

# Interpretation of results from Quantemol-EC

Greg Armstrong, Harin Ambalampitiya,  
Kateryna Lemishko, Sebastian Mohr, Anna Nelson,  
Jonathan Tennyson

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# Quantemol Electron Collisions (QEC)



- User-friendly interface for calculating electron-molecule collisions.
- Molpro quantum chemistry package provides molecular target orbitals.
- Molecular R-matrix (UKRmol+) code calculates cross sections.

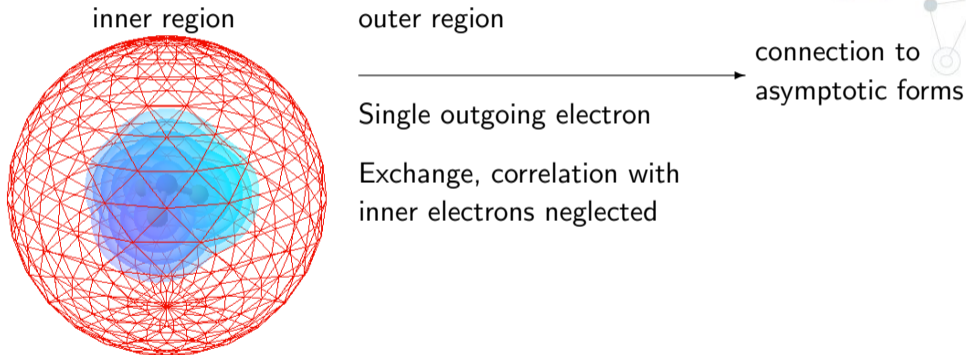


- Calculates cross sections and rates for various collisional processes including:
  - Elastic scattering.
  - Momentum transfer.
  - Electronic, rotational, vibrational excitation.
  - Dissociative electron attachment.
  - Ionization.

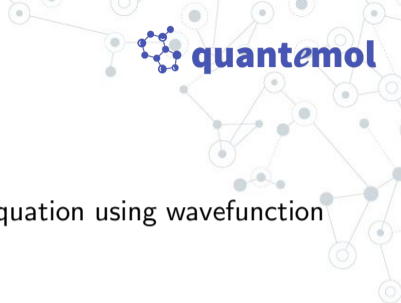


## R-matrix theory

- Space divided into inner, outer and asymptotic regions.
- Inner region confines the  $N$ -electron molecular target.



- Outer region wavefunction extends to large distances.
- Connection to asymptotic forms allows calculation of cross sections.



- Solve  $(N + 1)$ -electron time-independent Schrödinger equation using wavefunction expansion

$$\psi_k^{N+1} = \mathcal{A} \sum_{i,j} c_{ijk} \Phi_i^N(\mathbf{x}_1, \dots, \mathbf{x}_N) \eta_{ij}(\mathbf{x}_{N+1}) + \sum_m b_{mk} \chi_m^{N+1}(\mathbf{x}_1, \dots, \mathbf{x}_{N+1}).$$

- $N$ -electron target wavefunctions  $\Phi_i^N(\mathbf{x}_1, \dots, \mathbf{x}_N)$  calculated using MOLPRO basis sets and orbitals.



## R-matrix theory: outer region

- Solve for the radial wavefunction of a single outgoing electron ( $N + 1$ ):

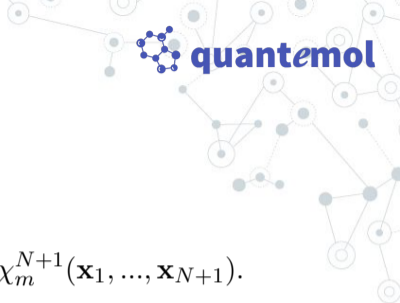
$$\Psi_j^{N+1} = \sum_i \bar{\Phi}_i(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) \frac{F_{ij}(r_{N+1})}{r_{N+1}}.$$

- At large distances ( $r_{N+1} = 100a_0$ ), solutions connect to asymptotic forms to calculate  $K$  matrix and eigenphase  $\delta(E)$ :

$$F_{ij}(r) \underset{r \rightarrow \infty}{\sim} \delta_{ij} \sin(k_i r + l\pi/2) + \cos(k_i r + l\pi/2) K_{ij},$$

$$\delta(E) = \sum_i \tan^{-1}(K_{ii}).$$

## Scattering models: Static exchange (SE)



- 1-state target representation (single  $\Phi^N$ )

$$\psi_k^{N+1} = \mathcal{A} \sum_j c_{jk} \Phi^N(\mathbf{x}_1, \dots, \mathbf{x}_N) \eta_j(\mathbf{x}_{N+1}) + \sum_m b_{mk} \chi_m^{N+1}(\mathbf{x}_1, \dots, \mathbf{x}_{N+1}).$$

- $\chi_m^{N+1}$  is a product of target state and virtual spin orbital for scattering electron.
- Cannot treat electronic excitation (no Feshbach resonances).
- Cannot treat target polarization.



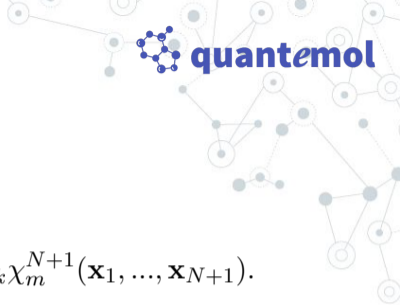
- 1-state target representation

$$\psi_k^{N+1} = \mathcal{A} \sum_j c_{jk} \Phi^N(\mathbf{x}_1, \dots, \mathbf{x}_N) \eta_j(\mathbf{x}_{N+1}) + \sum_m b_{mk} \chi_m^{N+1}(\mathbf{x}_1, \dots, \mathbf{x}_{N+1}).$$

- $\chi_m^{N+1}$  include single-electron excitations of target.
- Shape and Feshbach resonances can be resolved.
- Captures short-range polarization effects.



