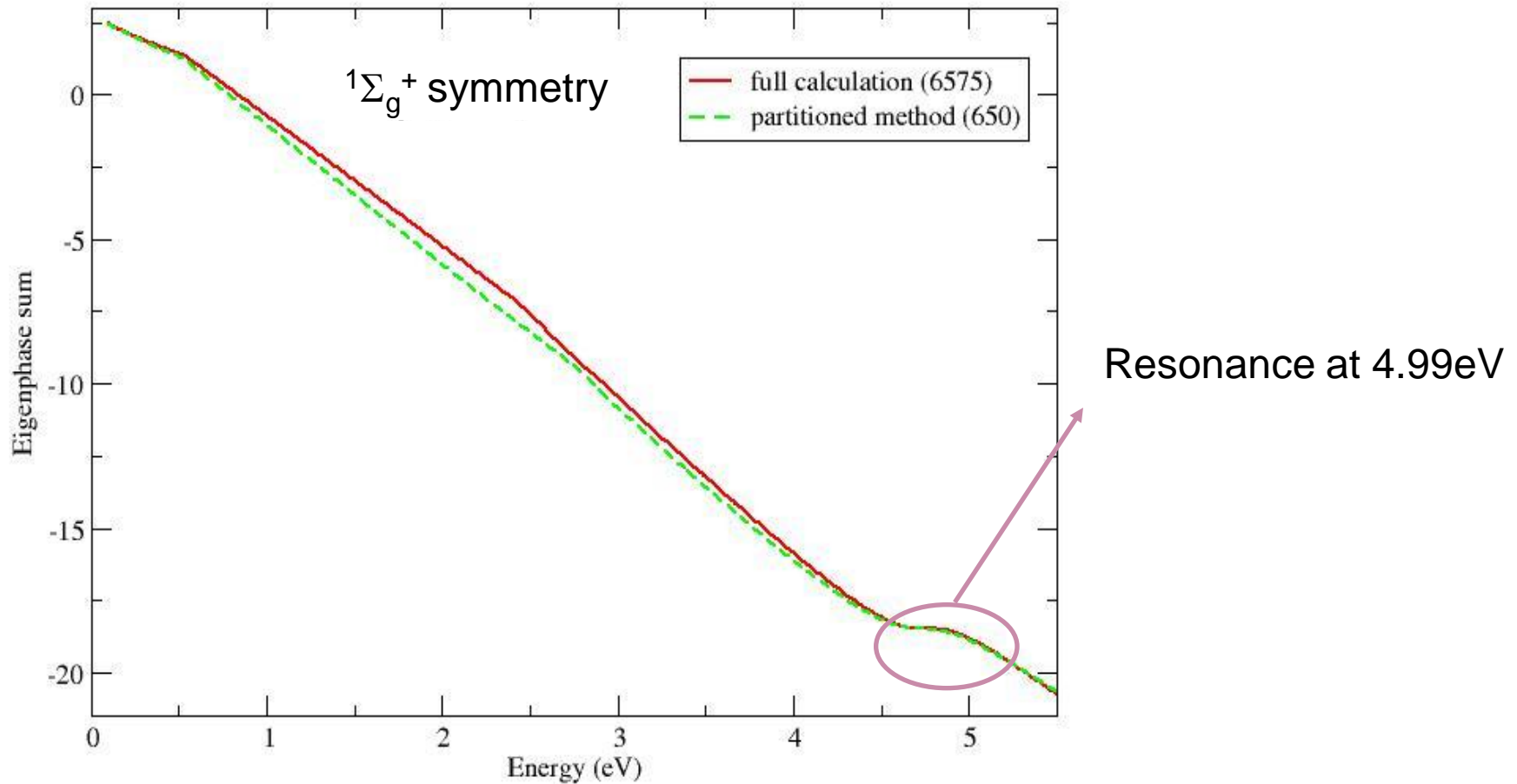
Needs

- ➡ Electron collisions from an anion
- ➡ Molecular R-Matrix with PseudoStates (MRMPS)
- ➡ Partitioned R-Matrix method