## Scattering models: Close coupling



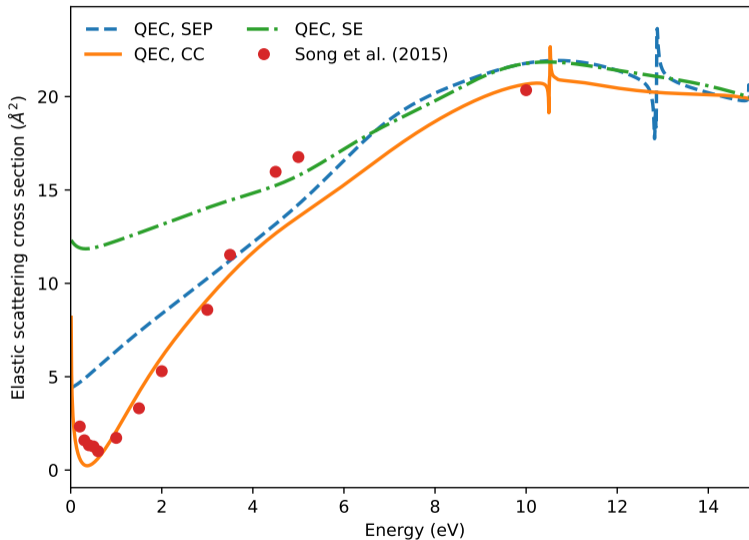
- multi-state target representation (set of  $\Phi_i^N$ ).

$$\psi_k^{N+1} = \mathcal{A} \sum_{i,j} c_{ijk} \Phi_i^N(\mathbf{x}_1, \dots, \mathbf{x}_N) \eta_{i,j}(\mathbf{x}_{N+1}) + \sum_m b_{mk} \chi_m^{N+1}(\mathbf{x}_1, \dots, \mathbf{x}_{N+1}).$$

- Complete active space for  $\chi_m^{N+1}$ .
- Shape and Feshbach resonances can be found.
- Applicable at energies up to first missing excitation threshold.

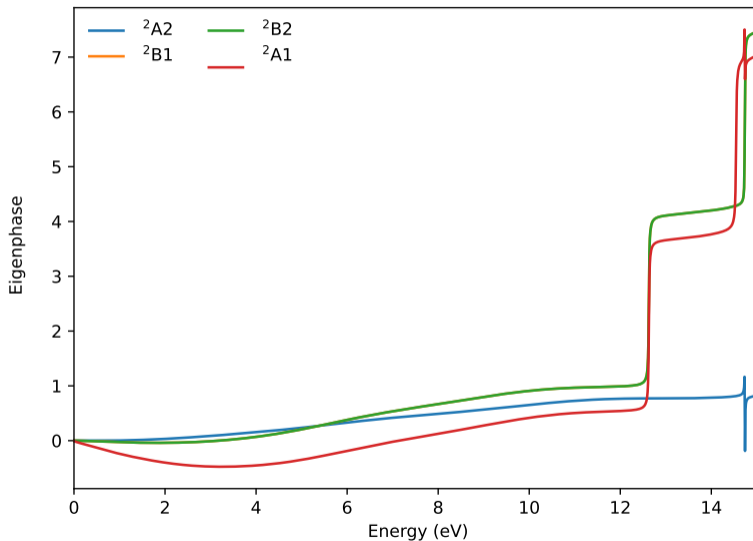


# Results: Elastic scattering cross section CH<sub>4</sub>

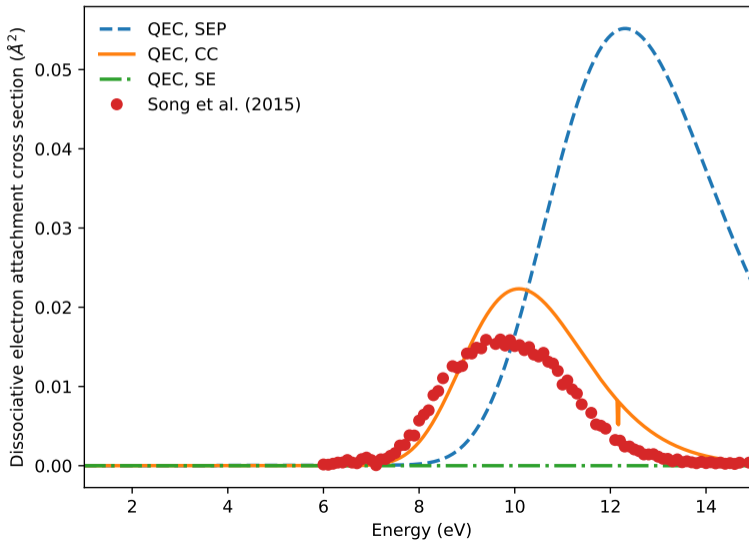


M.-Y. Song et al., J. Phys. Chem. Ref. Data **44** 023101 (2015).

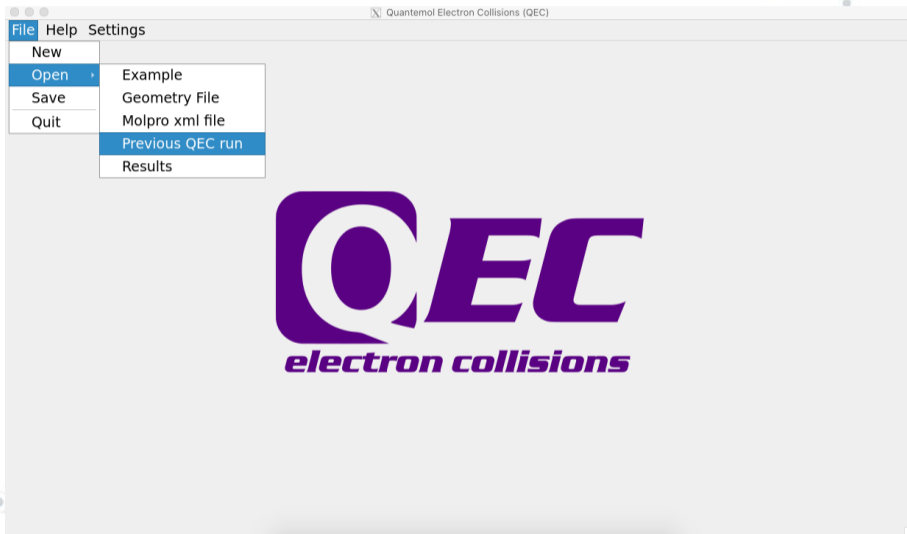
# Results: Eigenphases $\text{CH}_4$



# Results: Dissociative electron attachment cross section $e^- + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}^-$



# QEC Initial Setup



# QEC Molecule Setup

Quantemol Electron Collisions (QEC)

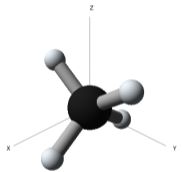
File Help Settings

## QEC Molecule Setup

Adding a few atoms? Click [here](#) to find out how to load an xyz file or Molpro xml!

Molecular Viewer

Show Axes Save Image



Buttons: Add Atom, Optimise, Center

### Molecular Coordinates (Angstroms)

Atom	X	Y	Z
1 C	0	0	0
2 H	0	-0.8836	0.6248
3 H	0	0.8836	0.6248
4 H	-0.8836	0	-0.6248
5 H	0.8836	0	-0.6248

Isotopes Delete Atom

### Bond Lengths (Angstroms)

Atom 1	Atom 2	R
1 C	H	1.0822
2 C	H	1.0822
3 C	H	1.0822
4 C	H	1.0822

### Bond Angles (Degrees)

Atom 1	Atom 2	Atom 3	Angle
1 H	C	H	109.4712
2 H	C	H	109.4712
3 H	C	H	109.4712
4 H	C	H	109.4712
5 H	C	H	109.4712

Buttons: Back, Next, Setup Next job, Show Job List, Run All jobs

# QEC Molpro basis sets and orbitals setup

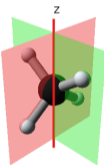
Quantemol Electron Collisions (QEC)

File Help Settings

**QEC Molpro Setup**

Molecular Viewer

Save Image



Point group identified as: C2v

Molpro Options

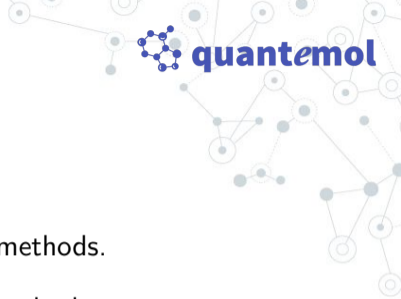
Orbital Type:  HFSCF  MCSCF

Basis Set: cc-pVDZ

Advanced Options

Back Next Setup next job Job list Run

# QEC Molpro basis and orbital sets setup



- Hartree-Fock (HFSCF) orbitals used with SE and SEP methods.
- Multi-configurational (MCSCF) orbitals used with CC method.
- Dunning (cc-pVXZ), Pople (W-XYZG), and Karlsruhe (def2-WXYZ) basis sets available.





# Advanced options for ions, radicals, large systems

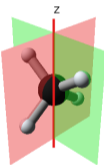
Quantemol Electron Collisions (QEC)

File Help Settings

**Q.EC Molpro Setup**

Molecular Viewer

Save Image



Point group identified as: C2v

Molpro Options

Orbital Type:  HFSCF  MCSCF

Basis Set: cc-pVDZ

Advanced Options

- Use an ECP
- Charge: 0
- Multiplicity: 1
- Symmetry: A1
- Memory (mw): 20

Back Next Setup Next job Show Job List Run All jobs

# QEC active space (CAS) settings

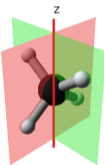
Quantemol Electron Collisions (QEC)

File Help Settings

### QEC Molpro Setup

Molecular Viewer

Save Image



Point group identified as: C2v

Molpro Options

Orbital Type:  HFSCF  MCSCF

Basis Set: cc-pVDZ

Advanced Options

- Use an ECP
- Charge: 0
- Multiplicity: 1
- Symmetry: A1
- Memory (mw): 20

MCSCF Calculations

Closed Orbitals:

A1	B1	B2	A2
1	0	0	0

Active Orbitals:

A1	B1	B2	A2
4	2	2	0

Back Next Setup Next job Show Job List Run All jobs

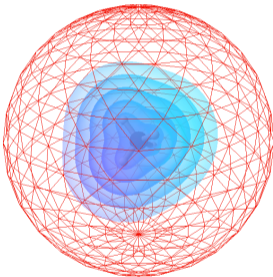
# QEC $R$ -matrix setup (SE)

Quantemol Electron Collisions (QEC)

File Help Settings

Molecular Viewer

Save Image



R-matrix Options

R-matrix sphere (Bohr): 10

Method: Static Exchange (SE)

Scattering Energy Grid:

Start energy (eV): 0.010

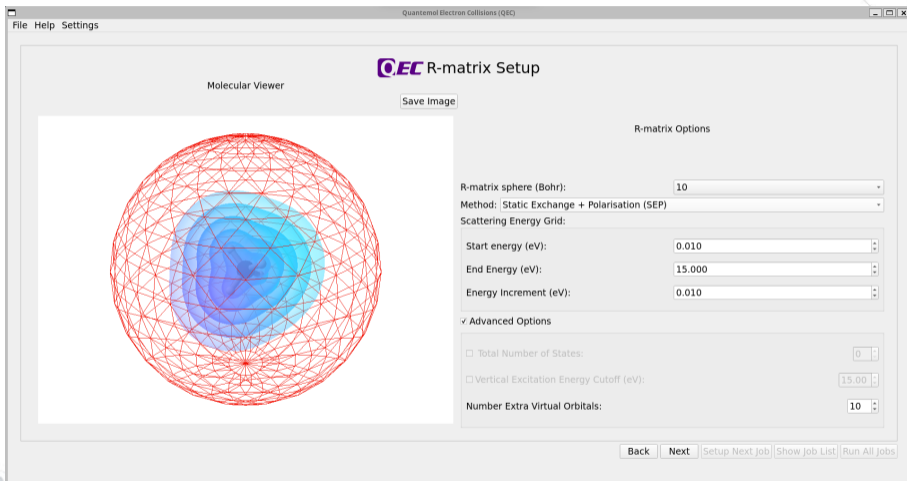
End Energy (eV): 15.000

Energy Increment (eV): 0.010

Advanced Options

Back Next Setup Next job Show Job List Run All jobs

# QEC *R*-matrix setup (SEP)

A screenshot of the "Quantemol Electron Collisions (QEC)" software interface. The window title is "Quantemol Electron Collisions (QEC)". The menu bar includes "File", "Help", and "Settings". The main area is titled "QEC R-matrix Setup" and is divided into two sections: "Molecular Viewer" and "R-matrix Options".  
The "Molecular Viewer" section on the left contains a 3D visualization of a molecule, represented by a red wireframe sphere with a blue and cyan density map inside. A "Save Image" button is located above the viewer.  
The "R-matrix Options" section on the right contains several input fields and checkboxes:  
- "R-matrix sphere (Bohr):" set to 10.  
- "Method:" set to "Static Exchange + Polarisation (SEP)".  
- "Scattering Energy Grid:" section with:  
 - "Start energy (eV):" 0.010  
 - "End Energy (eV):" 15.000  
 - "Energy increment (eV):" 0.010  
- "Advanced Options" section (checked) with:  
 - "Total Number of States:" 0  
 - "Vertical Excitation Energy Cutoff (eV):" 15.00  
 - "Number Extra Virtual Orbitals:" 10  
At the bottom right, there are buttons for "Back", "Next", "Setup Next job", "Show Job List", and "Run All jobs".

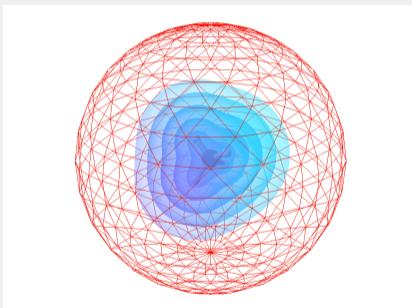
# QEC *R*-matrix setup (CC)

Quantemol Electron Collisions (QEC)

File Help Settings

Molecular Viewer

Save Image



R-matrix Options

R-matrix sphere (Bohr): 10

Method: Close Coupling (CC)

Scattering Energy Grid:

Start energy (eV): 0.010

End Energy (eV): 15.000

Energy Increment (eV): 0.010

Advanced Options

Back Next Setup Next job Show Job List Run All jobs

The screenshot shows the 'QEC R-matrix Setup' window. On the left, the 'Molecular Viewer' displays a red wireframe sphere with a blue and cyan density map inside. A 'Save Image' button is located above the viewer. On the right, the 'R-matrix Options' panel contains several input fields: 'R-matrix sphere (Bohr)' set to 10, 'Method' set to 'Close Coupling (CC)', and 'Scattering Energy Grid' with 'Start energy (eV)' at 0.010, 'End Energy (eV)' at 15.000, and 'Energy Increment (eV)' at 0.010. There is an unchecked 'Advanced Options' checkbox. At the bottom right, there are buttons for 'Back', 'Next', 'Setup Next job', 'Show Job List', and 'Run All jobs'.

# QEC *R*-matrix setup (CC)

Quantemol Electron Collisions (QEC)

File Help Settings

Molecular Viewer

Save Image

**QEC R-matrix Setup**

R-matrix Options

R-matrix sphere (Bohr): 10

Method: Close Coupling (CC)

Scattering Energy Grid:

Start energy (eV): 0.010

End Energy (eV): 15.000

Energy increment (eV): 0.010

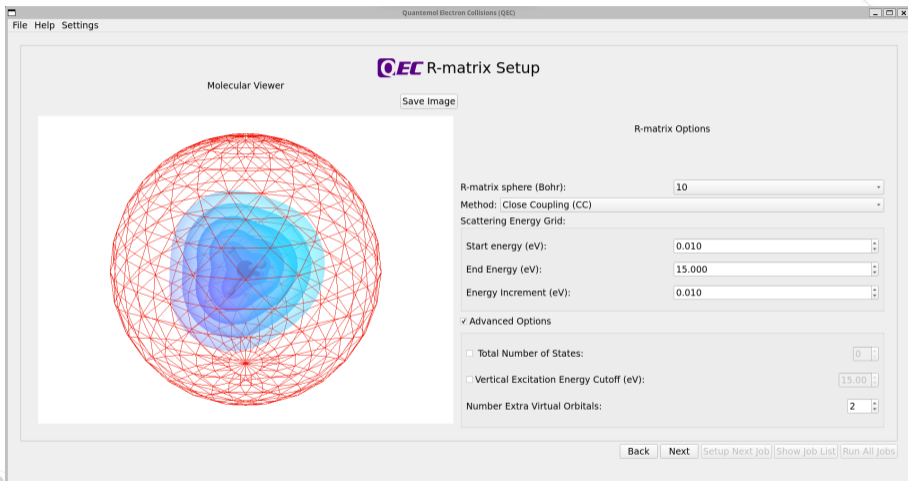
Advanced Options

Total Number of States: 0

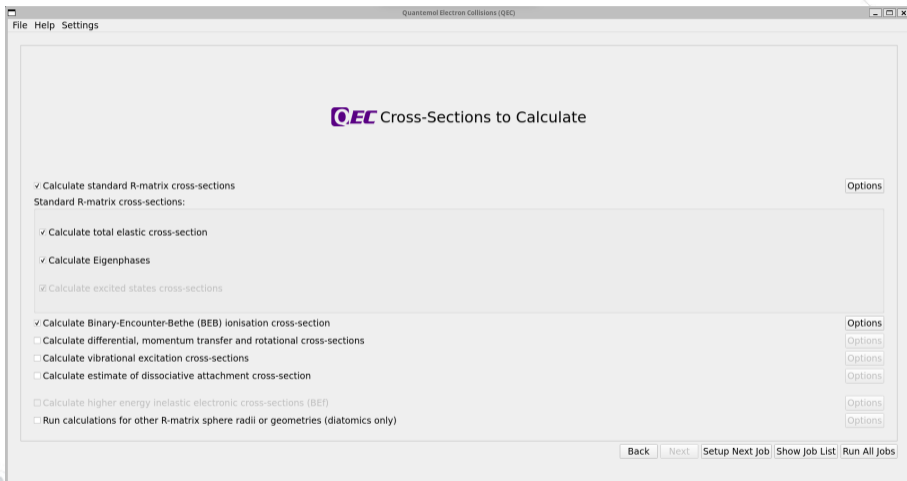
Vertical Excitation Energy Cutoff (eV): 15.00

Number Extra Virtual Orbitals: 2

Back Next Setup Next job Show Job List Run All jobs



# QEC cross sections to calculate (SE or SEP)



Quantemol Electron Collisions (QEC)

File Help Settings

### QEC Cross-Sections to Calculate

Calculate standard R-matrix cross-sections Options

Standard R-matrix cross-sections:

- Calculate total elastic cross-section
- Calculate Eigenphases
- Calculate excited states cross-sections

Calculate Binary-Encounter-Bethe (BEB) ionisation cross-section Options

Calculate differential, momentum transfer and rotational cross-sections Options

Calculate vibrational excitation cross-sections Options

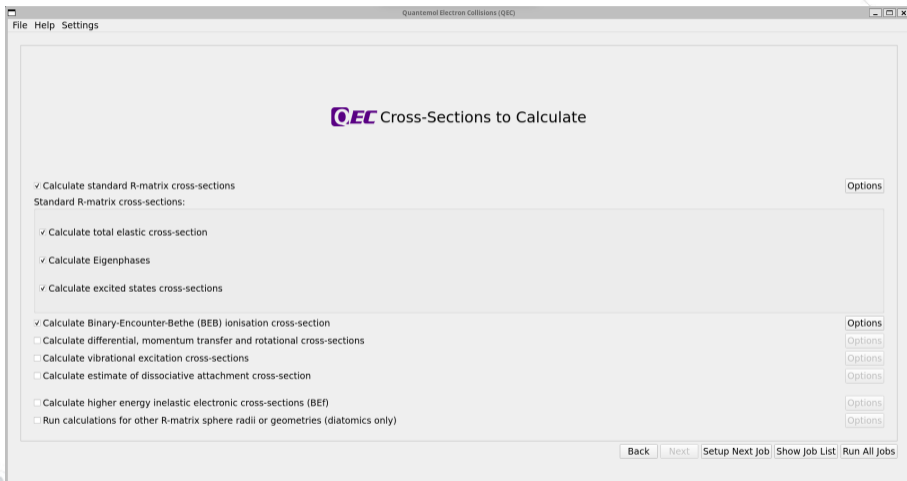
Calculate estimate of dissociative attachment cross-section Options

Calculate higher energy inelastic electronic cross-sections (BEI) Options

Run calculations for other R-matrix sphere radii or geometries (diatomics only) Options

Back Next Setup Next Job Show Job List Run All Jobs

# QEC cross sections to calculate (CC)



Quantemol Electron Collisions (QEC)

File Help Settings

### QEC Cross-Sections to Calculate

Calculate standard R-matrix cross-sections Options

Standard R-matrix cross-sections:

- Calculate total elastic cross-section
- Calculate Eigenphases
- Calculate excited states cross-sections

Calculate Binary-Encounter-Bethe (BEB) ionisation cross-section Options

Calculate differential, momentum transfer and rotational cross-sections Options

Calculate vibrational excitation cross-sections Options

Calculate estimate of dissociative attachment cross-section Options

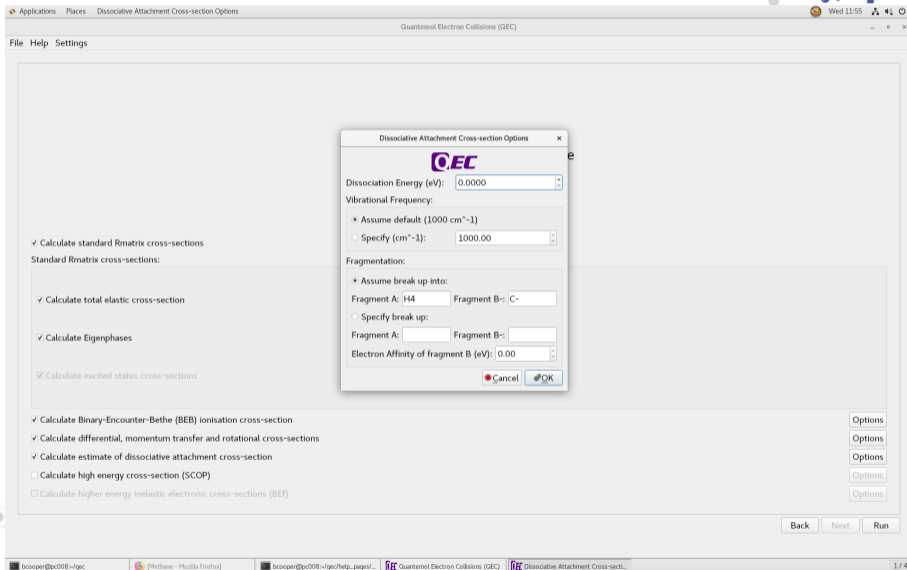
Calculate higher energy inelastic electronic cross-sections (BEI) Options