Electron – anion (C_2^-) scattering



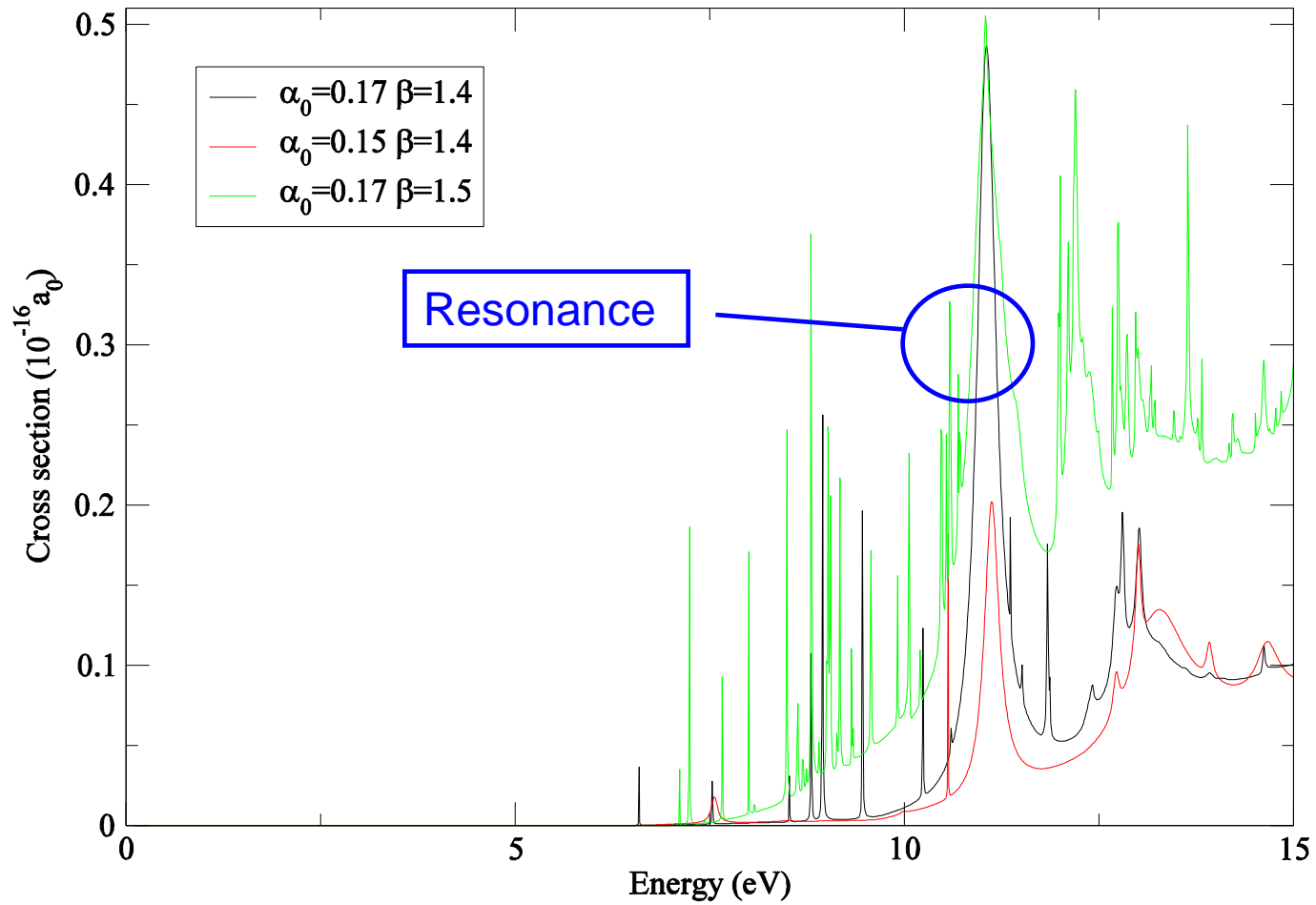
MRMPS, partitioned R-matrix calculation for electron - C₂⁻



Not all the solutions of the Hamiltonian matrix are needed to construct R-matrices.

Partitioned R-matrix method: [J Tennyson, J. Phys. B, 37, 1061 \(2004\).](#)