Run calculations for other R-matrix sphere radii or geometries (diatomics only) Options

Back Next Setup Next Job Show Job List Run All Jobs



# QEC cross sections to calculate (CC)



Applications Places Dissociative Attachment Cross-section Options

Quantemol Electron Collisions (QEC)

File Help Settings

**QEC**

Dissociation Energy (eV): 0.0000

Vibrational Frequency:

- Assume default (1000  $\text{cm}^{-1}$ )
- Specify ( $\text{cm}^{-1}$ ): 1000.00

Fragmentation:

- Assume break up into:

Fragment A: H4 Fragment B: C-

- Specify break up:

Fragment A: Fragment B: Electron Affinity of fragment B (eV): 0.00

Cancel OK

Calculate standard Rmatrix cross-sections

Standard Rmatrix cross-sections:

- Calculate total elastic cross-section
- Calculate Eigenphases
- Calculate excited states cross-sections

Calculate Binary-Encounter-Bethe (BEB) ionisation cross-section

Calculate differential, momentum transfer and rotational cross-sections

Calculate estimate of dissociative attachment cross-section

Calculate high energy cross-section (SCOP)

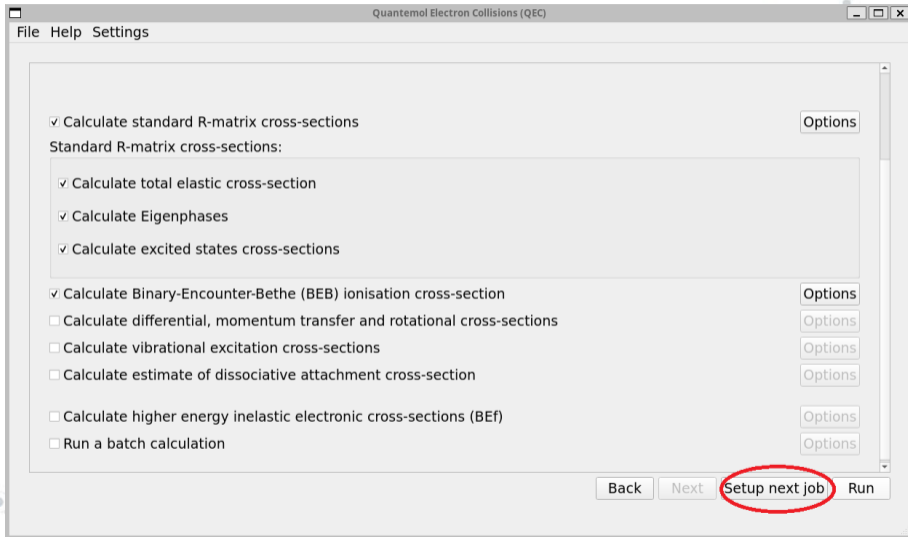
Calculate higher energy inelastic electronic cross-sections (BEF)

Options Options Options Options Options

Back Next Run

bcooper@pc008~qec [Methane - Mozilla Firefox] bcooper@pc008~qec/help\_pages/ QEC Quantemol Electron Collisions (QEC) QEC Dissociative Attachment Cross-sect... 1 / 4

# QEC cross sections to calculate (CC)



# QEC results output

Applications Places Quantemol Electron Collisions (QEC) Fri 11:18

Quantemol Electron Collisions (QEC)

File Help Settings

### Calculation Log

Molecular Information  
-----

Molecule: CH4  
Charge = 0  
Coordinates (Angstroms):  
H, 0.8906, 0.0, 0.6298  
H, -0.8906, 0.0, 0.6298  
H, 0.0, -0.8906, -0.6298  
H, 0.0, 0.8906, -0.6298  
C, 0.0, 0.0, 0.0  
Point group: C2v  
State Energy = -40.1987119763411 a.u.  
Dipoles:  
DX = 0.0 DY = 0.0 DZ = 6.50954984360297e-16 a.u.  
Polarizability = 13.00798937258466 a.u.

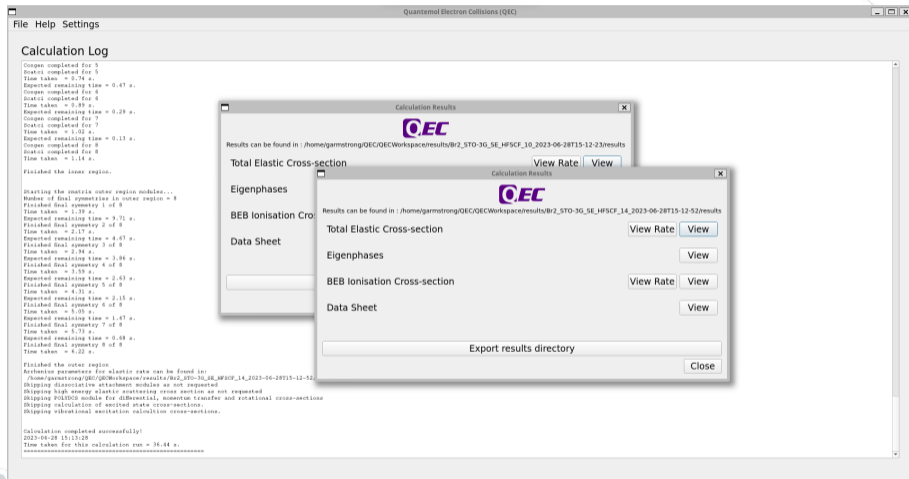
Molecular orbitals  
-----

Occupation	Symmetry	E (Hartree)
2.0	1	-11.216575
2.0	1	-0.941684
2.0	1	-0.542383
0.0	1	0.192926
0.0	1	0.273901
0.0	1	0.589527
0.0	1	0.888767
0.0	1	0.932712
0.0	1	1.131405
0.0	1	1.256294
0.0	1	1.892732
0.0	1	2.210392
0.0	1	2.542079
0.0	1	2.746448
0.0	1	2.792501
2.0	2	-0.542359
0.0	2	0.2739
0.0	2	0.589499
0.0	2	0.888757

Stop

bcooper@pc008~fqec bcooper@pc008~fqec/help\_pages/ [3] Brevet: Labour confirms it will n... bcooper@pc008~fqec/help\_pages quantemol-ec.pdf - Adobe Reader QEC Quantemol Electron Collisions (QEC) 1 / 4

# QEC results output



The screenshot displays the Quantemol Electron Collisions (QEC) software interface. The main window shows a "Calculation Log" with the following text:

```
Congen completed for 5
Scatol completed for 5
Time taken = 0.74 s.
Expected remaining time = 0.47 s.
Congen completed for 6
Scatol completed for 6
Time taken = 0.59 s.
Expected remaining time = 0.29 s.
Congen completed for 7
Scatol completed for 7
Time taken = 1.02 s.
Expected remaining time = 0.13 s.
Congen completed for 8
Scatol completed for 8
Time taken = 1.14 s.

Finished the inner region.

Starting the matrix outer region modules...
Number of final symmetries in outer region = 8
Finished final symmetry 1 of 8
Time taken = 1.39 s.
Expected remaining time = 9.71 s.
Finished final symmetry 2 of 8
Time taken = 2.17 s.
Expected remaining time = 4.67 s.
Finished final symmetry 3 of 8
Time taken = 2.94 s.
Expected remaining time = 3.86 s.
Finished final symmetry 4 of 8
Time taken = 3.59 s.
Expected remaining time = 2.63 s.
Finished final symmetry 5 of 8
Time taken = 4.31 s.
Expected remaining time = 2.15 s.
Finished final symmetry 6 of 8
Time taken = 5.05 s.
Expected remaining time = 1.47 s.
Finished final symmetry 7 of 8
Time taken = 5.73 s.
Expected remaining time = 0.68 s.
Finished final symmetry 8 of 8
Time taken = 6.22 s.

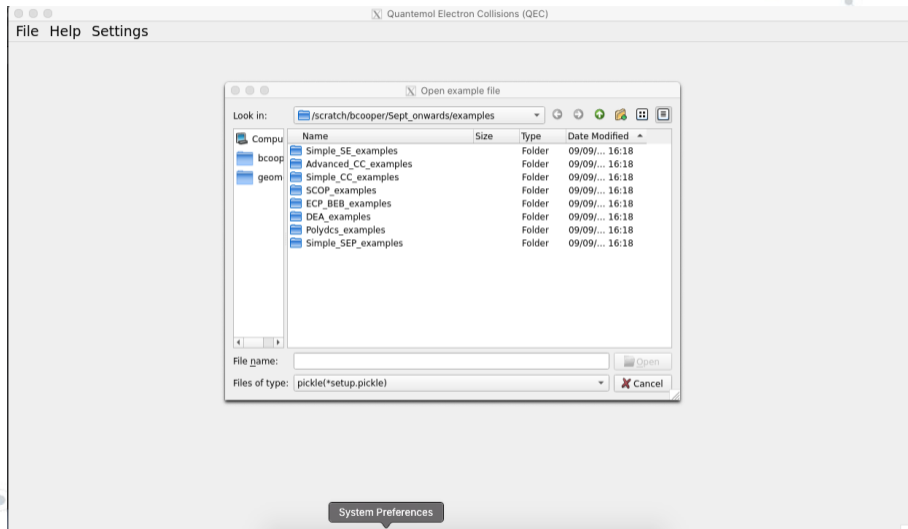
Finished the outer region
Archives parameters for elastic rate can be found in
/home/garmstrong/QEC/QECWorkspace/results/Br2_STO-3G_SE_HFSCF_14_2023-06-28T15-12-52
Skipping dissociative attachment module as not requested
Skipping high energy elastic scattering cross section as not requested
Skipping POLINDCS module for differential, momentum transfer and rotational cross-sections
Skipping calculation of excited state cross-sections.
Skipping vibrational excitation calculation cross-sections.

Calculation completed successfully!
2023-06-28 15:13:28
Time taken for this calculation run = 36.44 s.
*****
```

Two smaller windows are overlaid on the main window:

- Calculation Results (top):** Shows "Results can be found in : /home/garmstrong/QEC/QECWorkspace/results/Br2\_STO-3G\_SE\_HFSCF\_10\_2023-06-28T15-12-23/results". It has buttons for "View Rate" and "View".
- Calculation Results (bottom):** Shows "Results can be found in : /home/garmstrong/QEC/QECWorkspace/results/Br2\_STO-3G\_SE\_HFSCF\_14\_2023-06-28T15-12-52/results". It lists "Total Elastic Cross-section", "Eigenphases", "BEB Ionisation Cross-section", and "Data Sheet", each with "View Rate" and "View" buttons. At the bottom, there is an "Export results directory" button and a "Close" button.

# QEC example calculations



# Acknowledgements

- Harin Ambalampitiya
- Sebastian Mohr
- Kateryna Lemishko
- Sam Giltrap
- Anna Nelson
- Jonathan Tennyson



# QEC isotope selection

Quantemol Electron Collisions (QEC)

File Help Settings

### QEC Molecule Setup

Adding a few atoms? Click [here](#) to find out how to load an xyz file or Molpro xml!