Electron impact ionisation: several α 's



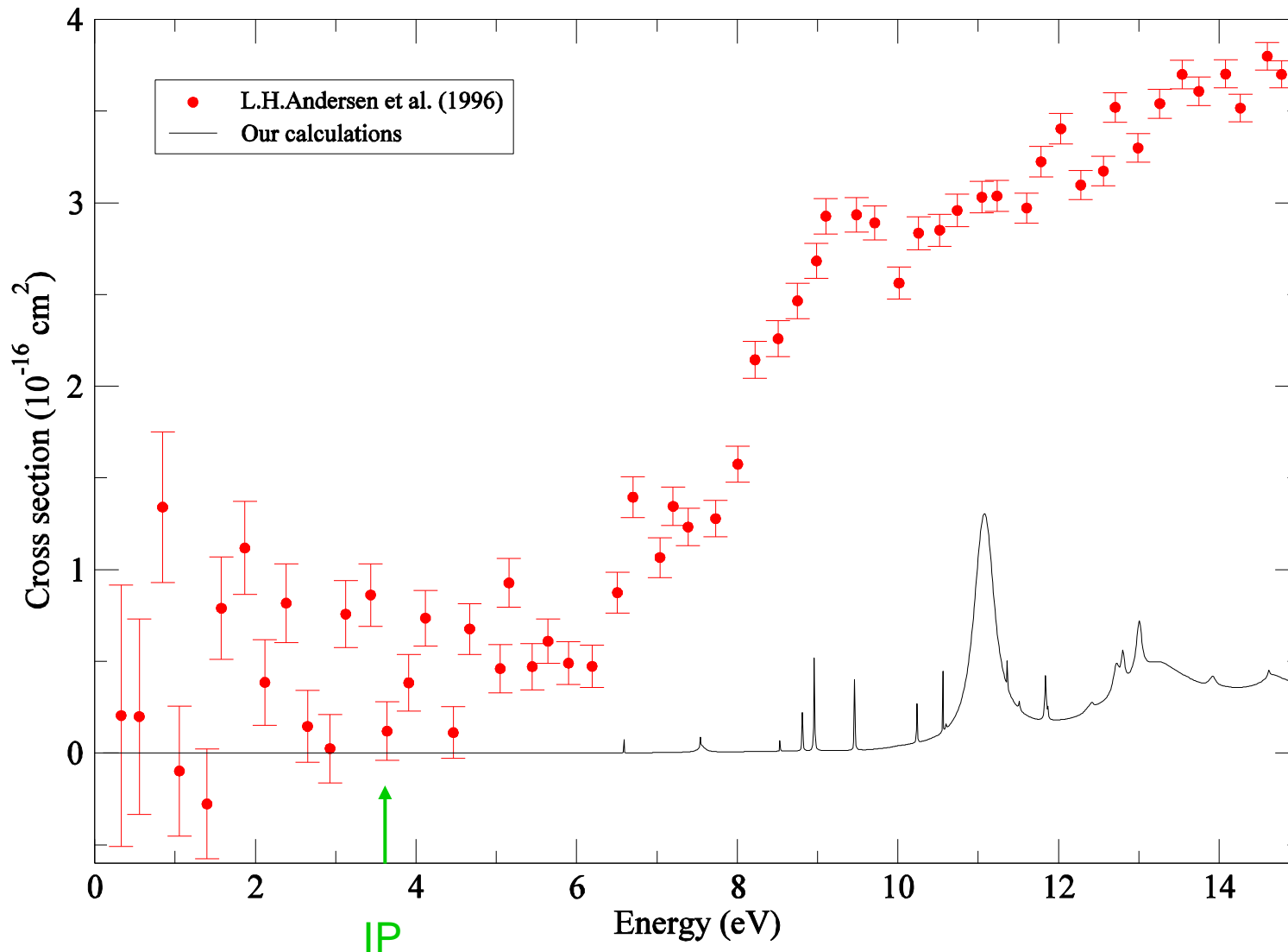
C_2^{2-} resonances

Find 3 broad resonances for

	E/eV	Γ /eV	
$^1\Sigma_g^+$	4.86	0.65	(also predicted by Sommerfeld et al (2000))
$^3\Pi_g$	9.71	1.14	
$^1\Pi_g$	10.92	0.52	

Find no resonance for $^1\Sigma_g^-$ symmetry
(predicted by Andersen et al (1996))