Molecular Viewer

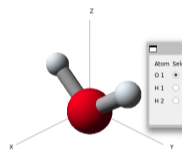
Atom	X	Y	Z
1 O	0	-0.0	-0.0647
2 H	0	0.7488	0.5139
3 H	0	-0.7488	0.5139

Atom 1	Atom 2	R
H	H	0.9463
H	H	0.9463

Atom 1	Atom 2	Atom 3	Angle
1 H	O	H	104.6117

Select Isotopes

Atom	Selected Mass	NIST Isotopes
O 1	<input checked="" type="radio"/> O 1: 15.999	<input type="radio"/> O 1: 15.99491 <input type="radio"/> O 1: 16.99913 <input type="radio"/> O 1: 17.99916
H 1	<input type="radio"/> H 1: 1.008	<input type="radio"/> H 1: 1.00782 <input checked="" type="radio"/> H 1: 2.0141 <input type="radio"/> H 1: 3.01605
H 2	<input type="radio"/> H 2: 1.008	<input type="radio"/> H 2: 1.00782 <input checked="" type="radio"/> H 2: 2.0141 <input type="radio"/> H 2: 3.01605



# Isotope selection



- Isotope library now available for all elements.
- Most abundant isotope selected as default.
- Important in astrophysical applications, where major astronomical and terrestrial isotopes differ.

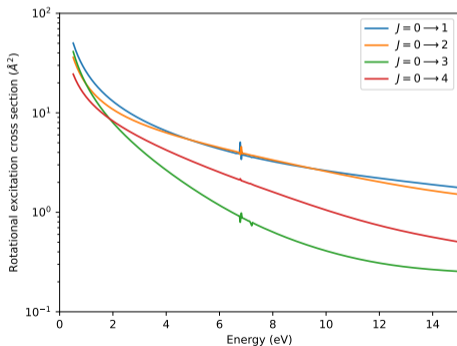




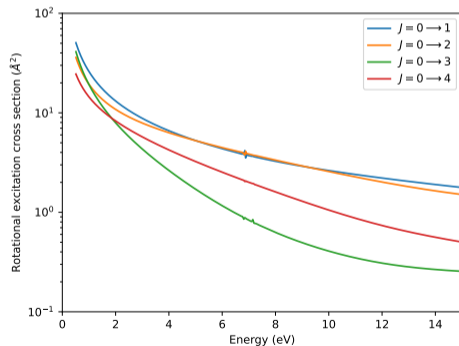
# Cross sections and dipole moments for $\text{ArH}^+$

<b><math>\text{ArH}^+</math> dipole moments</b>		
$^{36}\text{ArH}^+$	$^{38}\text{ArH}^+$	$^{40}\text{ArH}^+$
2.2233	2.2319	2.240

$^{36}\text{ArH}^+$



$^{40}\text{ArH}^+$



# MOLPRO basis sets for heavy elements



- Heavy: molecules containing elements Ar-Kr.
- Consider all-electron basis sets without core potentials.
- Dunning (cc-pVXZ) and Pople (X-YZWG) basis sets are commonly used.
- Pople basis sets only available for H-Ar.
- Include Karlsruhe bases in QEC for elements Ar-Kr.



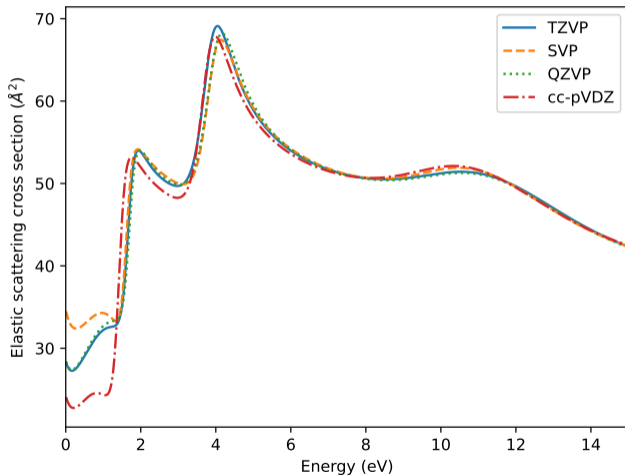
# Karlsruhe basis sets



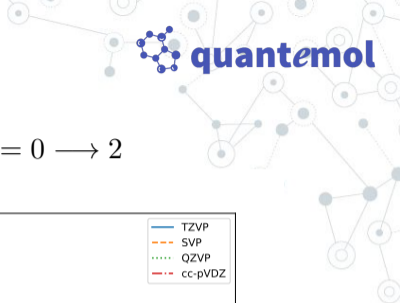
- Main hierarchy of Karlsruhe basis sets is:
  - def2-SVP — Split valence polarization.
  - def2-TZVP — Valence triple-zeta polarization
  - def2-QZVP — Valence quadruple-zeta polarization
- Analogous to cc-pV(D/T/Q)Z basis sets.
- Can include diffuse functions (similar to aug-cc-pVXZ).



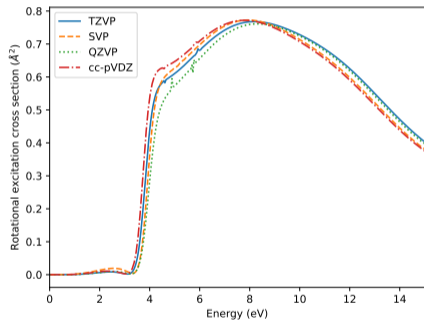
# Elastic scattering cross section for $\text{GeCl}_4$



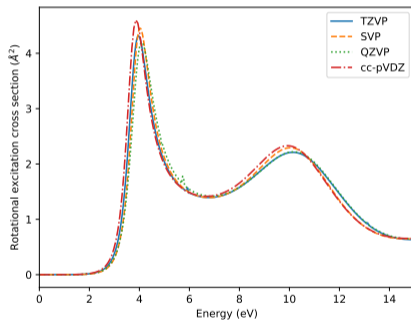
# Rotational excitation cross section for $\text{GeCl}_4$



$J = 0 \rightarrow 1$



$J = 0 \rightarrow 2$



# Vibrational frequencies for $\text{GeCl}_4$

$\text{GeCl}_4$				
NIST	cc-p		def2-	
( $\text{cm}^{-1}$ )	VDZ	VTZ	SVP	TZVP
396	399	404	403	407
134	126	124	130	126
453	470	472	478	475
172	171	171	175	172