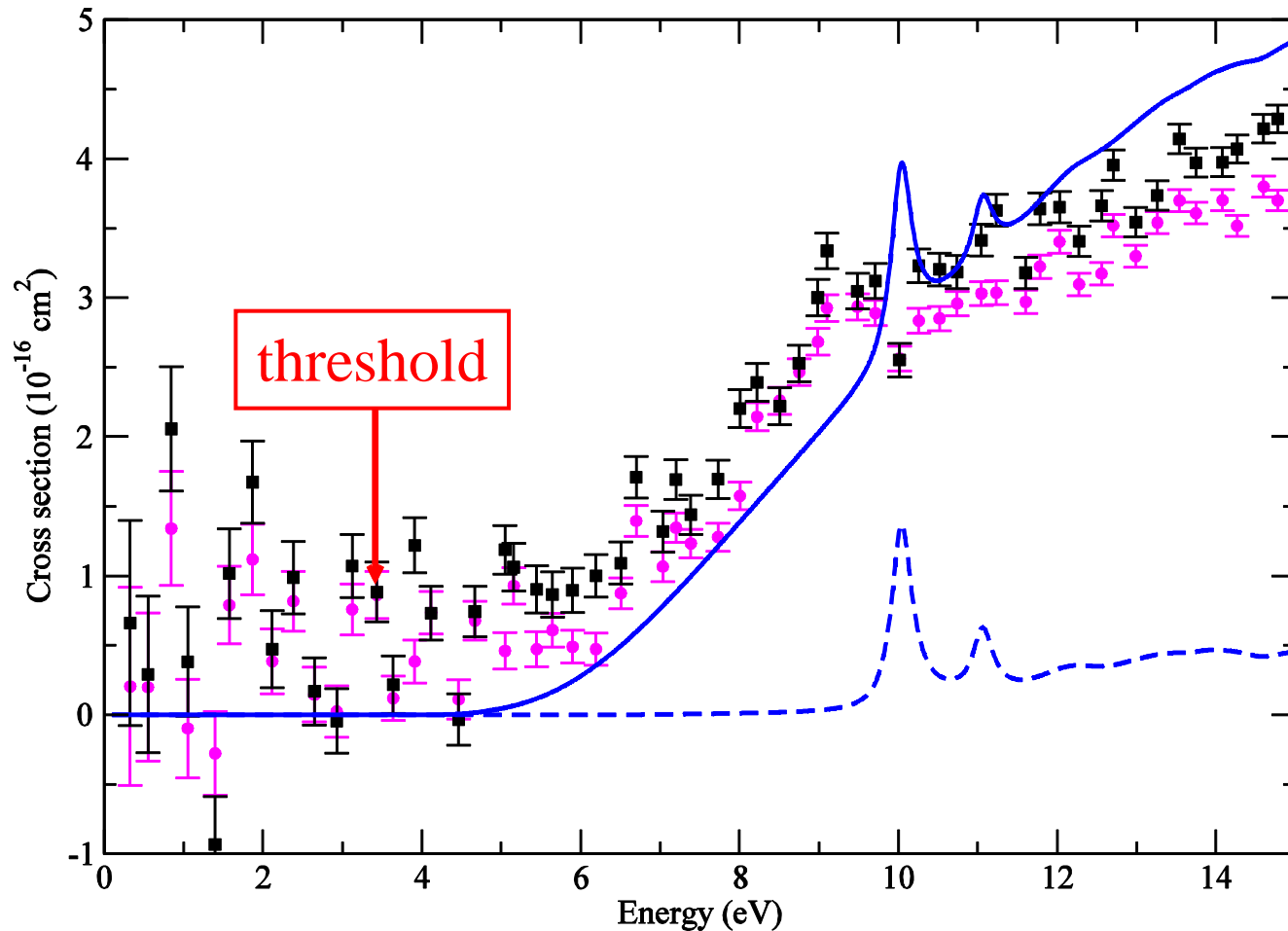
Electron impact electron detachment of C_2^-



Resonance mechanism?

- Unusual form of shape resonance
- Basic potential is strongly repulsive (Coulombic)
- Local minima due to polarisation potential
- Shape resonance with $l=0$ ($^1\Sigma_g^+$)
- $^3\Pi_g$ and $^1\Pi_g$ resonance a little too high:
presumably polarisation underestimated

Electron impact electron detachment of C_2^-



G Halmova & J Tennyson, Phys. Rev. Lett., 100, 213202 (2008)

G Halmova, JD Gorfinkiel & J Tennyson, J. Phys. B, 41, 155201 (2008)

Conclusions: electrons collisions

With the RMPS method for electron–molecule collisions we have:

- extend energy range of calculations
- treat near threshold ionisation
- improve representation of polarisation

Allows us to treat excitation to high electronic states and collisions with anions (e.g. C_2^-)

RMPS method also excellent for positron – molecule collisions but requires use of high l functions.

Recent developments:

- Positron-molecule collisions and positron annihilation
- Partitioned R-matrix method
- OpenMP and 64-bit implementations
- R-matrix with pseudo-states (RMPS)

Developments in progress

- MPI implementation for massively parallel machines
- Time-dependent approach for molecules in intense laser fields